THE CHEMICAL MODIFICATION OF POLYMER BLENDS BY REACTIVE PROCESSING.

KEVIN JAMES ARTUS

Doctor of Philosophy

THE UNIVERSITY OF ASTON IN BIRMINGHAM

OCTOBER 1994

THE UNIVERSITY OF ASTON IN BIRMINGHAM

THE CHEMICAL MODIFICATION OF POLYMER BLENDS BY REACTIVE PROCESSING.

KEVIN JAMES ARTUS

Doctor of Philosophy
October 1994

SUMMARY

The primary objective of this research was to examine the concepts of the chemical modification of polymer blends by reactive processing using interlinking agents (multi-functional, activated vinyl compounds ; trimethylolpropane triacrylates {TRIS} and divinylbenzene {DVB}) to target in-situ interpolymer formation between immiscible polymers in PS/EPDM blends via peroxide-initiated free radical reactions during melt mixing. From a comprehensive survey of previous studies of compatibility enhancement in polystyrene blends, it was recognised that reactive processing offers opportunities for technological success that have not yet been fully realised ; learning from this study is expected to assist in the development and application of this potential.

In an experimental-scale operation for the simultaneous melt blending and reactive processing of both polymers, involving manual injection of precise reactive agent/free radical initiator mixtures directly into molten polymer within an internal mixer, torque changes were distinct, quantifiable and rationalised by ongoing physical and chemical effects. EPDM content of PS/EPDM blends was the prime determinant of torque increases on addition of TRIS, itself liable to self-polymerisation at high additions, with little indication of PS reaction in initial reactively processed blends with TRIS, though blend compatibility, from visual assessment of morphology by SEM, was nevertheless improved. Suitable operating windows were defined for the optimisation of reactive blending, for use once routes to encourage PS reaction could be identified.

The effectiveness of PS modification by reactive processing with interlinking agents was increased by the selection of process conditions to target specific reaction routes, assessed by spectroscopy (FT-IR and NMR) and thermal analysis (DSC) coupled with dichloromethane extraction and fractionation of PS. Initiator concentration was crucial in balancing desired PS modification and interlinking agent self-polymerisation, most particularly with TRIS. Pre-addition of initiator to PS was beneficial in the enhancement of TRIS binding to PS and minimisation of modifier polymerisation ; believed to arise from direct formation of polystyryl radicals for addition to active unsaturation in TRIS. DVB was found to be a "compatible" modifier for PS, but its efficacy was not quantified.

Application of routes for PS reaction in PS/EPDM blends was successful for in-situ formation of interpolymer (shown by sequential solvent extraction combined with FT-IR and DSC analysis) ; the predominant outcome depending on the degree of reaction of each component, with optimum "between-phase" interpolymer formed under conditions selected for equalisation of differing component reactivities and avoidance of competitive processes. This was achieved for combined addition of TRIS+DVB at optimum initiator concentrations with initiator pre-addition to PS. Improvements in blend compatibility (by tensiles, SEM and thermal analysis) were shown in all cases with significant interpolymer formation, though physical benefits were not ; morphology and other reactive effects were also important factors. Interpolymer from specific "between-phase" reaction of blend components and interlinking agent was vital for the realisation of positive performance on compatibilisation by the chemical modification of polymer blends by reactive processing.

Keywords : Polymer blends, Reactive processing, Polystyrene, Interlinking agents, EPDM, Polymer modification, Compatibilisation, Interpolymer.

ACKNOWLEDGEMENTS

I most gratefully acknowledge the support given to me by my previous and present employers for the opportunity to carry out this research programme ; without both their financial assistance and acceptance of time away from industrial endeavours this study would not have been possible. I was initially at ICI Fibres in Gloucester when agreement was given for this experience of original research in an academic centre. I wish to thank Mr Nigel Hayman, Section Manager New Fibres and Fundamentals Research, and Dr Walter Burns, ICI Fibres Research Manager, for their personal involvement in the successful presentation of my case, and during my last year, for extension of the financial support from ICI by Mr Duncan Burns. Throughout these formative years with ICI, I wish to recognise the encouragement given by my Project Manager, Dr Robin Birch ; I am especially indebted for having shared in his ideals of individual development, inspirational research and "glad to be innovative" approach, in both good times and bad.

My present employers since February 1994, Cookson Group plc, recognised the personal importance of completing this study and have been keen for this to be achieved. I am most thankful for the accommodation and encouragement shown by Dr Robin Britton (Plastics Group Team Leader), Dr Steve Bold (Materials and Processes Assistant Director), and my new colleagues, at the Cookson Technology Centre in Oxford and at one of our principal operations in the United States of America, CAMAC Corporation.

This learning experience would not have been fractionally as satisfying without the guidance and expert supervision of Dr Sahar Al-Malaika, whose complete dedication and unfaltering energy in the quest for technological advances in polymer processing and performance will remain as examples of excellence with me forevermore ; I thank you for this enrichment and enlightenment which exceeds just the words and figures in this thesis.

Assistance from and discussion with other students and Research Fellows of the group has been much appreciated, but most especially that of Dr Hussam Sheena, whose technical knowledge, experience and understanding have been vital safety-nets throughout this work, always given freely without bias or over-emphasis and always of great help.

Greatest thanks of all are given to my wife Lynn for her loving acceptance of the many lost hours together throughout this study, which as a token of my eternal affection and appreciation, I dedicate to her and our children, Sophie and Robert, who perhaps one day may offer their own critical acclaim of the research herein.

LIST OF CONTENTS

LIST OF CONTENTS

LIST OF CONTENTS

LIST OF CONTENTS

LIST OF CONTENTS

LIST OF TABLES

LIST OF TABLES

LIST OF SCHEMES

LIST OF FIGURES

LIST OF FIGURES

LIST OF FIGURES

ABBREVIATIONS AND SYMBOLS

AA	:	acrylic acid
ASTM	:	American Society for Testing and Materials
BBR	:	bromobutyl rubber
BM	:	bis-maleimide
CPE	:	carboxylic acid-modified polyethylene
CTM	:	cavity transfer mixer
DBM	:	dibutyl maleate
dcp	:	dicumyl peroxide
DCPD	:	dicyclopentadiene
DMAE	:	dimethylaminoethanol
DMAEMA	:	(tertiary) dimethylaminoethylmethacrylate
DMTA	:	dynamic mechanical thermal analysis
DSC	:	differential scanning calorimetry
DVB	:	divinylbenzene
EPDM	:	ethylene propylene diene monomers (terpolymer)
EP(D)M	:	ethylene propylene (diene) monomers
EPR	:	ethylene propylene rubber copolymer
EVA	:	ethylene-vinyl acetate copolymer
FRI	:	free radical initiator
FRI:RA	:	free radical initiator : reactive agent molar ratio
FT-IR	:	Fourier Transform-Infra-Red analysis
GMA	:	glycidal methacrylate
gpc	:	gel permeation chromatography
H311	:	Huntsman Crystal Polystyrene grade 311
HIPS	:	high impact polystyrene
HPB	:	hydrogenated polybutadiene
HPB-b-PS	:	hydrogenated polybutadiene-block-polystyrene copolymer
IPN	:	interpenetrating polymer network
LDPE	:	low density polyethylene
LLDPE	:	linear low density polyethylene
MAA	:	methacrylic acid
MAH	:	maleic anhydride
MeOH	:	methanol
MFR	:	melt flow rate
MMA	:	methyl methacrylate
NBR	:	acrylonitrile butadiene rubber
NMR	:	nuclear magnetic resonance
NR	:	natural rubber
OPS	:	polystyrene-co-oxazoline copolymer
OsO_4	:	osmium tetroxide
PA	:	polyamide (nylon)
PA6	:	polyamide 6
PA66	:	polyamide 66
PB	:	polybutadiene
PC	:	polycarbonate
PE	:	polyethylene
PET	:	polyethyleneteraphthalate (polyester)
PE-g-PS	:	polyethylene-graft-polystyrene copolymer
PIP	:	polyisoprene
PO-g-MAH	:	polyolefin-graft-maleic anhydride adduct
PP	:	polypropylene

ABBREVIATIONS AND SYMBOLS

PPO	:	poly-(2,6-dimethyl-p-phenylene oxide)
PS	:	polystyrene
PST	:	dithiocarbamate-terminated polystyrene
PSTS	:	perthiocarbamate-terminated polystyrene
PSVP	:	poly(styrene-co-4-vinylpyridine) copolymer
PS-b-PE	:	polystyrene-block-polyethylene copolymer
PS-b-PMMA	:	polystyrene-block-polymethylmethacrylate copolymer
PS-co-MAA	:	poly(styrene-co-methacrylic acid) copolymer
PS-g-EP	:	polystyrene-graft-ethylene propylene rubber copolymer
PVC	:	polyvinyl chloride
PVDF	:	polyvinylidene fluoride
RA	:	reactive agent
RAPRA	:	Rubber and Plastics Research Association
RH	:	relative humidity
ROOR	:	organic peroxide
rpm	:	revolutions per minute
S634	:	Dow Styron Polystyrene grade 634
SEBS	:	styrene-ethylene butene-styrene triblock copolymer (ethylene butene unit is hydrogenated polybutadiene)
SEM	:	scanning electron microscopy
SGMA	:	styrene-glycidal methacrylate copolymer
SMA	:	styrene-maleic anhydride copolymer
SPD	:	solid phase dispersant
SPS	:	sulphonated polystyrene
T101	:	Akzo Chemie Noury Initiator Trigonox 101 (2,5-dimethyl-2,5-bis-tertiarybutylperoxy hexane)
TAIC	:	triallyl isocyanurate
tBAEMA	:	tertiary butylaminoethylmethacrylate
TEB	:	tensile energy to break
Tg	:	glass transition temperature
TPE	:	thermoplastic elastomer
TR	:	torque rheometer
TRIS	:	trimethylolpropane triacrylate
V2504	:	EXXON Vistalon EPDM grade 2504
XNBR	:	carboxylic acid-modified acrylonitrile butadiene rubber
Zn-S-EPDM	:	zinc neutralised sulphonated EPDM
dT_{10}	:	normalised final torque ($dT_{10} = T_{10} - T_3$)
dT_p	:	normalised peak torque ($dT_p = T_p - T_3$)
ε_b	:	extension to break point
ε_y	:	extension to yield point
σ_b	:	stress to break point
M_n	:	number average molecular weight
M_w	:	weight average molecular weight
Se	:	soluble EPDM portion on extraction of blend
Sp	:	soluble PS portion on extraction of blend (Table 5.8)
t	:	processing time
T_3	:	reference torque after 3 minutes processing
T_{10}	:	final torque after 10 minutes processing
T_p	:	peak (maximum) torque during reactive processing

CHAPTER 1.

GENERAL INTRODUCTION AND SCOPE OF THE WORK.

1.1 INTRODUCTION.

Many of today's commonplace materials, developed in the plastics age of yesterday, are now evolving into the higher performance species of tomorrow. Considerable research and development effort has been spent in maximising the ability of commodity polymers to satisfy the requirements of much more demanding (and higher value) applications. It has long been realised that novel polymer systems, incorporating existing materials in new ways, can provide more cost-effective solutions, avoiding the expense and introduction of further complications by the synthesis of new polymers or additives. Several technologies have emerged to exploit this concept and indeed some may be used in combination with even greater advantages ; promoting synergy to create "extra speciality plastics" from otherwise commodity polymers using conventional processing techniques in novel ways. Two such technologies are reactive extrusion and polymer blending. Both have great potential in their own right and it is now being realised how much greater this may be when they are employed together. This can be achieved over a wide range of scales, utilising large extrusion equipment for developed continuous processes or small batchwise internal melt mixers for laboratory-based research studies of the underlying principles.

A broad overview of reactive extrusion processes will be presented to indicate what can be achieved by this route, followed by brief discussion of the basic concepts of polymer blend compatibility, leading into the actual application of reactive processing for the chemical modification of polymer blends. The compatibility enhancement of polystyrene blends will also be reviewed and the use of reactive methods particularly emphasised, allowing for development of the overall research objectives and strategy from a position of greater understanding of the present topic of interest.

1.2 THE TECHNOLOGY OF REACTIVE EXTRUSION.

The processing technique of reactive extrusion uses a screw extruder simultaneously as a mixing unit and chemical reactor. Specific chemical transformations are actively promoted in-situ during extrusion rather than just physically thermoprocessing polymer. Reactive extrusion or reactive compounding has been used to produce many polymers by polymerisation of suitable monomer or pre-polymer mixtures and for the modification of even inert polymers.[1-3] Reactive blending is the term used specifically for the melt blending of polymer combinations, simultaneously undergoing chemical reaction. This is the topic of particular interest, but it will be useful to initially present a broad overview of the technology of reactive extrusion ; the capabilities of extruder systems, some of the processes carried out and in particular, polymer modifications by reactive extrusion.

1.2.1 Screw Extruders As Polymer Reactors.

Screw extruders, especially twin screw configurations, are very well suited to the task of acting as continuous polymer reactors.[1-6] In discussing the suitability of extruders as chemical reactors, some of the factors that come into play include the properties of molten polymer and the capabilities of screw extruders to handle and efficiently mix material undergoing physical and chemical changes in the absence of solvent ; the excellent thermal control of reaction mixtures due to rapid heat transfer within an extruder ; design flexibility for custom-engineered systems, allowing for suitable residence time with specific reaction schemes ; and the economic benefits of continuous operation and high space-time yields from a range of scales afforded by choice of extruder size.

A major advantage in using the extruder as a chemical reactor is that reaction takes place in the polymer melt in the absence of solvent[1] - this removes the requirement for

associated plant and unit operations for handling and removing solvent from product, reduces environmental impact, makes a process inherently safer, and significantly improves process economics by eliminating the cost of solvent consumption and processing.

1.2.2 Reactive Extrusion Processes.

Reactive extrusion has been used to carry out many polymerisations and polymer transformations.[1,2,4] The type of processes carried out, summarised according to the overall aim, are shown in Table 1.1, which includes feed components and final products for each to further clarify these arbitrary groups.

Processes (V) and (VI) were to be utilised in the present research and will be elaborated on further ; the others warrant just brief comment.

Table 1.1 **Reactive Extrusion Processes.**

Process	Feed Components	Product
I. Bulk Polymerisation	Monomer(s) and/or low MW prepolymer	High MW polymer
II. Graft Polymerisation	Polymer + monomer	Graft copolymer
III. Controlled Degradation	High MW polymer + O_2 or ROOR	Lower MW polymer
IV. Coupling / Branching	Single polymer + condensing/coupling/ brancing agent	Chain-extended or branched higher MW polymer
V. Polymer Modification	Single polymer + reactive agent(s)	Polymer with new or modified functional groups
VI. Interpolymer Reaction	Polymer blend (+ reactive agents)	Compatibilised polymer blend or random/block copolymers

I) **Bulk polymerisation** processes have been developed for the continuous extrusion of many different polymers. Polyurethane elastomers are common addition polymers produced by this route.[1] Condensation polymers such as polyamides, polyesters and polyetherimide can also be prepared[1,2] ; and many styrenic, acrylic, acrylate and alkene polymers and copolymers are given by free radical polymerisations of ethylenically unsaturated monomers via reactive extrusion,[1,2,4,6] such is the versatility of this technology.

II) **Graft polymerisations** in which monomer is reacted to build up side chains of substantial length from occasional graft sites on a host polymer have been effected during an extrusion process.[1] Graft length not only depends on reaction kinetics and mechanisms (often free radical), but also the conditions of the extrusion system.[4,6] This is different to polymer functionalisation or modification in which the degree of polymerisation from graft sites is typically very low. Styrenic copolymerisations may be carried out in this way, with an elastomer present in the extruder feed to achieve efficient rubber toughening of the ultimate plastic matrix through grafting.[2]

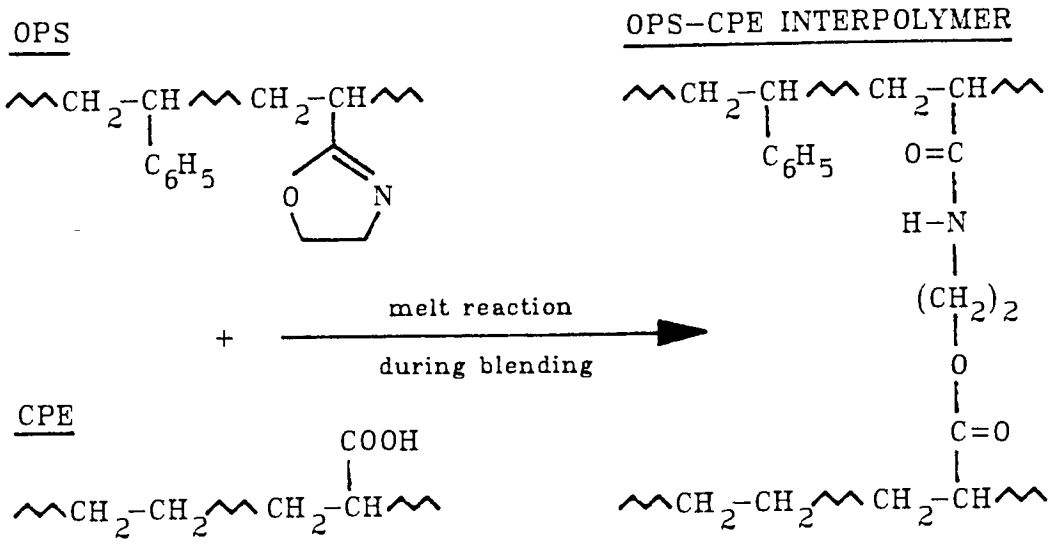
III) **Controlled degradation** and IV) **Coupling/Branching** processes have been used to alter the molecular weight distribution and chain topography for many polymers. The molecular weight of PP may be considerably reduced if a specific initial MW experiences sufficient shear in the presence of oxygen or peroxides ; the distribution is considerably narrowed by this route to generate products with designed specifications.[1,3,5] Conversely, chain extensions of polyamides and polyesters can be brought about using tertiary phosphite condensing agents as polyfunctional coupling agents.[1]

V) **Polymer Modification** introduces new, or modifies existing functional groups in polymers by reactive extrusion. This typically produces lone functional units that are not required to react further until its desired chemical effect is wanted.[1] Over a slightly larger scale, particular monomer units within the polymer chain may be modified to improve specific properties, eg the heat resistance of acrylic polymers by imidisation with aminating agents.[3] Because of the potential for incorporating modified, reactive polymers in blend systems, possible modifications have thus been explored in more detail, in the next section (1.2.3).

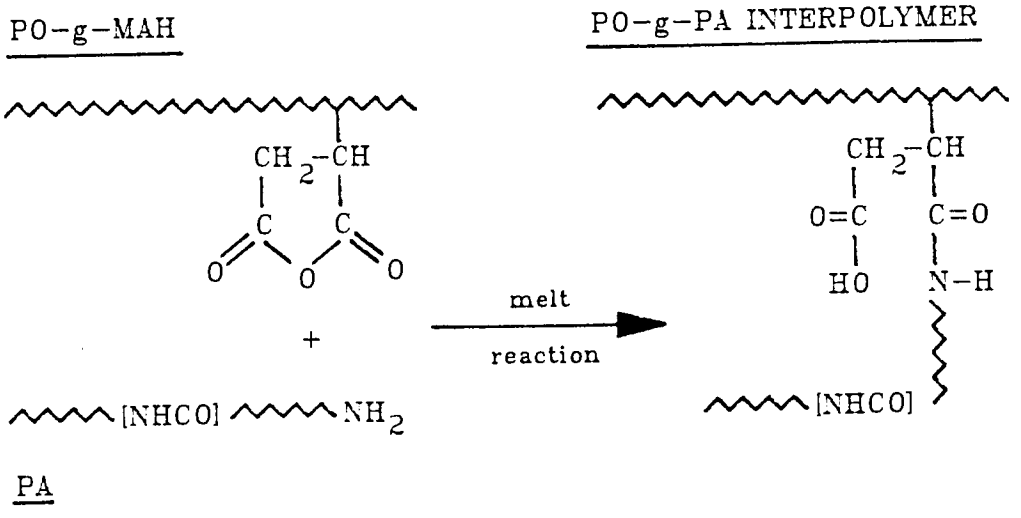
VI) **Interpolymer reactions** may occur during extrusion of polymer blends if the components have suitable co-reactive functionalities resident in the polymers. These may be from functional monomer units introduced at polymerisation or even by modification from previous reactive extrusion process. One example is the polystyrene copolymer with 1% vinyl-oxazoline monomer (OPS), produced by Dow Chemicals Limited, which has been shown to give reaction with many other functionalities.[1,7] Its coupling reaction with carboxylated polyethylene (CPE) is shown in Scheme 1.1.[8,9]

A more commonly reported interpolymer reaction uses maleic anhydride modified polymers, which can also be prepared by reactive extrusion[10-12] (see 1.2.3). Maleanised polyolefins or elastomers are often compounded with polyamides to raise impact properties.[13-17] Compatibilised polymer alloys are produced by interpolymer reaction between the functionalities, leading to improved property profiles from otherwise incompatible blends. It has been proposed that such reactions of maleic-adducts occur through the terminal amine groups of the polyamide[17,18] (Scheme 1.2).

Scheme 1.1 Interpolymer reaction of Polystyrene-co-oxazoline (OPS) and Carboxylated Polyethylene (CPE).



Scheme 1.2 Interpolymer reaction of Maleic Anhydride - Polyolefin Adduct (PO-g-MAH) and Polyamide (PA).



Graft, block or even random, copolymers can be produced in blends if reaction is highly favoured. Interchange reactions of condensate polymers have been reported,[19-23] especially between polyester and polycarbonate blends, which can yield fully random copolymers. The mixing conditions, polycondensate nature, and the presence of residual catalysts all have a significant effect on interpolymer reaction in the melt.

Chemical interlinking of polymers in blends can also be achieved by the in-situ generation of reactive sites during compounding ; perhaps by the reaction of macro-radicals, resulting from either intensive shear and thermal stresses during mixing, or the addition of organic peroxides.[24] Using these principles, the mechanochemical synthesis of block copolymers from blends of non-functional polymers, eg polyethylene and polystyrene, have been described.[25-26] Addition of a reactive agent can also induce interpolymer reaction ; as with organic phosphites in blends of polyester and polyamides to yield block or graft copolymers.[27]

Cross-linking principles and chemistry from rubber technology have been used in reactive extrusion processes known as dynamic vulcanisation. Interpolymer formation is targeted in blends of elastomers and plastics to produce copolymer-like alloys, which behave similarly to vulcanisates in service, but have the supreme advantage of being melt processable[28-30] : thermoplastic elastomers (TPEs). The work of Coran and Patel, using many different elastomers and thermoplastics,[28,31-33] was significant in realising the potential of this concept, with many commercial products now being offered.[34]

1.2.3 Polymer Modification By Reactive Extrusion.

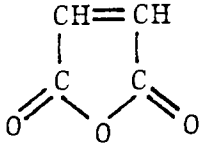
Reactive extrusion provides a convenient route to a range of polymer modifications. These offer changes to the chemical composition and can thus alter specific properties of the material.[10,35-37] However, one major constraint is that other important performance characteristics of the polymer should not be significantly different to those of the virgin material. In particular, modification must be effected in such a way to avoid drastic changes in molecular weight.

Polymer modifications are carried out for many reasons, especially on inert, non-polar polymers. Incorporating particular functional groups can dramatically improve adhesion to metal, plastic and glass surfaces,[37] inorganic fillers[36] and glass fibre.[10,36] Dyeability, paintability, printability and hydrophilicity can be altered and increased nucleation has also been reported.[37] Compatibility with other polar polymers in blends can also be achieved by this route ; interphase adhesion is raised through specific interactions of functional groups in both polymers.[1,3]

Subsequent reaction of modified polymer has been exploited by the use of novel reactive thermal and photo-antioxidants, substantially improving additive performance in demanding environments.[10,35] Stability may also be increased by the promotion of cross-linking reactions of functionalised polymer ; in the Dow Corning Sioplas technology, reactively extruded vinyl -silane-modified polyolefins are cross-linked by moisture to give polymer with improved chemical resistance.[1]

Many reactive modifiers contain at least one centre of unsaturation which can undergo addition reaction with polymer macro-radicals generated during extrusion.[1,2,10] Functionalisation of numerous polymers has been reported with many such reagents ; this is exemplified in Table 1.2.

Table 1.2 Vinyl-Containing Reactive Agents Employed For Polymer Functionalisation.

	Reactive Agent	Polymer	References
I	Maleic Anhydride (MAH) 	PE	11,13,38
		LDPE, LLDPE	12
		PP	10,11
		EPR	14
		HPB	2
		PS	39
		SEBS	40
II	Dibutyl Maleate (DBM) $CH-COO(CH_2)_3CH_3$ ‖ $CH-COO(CH_2)_3CH_3$	EPR	41
III	Vinyl Silane $CH_2=CH-Si(OMe)_3$	PE, HDPE	1,42
IV	Acrylic Acid $CH_2=CH-COOH$	PP, PE	1,10
		EPR, EVA	1
V	Methacrylic Acid $CH_2=C(CH_3)-COOH$	PE, PP,	1
		EPR, NR	
VI	Methyl Methacrylate $CH_2=C(CH_3)-COOCH_3$	EPDM, EPR,	1
		PB	
VII	Butyl Acrylate $CH_2=CH-COO(CH_2)_3CH_3$	PE, PP	1
VIII	Glycidal Methacrylate $CH_2=C(CH_3)-COCH_2CH(O)CH_2$	PE, PP	43

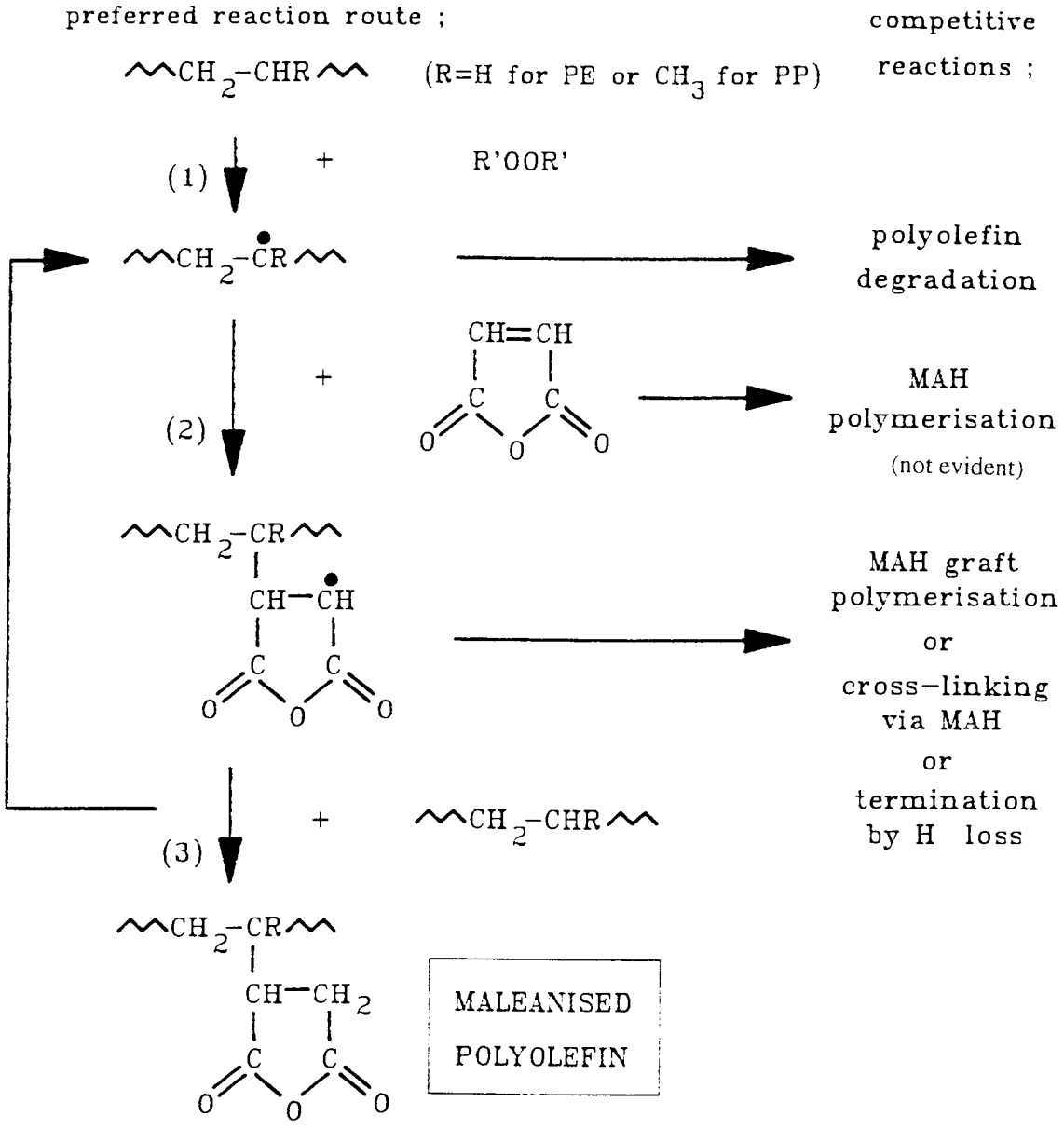
Addition reactions of the above reagents are extremely well suited to reactive extrusion processes. Macro-radicals are readily formed under the conditions of temperature and shear experienced, and especially with added organic peroxides. Propagation occurs rapidly due to the reactivity of the macro-radicals and clean additions are usually achieved, without the generation of low molecular weight by-products. Suitable termination then gives the required modified polymer adduct.

However, the desired adduct formation is in direct competition with such other reactions as degradation of polymer, homopolymerisation of modifier, cross-linking of polymer adduct and radical scavenging by free oxygen and stablisers often present in the polymer.[10] Successful adduct reactions can thus only be achieved by an understanding and subtle control of such interfering chemical processes.

Functionalisation of hydrocarbon polymers with maleic anhydride (MAH - **I**) via reactive extrusion is a well documented example,[2,10-12] giving scope for additive attachment, increased glass fibre adhesion and improved compatibility with polar polymers. The active unsaturation in MAH allows addition of macroalkyl radicals, leading to subsequent formation of the desired adduct product.[10,11] Scheme 1.3 shows this MAH reaction with polyolefins, along with some indication of competitive processes.

Mechanistic studies have shown the need for active unsaturation,[10] the preferred route to the succinic anhydride adduct[11] and the effects of organic peroxide initiators.[12] The role of MAH homopolymerisation and cross-linking is disputed,[18] but graft polymerisation does not typically occur so that individual pendant functionalities are given.[11] Reaction is very dependent on feed composition and extrusion conditions, such that it is often unclear as to what maximum level of grafting can be achieved due to the possibilities of competitive effects.

Scheme 1.3 Maleic Anhydride Modification of Polyolefins.



Legend.

(1) Initiation by organic peroxide

(2) Addition of MAH to macroalkyl radical

(3) Termination of adduct radical

Maleanised polymers can undergo further reaction with nucleophiles at the pendant anhydride centre during subsequent extrusion.[1] A typical interpolymer reaction with amine-containing polyamide has already been shown (Scheme 1.2) ; these are extensively documented.[2,14-17] Improvements in adhesion to glass fibre coated with amino-silane coupling agent also arise by similar reaction.[10]

Dibutyl maleate (DBM - **II**) has been grafted onto ethylene-propylene rubber (EPR), using a cavity transfer mixer in tandem with an extruder to obtain addition levels of almost 6% by weight of polymer.[41] This was claimed to be due to the highly efficient mixing equipment used and the lack of graft or homo-polymerisation of the DBM modifier.

Other vinyl-containing reactive agents have also been widely employed for functionalisation. Previously mentioned, is the use of vinyl-silane (**III**) with polyethylene.[1] Polybond 1001 is another commercial product, from BP Performance Polymers Inc., which is a grade of reactively extruded polypropylene containing 6% grafted acrylic acid (**IV**).[36] The reaction route is similar to that for MAH, but in this case graft polymerisation is more prevalent so that between two and ten acrylic acid units build up off each graft site.[36] Analogous vinyl acids and esters (**V-VII**) have also been used with a range of polyolefins[1,2,3] (Table 1.2), although for this group of compounds, homopolymerisation occurs much more readily than with maleic anhydride.[1]

One particularly interesting modifier, which has not been as widely used as it could be, is glycidal methacrylate (GMA - **VIII**). High level binding with little cross-linking of EPR and EPDM has been demonstrated, along with subsequent melt reactions of the epoxy-grafted functionality with both electrophiles and nucleophiles.[43]

Exciting opportunities in this area are being generated by research at Aston University using the vinyl chemistry discussed above, in combination with an additional reactive component to promote particularly efficient modification reactions. The use of a second polymerisable monomer, termed an **interlinking agent**, is believed to result in fully bound, non-migratory modifiers.[44] Such reagents are multi-functional acrylates (eg **IX**, **X**) or other compounds containing multiple vinyl groups (eg **XI**). It is hoped that this present research will contribute to the use and understanding of this interlinking agent technology, particularly for application in the reactive processing of polymer blends.

IX $\mathbf{C_2H_5\text{-}C\text{-}(CH_2OCOCH{=}CH_2)_3}$

trimethylolpropane triacrylate (TRIS)

X $\mathbf{CH_2{=}CHOCOCH_2CH_2OCOCH{=}CH_2}$

ethylene glycol diacrylate

XI $\mathbf{C_6H_4\text{-}(CH{=}CH_2)_2}$

divinyl benzene (DVB)

1.3 POLYMER BLEND COMPATIBILITY.

Polymer blending has been attempted as a way to negate undesirable factors of the component materials and obtain systems with novel property profiles. Occasionally compositions have been found that act with synergy to produce better specific properties than expected from the component contributions alone. However, the majority of polymer combinations are found to phase-separate into heterogenous mixtures and thus do not exhibit these enhanced features. Such multiphase blends may still be deemed to be "compatible" if their characteristics allow use under certain conditions, which may in part result from their complex morphology. Compatibility is thus a quite arbitrary term. The more absolute definition is given by miscibility, which considers the degree of intimacy of polymer chains on a molecular scale and is determined by the thermodynamics of the system. The consequences of miscibility level are manifested in the properties of a blend, which dictate the limits of application (or compatibility).

For this present research on the chemical modification of blends, it was necessary to gain an understanding of the concepts of miscibility, their consequences, characterisation and how compatibility may be changed. The results of this learning will be briefly presented.

1.3.1 Thermodynamic Definition Of Miscibility.

From basic thermodynamics, the miscibility of a mixture is governed by the Gibbs free energy of mixing, which is related to changes on mixing in enthalpy and entropy according to equation {1.1}. For a system to be fully miscible, showing homogeneity by intimacy on a molecular level, then the total free energy must be negative (equation {1.2}). Further analysis of these functions have been made according to the principles of Flory and Huggins[19,45-48] (equations {1.3} to {1.5}).

$$\Delta G_m = \Delta H_m - T\Delta S_m$$ equation {1.1}

$$\Delta G_m < 0$$ equation {1.2}

$$\Delta H_m = RT\,(V_A + V_B)\,\phi_A\,\phi_B\,\alpha_{AB}$$ equation {1.3}

$$\Delta S_m = -R\,(V_A + V_B)\left[\sigma_A \frac{\phi_A}{M_A}\ln\phi_A + \sigma_B \frac{\phi_B}{M_B}\ln\phi_B\right]$$ equation {1.4}

$$\left[\frac{\delta^2 \Delta G_m}{\delta\phi^2}\right]_{T,P} > 0$$ equation {1.5}

Symbols :

ΔG_m – Gibbs free energy of mixing

ΔH_m – enthalpy change on mixing

ΔS_m – entropy change on mixing

R, T & P have their usual significance

α_{AB} – interaction parameter between polymers A & B

V_i – volume of component i in the mixture

ϕ_i – volume fraction of component i

σ_i – molecular density of component i

M_i – molecular weight of component i

Enthalpy of mixing has been shown to be independent of molecular size and is primarily a measure of the energy change associated with the net intermolecular attractions (equation {1.3}). However, the entropy term, reflecting changes in the randomness of the system, is an inverse function of the molecular weight of each component (M_i, equation {1.4}) due to the intrinsic order in a system from limited possible arrangements of linked segments.[48] To allow miscibility at equilibrium with endothermic mixing (positive enthalpy), entropic change must be greater than the resulting enthalpy to produce a negative Gibbs free energy value. This is unlikely for high polymers because of the above relationship between entropy and molecular weight (equation {1.4}). Thus, when each different polymer is preferentially attracted to itself (endothermic mixing), an immiscible blend results.

Exothermic mixing however, provides a negative value for enthalpy, from the release of energy by the formation of stronger inter-molecular attractions on mixing. Thus miscibility may only be expected for high molecular weight polymers when specific interactions are greater in the blend than within isolated components.[19,45,47]

By considering the variation in free energy with blend composition for different levels of molecular interaction, it has been realised that there are certain conditions where the sum free energy can be lowered if a homogeneous mixture undergoes phase separation (equation {1.5}).[47] This is an even more rigorous thermodynamic definition of miscibility, which also encompasses the previous conditions assessed.

Further thermodynamic analyses have been made by the manipulation of interaction parameters, equations of state and statistical methods.[52] These have also been examined by experiment in attempts for justification. However, it can be argued that because of the high viscosity of polymer and the very dynamic nature of melt processing,

thermodynamic equilibrium may not always, if ever, be achieved by this route.[45,49] Melt systems are thus real, rather than ideal, for which thermodynamic analyses are much more limited. However, for such real systems, thermodynamic factors do suggest that :

i. - blends of high polymer are not expected to be miscible ;

ii. - mixtures of non-polar (non-interacting) polymers are typically immiscible ;

iii. - polar polymers offer greater opportunities for miscibility ;

iv. - specific interactions capable of causing exothermic mixing encourage miscibility ;

v. - miscibility is achieved by favourable changes in enthalpy and entropy.

In the reactive processing of polymer blends, interpolymer reaction will alter many of the above factors, particularly in terms of the degree of interaction between components and hence the enthalpy and entropy of the system. Such changes would be expected to be favourable, encouraging miscibility. However, perhaps because of the non-equilibrium conditions, thermodynamic analysis specific to this problem may as yet be unavailable.

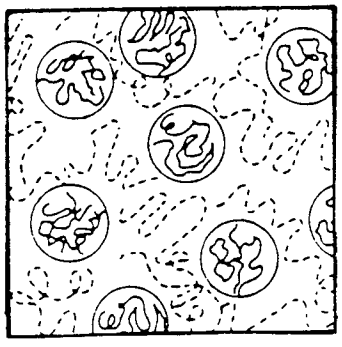
1.3.2 Practical Definition Of Miscibility.

In practice miscibility is not as "black-and-white" an issue as predicted from thermodynamic criteria, most probably because equilibrium conditions are rarely met. There is thus a large grey area between the two limiting cases, encompassed by the term **partial miscibility**. This may occur in a blend which is miscible when one polymer is in excess, but as proportions progress to equality, phase separation becomes favoured. A characteristic of this state is that molecular mixing occurs only at the interface of the two phases, giving an ill-defined boundary with improved adhesion between domains.[45] The three levels of miscibility may thus be clearly pictured by the degree of molecular mixing (Figure 1.1). This gives a more practical definition of miscibility level, since the degree of molecular mixing may be inferred by the blend characteristics.

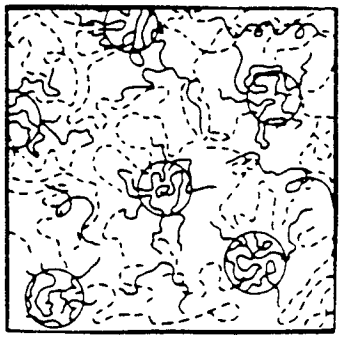
Figure 1.1 Degrees of Molecular Mixing in Polymer Blends.

a) miscible blend
– homogeneous

b) immiscible blend
– distinct phases



c) partially miscible blend
– phases poorly defined



1.3.3 Characteristics of Miscibility Level.

The characteristics and properties of any blend will depend primarily upon the level of miscibility achieved and the morphology thus generated. Composition, crystallinity of either component and the properties of the constituent materials also play a part, but some broad generalisations on the consequences of miscibility level may still be made. This is shown in Table 1.3 (for binary polymer blends). No further exemplification of this need be made here since this has been well presented in many reviews of this topic.[19,45,47,50-53]

Table 1.3 Characteristics of Polymer Blends According to Miscibility Level.

Characteristics	Type of Polymer Blend		
	Miscible	**Immiscible**	**Partially Miscible**
Thermodynamics	negative Gibbs Free energy	positive Gibbs Free Energy	?
Number of phases	one (unless crystalline)	multiple	multiple
Morphology	homogeneous	heterogeneous	heterogeneous
Interphase boundaries	indiscernable	distinct	poorly defined
Interphase adhesion	not applicable	poor	good
Optical clarity	transparent	opaque	opaque
Transition behaviour	single Tg - composition dependant	multiple Tgs - identical to components	multiple Tgs - shifted from components
Mechanical properties	additive or exhibit maximum	generally poor	improved over immiscible blend
Toughness	may be reduced	morphology dependent	improved over immiscible blend

1.3.4 Determination of Miscibility Level.

The methods used to determine miscibility level typically rely on the measurement of characteristics listed in Table 1.3. Optical transparency may be used as a rough indication for miscibility, so long as component refractive indices differ by more than 0.01 and phase size is not below 100nm.[19] Other radiation scattering techniques have been reported (with both X-ray and neutron sources[19,45,50]) ; an advantage of these methods is that samples can be examined under steady-state conditions and are thus more likely to be at equilibrium. Determination of transition behaviour correlates particularly well with morphology and miscibility level : measurement of thermal, mechanical, dilatometric or dielectric properties have all been used.[19,45,50,54] Thermal methods are particularly good ; dynamic mechanical thermal analysis (DMTA) being very sensitive to changes in Tg, with phase domains down to 10nm discernible if each component is resolvable by a sufficient difference in Tg.[47] Spectroscopic methods have also been used, more to clarify the nature of specific interactions, than to actually decide on miscibility level. Fluorescence spectroscopy yields information on interactions at the angstrom scale, infra-red at the order of tens of angstoms[49] and NMR can resolve phase domains over 3nm in size using spin-lattice relaxation times.[47]

Many studies have inferred miscibility level from changes in physical characteristics, which may not be completely justified. Indeed, increased interfacial adhesion may manifest itself by improved bulk properties, but many other factors, especially morphology, significantly alter mechanical strength. The validity of such studies however, may be recognised in the demonstration of blend systems for particular applications and are thus quite relevant in the technological terms of compatibility.

1.3.5 Compatibilisation of Polymer Blends.

In accordance with the previous discussion on miscibility, polymer blend compatibilisation has more to do with improving the performance of blends than the achievement of thermodynamic miscibility. This was expressed by Coran and Patel[32] in their definition ;

"technological compatibilisation ... is the result of a process or technique for improving ultimate properties and by making polymers in a blend less incompatible ; it is not the application of a technique which induces thermodynamic compatibility".

Indeed with many blends it is the multiphase morphology that gives interesting properties in a polymer combination. Fully immiscible blends are not advantageous, due to poor interphase adhesion. Compatibilisation aims to overcome this deficiency by the reduction of immiscibility, to gain the benefits of a heterogeneous, partially miscible system with improved interfacial adhesion. Several strategies have been attempted to achieve this ideal ; these will be summarised in the following examples.

a) **Control of Blending** - efficient dispersive and distributive mixing may reduce phase segregation, as claimed by RAPRA for their CTM (cavity transfer mixer)[55,56] and as reported for other mixing processes.[57-59] By subtle control of rheology at extrusion, balanced by selection of composition, blends can be formed having co-continuous network structures. These are termed thermoplastic interpenetrating polymer networks (IPNs) and have been exploited in novel fibres and extruded products[60,61] and the Kraton range of thermoplastic elastomers developed by Shell.[62]

b) **Introduction of specific interactions** - in this way total miscibility can actually be achieved in certain systems. The different types of specific interaction used include hydrogen bonding, dipole-dipole / ion-dipole interactions, charge transfer and acid-base

complexion.[45,49,63] Repulsive forces have also been used to produce miscibility windows in particular copolymer blends by satisfying thermodynamic requirements.[64] Selection of appropriate polymer combinations is a rather limited way of obtaining miscible systems (eg PVDF and PMMA, PPO and PS),[19] as is the introduction of specific monomer units at polymerisation to interact with analogous polymer when mixed.[64] Co-crystallisation is another important phenomenon in blends of polyolefins which yield thermoplastic elastomers ; by the formation of thermo-labile crosslinks, arising from common regions of crystallinity in the blends, as with PP and EPR, for example.[65,66]

c) **Use of copolymers** - this well researched method uses the addition of small amounts of block or graft copolymers (often <5%) with segments at least partially miscible with both major components to act as polymeric surfactants.[19,45,67-69] It is postulated that the copolymer segments lie within the phase that they are compatible with and, since they are covalently linked to dissimilar units, compatible with the second phase, arrange themselves in the interfacial regions. This decreases interfacial tension leading to considerable reduction in phase size. The consequence is improved interphase adhesion and thus enhanced mechanical properties. **Copolymer compatibilisers**[67,69,70] are typically the products of specific copolymerisation methods, however mechanochemical coupling of dissimilar polymers has successfully yielded copolymer-like interfacial agents termed **solid phase dispersants** (SPD).[25,26,70-73] Studies of both agents have placed particular emphasis on the morphological changes and improvements in the physical properties achieved in highly incompatible mixtures, for example PP/LDPE blends.[74-76] Many other studies have involved PS blends and copolymers ; these will be discussed further in Section 1.4.1.

d) **Reactive Compatibilisation** - this has employed chemical reactions between immiscible components during blending, either directly or via a third component, to facilitate improvements in compatibility. Beneficial changes in morphology, interphase adhesion and thus mechanical properties, have been attributed to interpolymer reaction (Section 1.2.2). It is postulated that the targeted chemical processes are most prevalent in the interfacial regions and that even minor yields of in-situ formed copolymer can act as particularly effective compatibilisers. This method has been used in a wide range of different blend systems ; many of these have been detailed in a comprehensive review by Xanthos.[77] The application of this technique in polystyrene blends will be further detailed in Section 1.4, though a selection of other blend systems may be useful examples to indicate the strategies attempted.

Several routes to reactive compatibilisation have been assessed, apparently depending on the inherent reactivity of the blended polymers. In blends of condensate polymers, exchange reactions occur readily (eg PET/PC transesterification), leading to progressive miscibilisation via block and eventually random copolymer formation.[19,45,19-23] The action of melt blending under conditions of high shear can be sufficient to cause mechanochemical degradation ; cross-recombination between blend components may then result in enhanced compatibility, as found by Scott at al with LDPE/PVC mixtures.[78] However, when an immiscible blend includes one or more inert components (eg polyolefins), chemically modified equivalents may offer a solution. Total replacement of the inert phase is not always necessary to achieve the desired effect ; addition of a minor amount of the reactive compatibiliser may produce enough in-situ interpolymer upon reaction to stabilise the blend. Such reactive copolymers may be prepared by

copolymerisation with co-monomer containing a reactive functionality for later expression in a blend, for example the OPS (styrene-oxazoline) copolymer[1,7-9] previously detailed (Section 1.2.2).

In another instance, the polyethylene phase in blends with nylon 6 was replaced with poly(ethylene-co-methacrylic acid {MAA}), producing substantial changes in the degree of compatibility according to the MAA content of the copolymer. This was due to reaction between acid and amine groups in the polymers.[79] Polymer modification by reactive extrusion (Section 1.2.3) has also provided useful reactive compatibilisers ; the maleanised polyolefins for example.[13-17] Polypropylene with grafted acrylic acid (PP-g-AA), produced by reactive extrusion, has been examined in blends with nylon 6[80] and also polyethylene terephthalate[81] (PET), though interpolymer reaction was only confirmed in the nylon blend.

Low molecular weight reactive additives have not been as generally applied as polymeric modifiers, most examples of this route being in the field of rubber technology : involving high rubber content blends and curatives used for elastomer cross-linking.[77] This may in part be due to the significance of the dynamic vulcanisation technique championed by Coran and Patel.[28,31-33] Therefore this appears to offer an opportunity which has not yet been fully realised, namely the simultaneous application of polymer modification by reactive extrusion during the melt blending of appropriate polymer combinations. Further expansion and exemplification of this concept is to be a primary objective of the current research.

1.4 COMPATIBILITY ENHANCEMENT IN POLYSTYRENE BLENDS.

Polystyrene is an important commodity plastic widely used in many applications, particularly in disposable packaging and other domestic articles.[82,83] The basic grade material, known as general purpose or crystal PS, is a substantially linear, completely amorphous thermoplastic. It is readily available at low price, has excellent processability and reasonable service properties. PS is hard, rigid and fully transparent to visible light. However, its principle limitations are low resistance to crazing and brittle fracture, intolerance to boiling water and mediocre oil and chemical resistance. Nevertheless it has found wide acceptance in many less demanding applications so that world wide consumption is huge.

In the field of polymer blends it is not surprising to find that polystyrene has been a popular choice for mixing with other polymers.[82] Primary reasons for blending have been to overcome the limitations of PS, extend its other properties and to engineer novel materials with unique property combinations. In attempts to improve the mechanical properties of PS, the consistent aim has been to maintain its high modulus, whilst increasing ductility and impact resistance. Recently the focus has been on the recycling of mixed plastic wastes, to which polystyrene makes a very significant contribution, being used in large volumes in packaging and disposable goods. Blends have been made with other commodity and even engineering thermoplastics in attempts to improve performance of blended constituents, processability of difficult materials and the economics of speciality products. Elastomers have also been used as a second component with PS,[84] though the best route to impact resistance is by styrene copolymerisation around a finely dispersed rubbery phase (ie HIPS), rather than simple blending. PS/elastomer blends however may have some potential in the generation of novel thermoplastic elastomer (TPE) compositions.

The majority of common plastics and elastomers are totally immiscible with PS, yielding multiphase blends which are inherently weak due to low interfacial adhesion. A notable exception is the PS/polyphenylene oxide (PPO) combination which is a very rare example of complete miscibility over the full composition range.[19,82] Physical properties follow nearly linear relationships with composition in such miscible systems. PS/PPO blends have been successfully exploited as a range of commercial products under the Noryl trademark (General Electric Corporation)[83] since 1965. However, many more mixtures of PS and other polymers do not offer such opportunities due to the inferior properties from gross incompatibility.

In the previous section on polymer blend compatibility (1.3), routes to the compatibilisation of immiscible blends were described (1.3.5). Literature on the application of these methods, specifically in blends containing general purpose polystyrene, has been critically reviewed and will now be presented. An almost universal objective has been to achieve a degree of partial miscibility between PS and the other component. Total miscibilisation may not produce the desired effect ; indeed it is often the strengthened and stabilised multiphase morphology of a partially miscible, compatibilised blend that generates the unique characteristics. This is in agreement with the concept of "technological compatibilisation" proposed by Coran and Patel[32] quoted previously (1.2.5). The general principle behind previous work in this area is thus clear ; how it has been attempted and the effectiveness that has been achieved will be presented.

1.4.1 Copolymer Compatibilisation.

The use of copolymers to raise the compatibility of immiscible blends has been a popular topic for research, and a similarly popular subject for review.[19,45,67-69] Copolymer, incorporating segments compatible with both phases, is believed to act as a "polymeric emulsifier" between phases within the interfacial zone to strengthen and

"polymeric emulsifier" between phases within the interfacial zone to strengthen and promote greater adhesion[85] Such copolymer compatibilisers[67-69] or solid phase dispersants[71,72] have been extensively investigated in blends of polystyrene and other hydrocarbon polymers ; optimising copolymer molecular structure according to the effects upon ultimate properties of the blend.[86,87] Graft, pure diblock, tapered diblock and triblock copolymers have all been considered and found to have variable effectiveness. Some "off-the-shelf" commercial copolymer products have been evaluated, but controlled copolymerisation methods have been crucial in providing specific copolymer architectures to optimise and examine the compatibilising mechanisms involved.

1.4.1.1 Graft Copolymers.

Early work by Locke and Paul[88] demonstrated that the mechanical properties of incompatible PS/LDPE blends could be significantly improved by the addition of PE-PS graft copolymers (produced by irradiation of PE and styrene mixtures). The mechanism proposed was of higher interfacial adhesion and was substantiated by a decrease in the blend domain size with copolymer addition. The graft copolymer molecular structure was believed to be important, the magnitude of change being found to depend upon the polymerisation conditions under which the PE-g-PS had been formed. It was recognised that control of copolymer structure was of prime importance in optimising compatibilisation and minimising the graft copolymer addition.

Further work on PS/LDPE blends, by Heikens et al[86,89-92] confirmed improvements in ultimate mechanical properties and reduced phase sizes with PE-g-PS copolymers. The greatest changes were achieved by replacing the PE phase entirely with copolymer, although useful properties could be obtained by the addition of disproportionately low amounts of graft (ie 5% of PE component).[89] Morphological studies related reduction in domain size to the interfacial action of copolymer, observed as irregularities on the surface

of the dispersed phase[90,91] and increased adhesion between blend components, confirmed by peel test measurements.[90] Another graft copolymer (PS-g-EP) was used in PS/amorphous ethylene-propylene rubber (EPR) blends with similar advantageous results[86,93] ; though the extensive improvements in blend impact strength may have been due to the elasticity of the non-crystalline cross-linked EPR phase, not any greater efficiency in the interfacial action of the SPD.

1.4.1.2 Graft vs Diblock Copolymers.

Later work by Heikens et al compared directly the effectiveness of different graft copolymer molecular structures against a series of PS-b-PE diblock copolymers, introduced to assess the merits of their potential for compatibilisation of the PS/PE system.[86,92] Copolymer structures and resulting improvements in impact strength of 85/15 PS/PE blends with 5% of the PE phase as copolymer are given in Table 1.4. Above 10% PE all blends with copolymer gave increased impact resistance, coupled with a strong decrease in dispersed phase domain size (except for the microgel which was seen as discrete particles). The most effective compatibiliser proved to be the tapered diblock which had a random PS/PE central segment between approximately even molecular weight end blocks of PS and PE. The uneven tapered diblock and high MW partly cross-linked graft network were next best. Ultimate tensile properties were not reported, though the concept of comparing the experimental curves for modulus variation with blend composition to model systems was developed as a tool for morphological analysis.[86,92] From this, graft copolymers were considered to provide purely an interfacial contribution to modulus effects, by improving the adhesion between dissimilar phases.

Table 1.4 **Comparison of impact strength effectiveness of graft and block copolymer compatibilisers in 85/15 PS/PE blends (5% PE phase as copolymer).**[86,92]

Copolymer Molecular Structure	Mn ($x\ 10^{-3}$)	Relative Impact Strength (85/15 PS/PE = 1.0)
PE-g-PS Regular Graft	110	1.73
Partly Cross-Linked Graft (59% gel)	-	2.26
Fully Cross-Linked Graft (100% gel - "microgel")	-	1.53
PS-b-PE Pure Diblock	58 - 42 (PS - PE)	2.13
Uneven Tapered Diblock	14 - 10 - 54 (PS - PS/PE - PE)	2.26
Even Tapered Diblock	22 - 22 - 25 (PS - PS/PE - PE)	3.40

Diblock copolymers exhibited different behaviour which was explained by a more complex morphology ; limited interfacial activity was believed to account for the reduction in domain size, but the existence of a third discrete phase was also proposed, containing superstructures of alternating PS and PE blocks.[86] Specific physical and rheological characteristics of the block copolymers were required to substantiate this microstructure, appearing as if performance improvements were somehow due to the properties of this minor third phase rather than its compatibilising action between the major components. Subsequent work by the same group using dynamic mechanical analysis[94] and on deformation mechanisms[95] further probed the effect of tapered diblock. PE and PS adhesion was shown to be greatly increased and that this could be achieved by minor amounts of diblock (<1% total blend). A complex morphological argument was no longer needed to explain the diblock effects, since high interfacial activity was confirmed by these measured gains in adhesion.

From these detailed mechanical studies it could also be seen that compatibilisation does not always result in beneficial changes ; with high interphase adhesion the modulus of blends was reduced below that of the PS almost in accordance with the amount of softer phase included. Similarly, brittle failure could still occur if the minor PE phase was too highly dispersed by high copolymer activity.[95] Thus it should be realised that physical properties are only indirectly related to the compatibility level of a blend, more significant factors are the inherent properties of each component and the response of the blend morphology to applied stresses.

1.4.1.3 Triblock Coplymers.

Triblock copolymers have also been examined.[71,72,96,97] Kraton G (Shell Chemical Co.) is a commercially available thermoplastic elastomer with polystyrene end blocks and a hydrogenated polybutadiene midblock, equivalent to ethylene-butene copolymer (SEBS). This was identified by Paul as having potential for the compatibilisation of PS/HDPE blends.[96] Adhesion of SEBS to both PS and HDPE was proven by peel test measurements and considerable improvement in blend ductility was indeed shown, but at the cost of reductions in both tensile strength and modulus. At the high copolymer levels used (to 30%), the blend characteristics were possibly influenced by a SEBS phase rather than just interfacial activity between PS and HDPE. Scott et al used SEBS as a very effective SPD in PS/LDPE blends,[71,72] producing considerable gains in ultimate tensile properties and exceptional impact resistance, albeit at high SPD content (20-50%). A similar pattern of change, with low addition of SEBS (2%) to PS/LDPE has also been produced, but not with the same magnitude.[97] However, the significant disadvantage found with SEBS was that it is a sensitiser to photo-oxidative degradation in the PS/PE blends, being rapidly consumed with a corresponding loss of effect.[98]

In other work by Scott, mechanochemically synthesised copolymer, from the processing of PS and LDPE with peroxide, was used as a SPD.[25] Block copolymer was presumed to have been formed, which when subsequently mixed with virgin PS and LDPE gave fair improvement in blend properties, but was not as effective as the SEBS also used.

1.4.1.4 Optimised Block Copolymers.

Extensive research on the emulsifying action of block copolymers in PS/PE melt blends has been carried out by Fayt and co-workers.[85,99-102] Hydrogenated polybutadiene-polystryene diblock copolymers (HPB-b-PS) were prepared with well controlled molecular characteristics, giving both pure and tapered diblock structures for use in many PS/PE blends (Table 1.5). The intention of unambiguously demonstrating the interfacial activity of these block copolymers was realised, resulting in a near complete rationale for their morphological action[103] and determination of the optimum conditions for the enhancement of mechanical performance.[87]

Table 1.5 **Hydrogenated polybutadiene-polystyrene block copolymer compatibilisers examined in PS/PE blends.**

Molecular Structure	Mn ($x10^{-3}$) PS - PS/HPB - HPB			References Cited		
				PS/LDPE	PS/LLDPE	PS/HDPE
Pure Diblock	25	-	33	85, 87		
Pure Diblock	75	-	80	85, 87, 103		87, 99
Pure Diblock	130	-	145	87		
Tapered Diblock	26	22	32	87, 100, 103	87	
Pure Diblock	40	-	40	87, 103	87	
Tapered Diblock (ex Solprene 410)	22	15	25	87, 103	87	87, 103
Tapered Diblock	22	22	25			96
Pure Diblock (HDPB "hard" block)	10	-	39 (HDPB)			101
Triblock (PS-b-PIP-b-HPB)	65	15 (PIP)	50	102, 103		
Triblock SEBS (Kraton G)	-	-	-	87		

In all cases addition of diblock significantly reduced phase size, dramatically increased interfacial adhesion and firmly stabilised the fine morphology against coalescence during further processing.[103] Direct observation of copolymer as a regular continuous layer around dispersed phase particles was made (via OsO4 staining of a polyisoprene {PIP} segment introduced in the centre of a HPB-b-PS diblock).[87,103] A dark layer around the dispersed phase was seen with transmission electron microscopy. The thickness of the layer was consistent with the PIP chain length, confirming block alignment within the interfacial region. Further to location at the junction of PS/PE phases, copolymer inclusion was also found in the PE phase as dispersed micro-domains on a much finer scale than the blend phase size. This was similar to the structures proposed by Heikens[86] to explain modulus effects at high diblock content. Dominance of this micellar third phase, could be avoided if only just sufficient tailored coplymer was employed for interfacial action ; this was later shown to be around 2% for optimum improvements in physical properties of the blends.[102]

All HPB-b-PS diblock coplymers gave significant increases in tensile properties of PS/PE blends and were believed to be superior in effect when compared to all other types (graft, tri- & multi-block and star-shaped copolymers).[87] Diblocks were considered capable of greater anchoring into each homopolymer phase, enhancing ductility and considerably raising energy to break.[85,87,99] By using higher molecular weight pure diblocks mechanical performance could be further increased, with large gains in extensibility, but minimal improvement in strength.[85,87] This effect was contrary to the "block length rule" for solution cast systems, but it was felt that this requirement was outweighed considering the dynamic, non-equilibrium nature of melt-blending.[87,103] With tapered diblocks (having a central transition zone of random PS/HPB), ultimate strength

could be significantly increased at the expense of ductility.[87,100] Greater interfacial action was found for tapered diblocks, giving higher adhesion between phases.[87,103] This was proposed to be from enhanced molecular mixing, by reduced "blockiness" driving more tapered copolymer into the interfacial zone rather than forming dispersed micro-domains of pure diblock in the other phases.[100] Such was the net positive effect that the most suitable diblocks were found to promote synergistic rises in blend properties above those of the base polymers[87] ; adequately demonstrating the power of this technique.

1.4.1.5 PS Replacement by Graft Copolymers.

Another approach involving the use of graft copolymers has been the total replacement of the second phase by a PS-grafted version (as indeed found by Heikens to be very effective[89]). Earlier work by Natta et al[104] using styrene-grafted ethylene-propylene elastomers blended with PS demonstrated the benefits of this modified rubber by:

"the formation of vitreous and elastomeric microphases, rather than macrophases ..... and better adhesion between these".

More recently, Shaw and Singh replaced the entire EPDM component in blends with PS by styrene-grafted elastomer copolymers.[105-107] The best gain in tensile strength was from EPDM modified with styrene monomer, but for impact strength improvement both styrene/MMA and styrene/MAH grafts were better modifiers. The evidence for differences in compatibilisation was limited : morphologies were altered according to the copolymer graft used but a coherent argument for this was not developed.

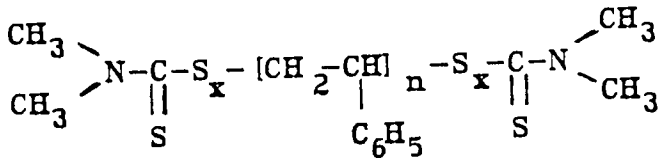
1.4.2 Polystyrene Functionalisation.

The molecular structure of polystyrene provides for very little interaction with other polymers due to the absence of any polar groups or centres of any great reactivity. Attempts have been made to overcome this by the introduction of functional groups into the relatively inert PS. Some modifications have been carried out to target interactions in a blend with another particular polymer, whereas the general use of commercially available functional PS has also been investigated. One route has been the addition of co-monomers to styrene during polymerisation to produce functionalised polystyrene copolymers. Modification of pre-formed polymer by an additional reactive process in solution, the bulk, or melt state to yield modified polystyrene prior to blending has also been examined. Both of these two approaches will be considered in the following parts.

1.4.2.1 Functional Polystyrene Copolymers.

Reactive di- and per-thiocarbamate end groups were introduced into polystyrene (XII) by Slusarski and Kuczynski[108] by the termination of styrene polymerisation with sulphur and sulphur containing compounds. These were intended to react with unsaturated elastomers by cleavage at unstable S-C bonds during melt blending, and then enhance compatibility through interfacial grafting. Changes in morphology, thermal properties and mechanical properties for blends with butadiene-acrylonitrile rubber (NBR) were demonstrated, proving the value of these exotic modifications.

XII



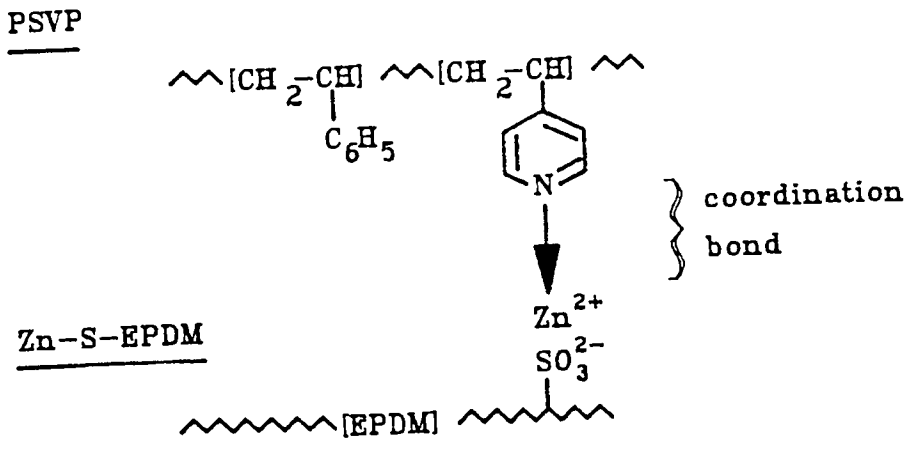
x=1 dithiocarbamate (PST)

x>1 perthiocarbamate (PSTS)

Polystyrene-co-4-vinylpyridine copolymer (PSVP), prepared by emulsion copolymerisation, has been shown to become miscible with zinc neutralised sulphonated EPDM (Zn-S-EPDM) by interpolymer complex formation.[109,110] Coordination-type interaction (Scheme 1.4) between the pyridine group and transition metal was confirmed by infra-red analysis and gave an almost single phase system at the stoichiometric ratio of interacting moieties. Over a wider range of compositions, PSVP/Zn-S-EPDM blend characteristics were significantly different to the grossly immiscible PS/Zn-S-EPDM blends and thus demonstrated the attainment of partial compatibility.

Reactive compatibilisation of PS/PE blends and the improvement of rubber toughening in PS/NBR mixtures have been detailed by Baker and fellow researchers in their work on oxazoline-containing polystyrene copolymers (OPS).[8,9,111,112] Co-reactive carboxylic acid-modified polymers (CPE and XNBR respectively) were coupled with OPS during melt mixing to form in-situ compatibiliser and thus modify blend properties. From

Scheme 1.4 Coordination-type Interaction Between PSVP and Zn-S-EPDM.



initial work on OPS/CPE blends, changes in torque behaviour, phase structures and thermal properties were all attributed to this coupling reaction[8] (Scheme 1.1 - Section 1.2.2). The presence of interpolymer product was supported by solubility studies on the alloys and detection of amido-ester linkages, as expected from model studies. Reaction rate was found to be limited by mass transfer rather than kinetic factors and the mechanical properties of certain blend compositions could be enhanced.[9]

In the PS/XNBR blend, major increases in impact strength were obtained only at low OPS levels.[112] At high OPS content, the dispersed phase size was readily reduced below the optimum for rubber toughening and thus impact resistance was correspondingly lowered. Attempts to control phase size and hence the characteristics of compatibilised products, involving optimisation of PS/OPS/PE/CPE compositions and blending sequence,[111] did not provide a predictive formula for product selection. Nevertheless some useful general concepts were exemplified ;

- mechanical property improvements were highly dependent on blend composition; at high PS gains in strength only could be expected, whereas high PE large increases in extensibility were coupled with respectable tensile strength.

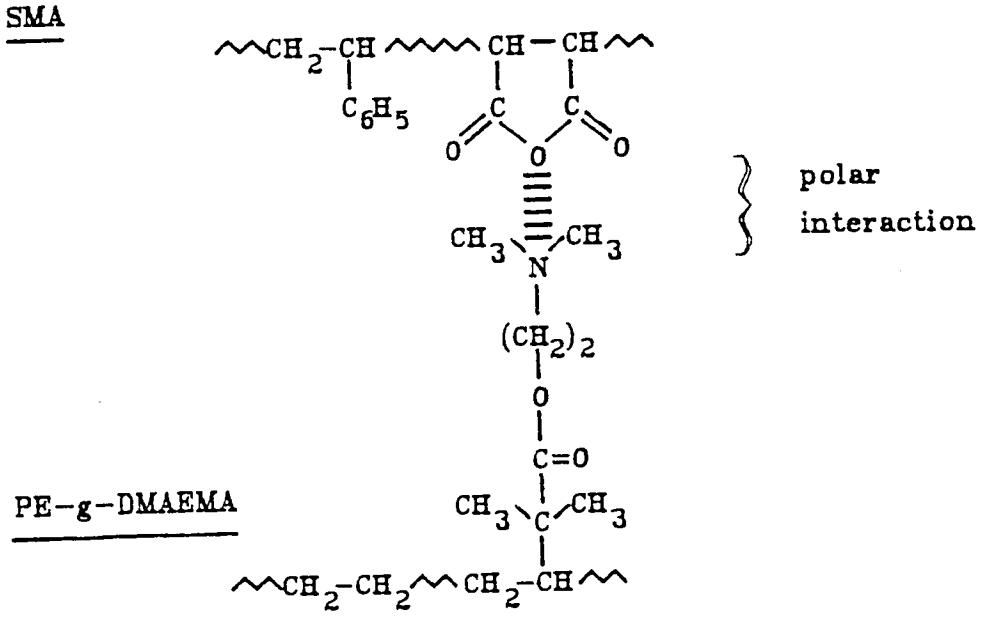
- low concentrations of reactive components were effective ; the greatest tensile strength was not with OPS alone but when diluted with inert PS.

- pre-reacted OPS/CPE mixtures and direct blending of unreacted components were both shown to improve compatibility, though "in situ" reactive compatibilisation was far superior.

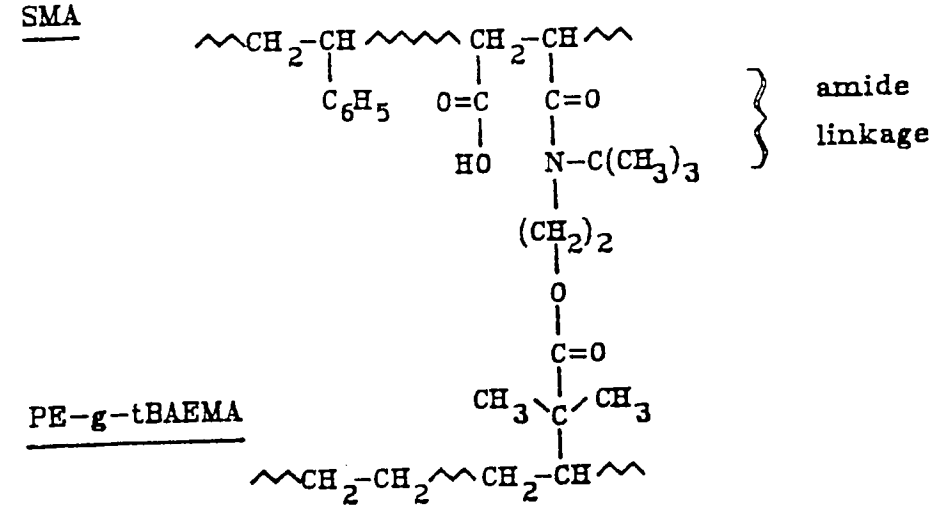
Recent research by Baker has employed polar interactions between acid and base functionalities on polymer to induce compatibilisation in PS/PE blends.[113,114] Styrene-maleic anhydride copolymer (SMA) contained acidic groups to interact with tertiary

dimethylaminoethylmethacrylate (DMAEMA) or secondary t-butylaminoethylmethacrylate (tBAEMA) amine groups grafted to PE. Dramatic reductions in phase size were found as evidence for compatibilisation and were attributed to the lowering of interfacial tension by strong polar interactions between the PSMA and modified PE (Scheme 1.5a). With the

Scheme 1.5a Polar Interaction Between SMA and PE-g -DMAEMA



Scheme 1.5b Possible Interpolymer Product From Reaction Between SMA and PE-g-tBAEMA.



tertiary amino PE (PE-g-DMAEMA) there was no evidence for any covalent bonding.[113] Slightly more compatibilisation by PE-g-tBAEMA was believed to result from limited reaction of the secondary amine (Scheme 1.5b). PSMA-g-tBAEMA-g-PE compatibiliser was believed to have been produced in-situ, supported by major changes in rheological and thermal properties. Physical property improvements were moderate and again highly dependant on blend composition (in a similar fashion to the work of Baker and Saleem with OPS/CPE[111]).

1.4.2.2 Modified Polystyrene.

Oxidised polystyrene containing peroxide groups was also used by Slusarski and Kuczynski in blends with NBR.[108] Unsaturation in the elastomer was reactive to the modified PS improving blend compatibility, though not to the same extent as the organosulphur-terminated copolymers previously mentioned (Section 1.4.2.1).

Sulphonation has been a popular method of polymer modification and has recently been reported for use with PS to improve compatibility in blends. Molnar and Eisenberg found that the compatibility of PS/nylon 6 blends was improved by the introduction of sulphonic acid groups into the PS (SPS),[115] probably by protonation of amide and amine nitrogens in the nylon. Only low levels of sulphonation were necessary, but simultaneously with compatabilisation, acid catalysed degradation of the PA6 occurred, reducing molecular weight by hydrolytic chain scission. However, the more strongly interacting lithium neutralised SPS enhanced miscibility without causing hydrolysis, though this was for a solution rather than melt blend.

Sulivan and Weiss have successfully employed ionomeric and sulphonic acid modified PS (SPS) in melt blends with an amorphous polyamide.[116] Light sulphonation produced considerable reduction in phase sizes and shifts in thermal transitions as

compatibility was enhanced, to the extent that single phase, single Tg, fully miscible blends were possible at high SPS contents. Hydrogen bonding between sulphonic acid and amide groups was identified by infra-red spectroscopy as the mechanism of this powerful miscibilising interaction.

1.4.3 Mechanochemical Grafting.

Copolymer synthesis by mechanochemical reaction has been shown by many methods[24] ; of particular interest is the formation of block copolymers when two polymers are intensely blended in a shearing mixer. Under these conditions mechanochemical scission leads to radical initiated block interchange and reduction in blend immiscibility.[78] The further addition of radical initiators is complementary to this process and has been used by several groups in polystyrene blends.

Scott et al[25] melt mixed PS and LDPE in the presence of cumene hydroperoxide and achieved high yield of interpolymer product. Properties of this compatibilised system were not detailed, as the aim was to use this as SPD in further blends (see Section 1.4.1). Similarly this process was attempted in PS/natural rubber blends by Slusarski and Kuczynski,[108] but resulting compounds were found to be non-advantageous. Polystyrene was included in an extensive series of blends between elastomers and plastics in the work on "dynamic vulcanisation" by Coran.[28] In blends with eleven elastomers and suitable initiating agents the resulting property combinations were not particularly useful, so did not warrant detailed examination for interpolymer grafting and "technological compatibilisation."

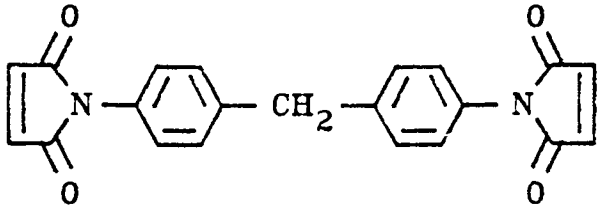
Greater success with mechanochemical grafting was achieved by Pukanszky et al in melt blends of PS and ethylene-propylene-(diene) co- and ter-polymers [EP(D)M] using Lewis acid initiators.[117,118] Complex physical and chemical transformations occurred

upon addition of $AlCl_3$ to PS and EP(D)M when processed separately, attributed to a sequence of carbocationic induced degradative reactions.[119,120] When applied to the blends, grafting between components was generally dominant to competitive degradation and cross-linking reactions, according to the amount and structure of the unsaturated units in the EPDM.[117] Further optimisation of the system showed the influence of the high reactivity of the EPDM phase : grafting with PS was prevalent at high Lewis acid addition, but with less initiator cross-linking of the elastomer itself was more extensive.[118] Torque changes were related to the coupling reaction and degradative processes were excluded. Blends containing chemically coupled components showed minor improvements in mechanical properties ; suspected to be from "increased solubility" of the grafted rubber in the PS phase - ie compatibilisation via mechanochemical grafting.

1.4.4 Addition of Reactive Agents.

The effect of a highly reactive difunctional agent has been compared directly with copolymer compatibilisation in blends of PS and LDPE by Lambla et al.[97] Peroxide initiators were not incorporated since they were believed to cause chain degradation and lower the mechanical strength of PS. Bis-maleimide (XIII) was used for its reactivity towards tertiary hydrocarbon sites and showed some limited gains in mechanical properties, though not as great as for SEBS copolymer addition (Section 1.4.1).

XIII

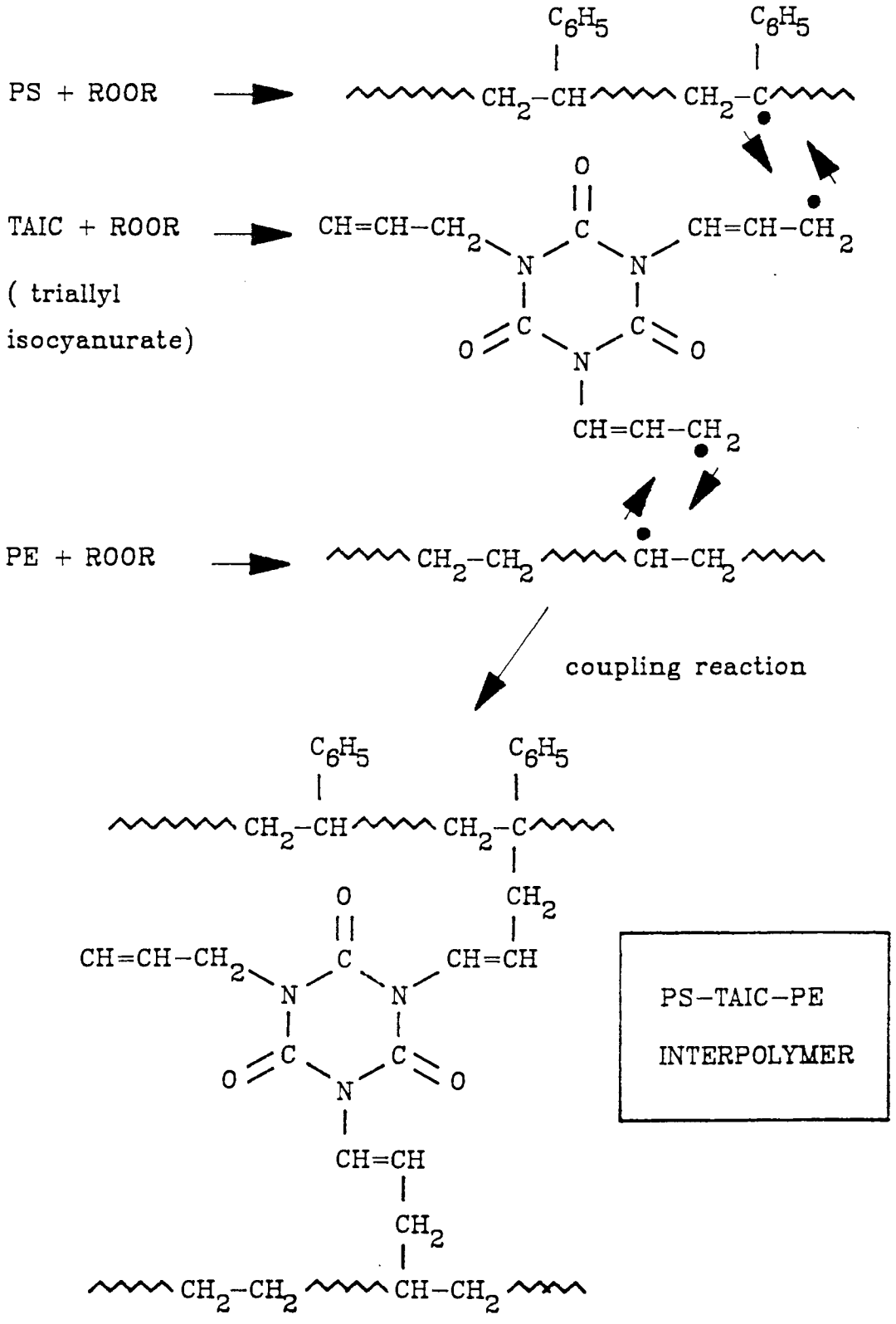


bis-maleimide

The reactive extrusion of PS/LLDPE blends with dicumyl peroxide (dcp) and triallyl isocyanurate (TAIC) coupling agent was investigated by Rudin and van Ballegooie[121,122] to assess the benefits of in-situ PS-PE graft formation. The yield of PS-TAIC-PE graft was found to strongly depend on the level of coupling agent, which caused correspondingly higher torque on extrusion. Phase size was reduced and interfacial adhesion appeared to be raised in reactive blends, indicating enhanced compatibility. Improvement in physical properties were not large, although graft formation clearly gave a net positive effect. PS copolymer of enhanced reactivity (due to an easily abstractable aldehydic hydrogen from ortho-vinylbenzaldehyde copolymerised with styrene) was shown to give more PS-PE graft product and slightly higher compatibilisation, though without any greater mechanical properties. With high molecular weight PS although grafting levels were similar to low molecular weight analogues and interphase compatability was also enhanced, physical properties were generally not improved. A semi-continuous two phase morphology was generated in blends with the more viscous (high MW) PS and this had a more dominant effect on the mechanical properties than interfacial stabilisation by chemical grafting.

Subsequent work by Rudin and Teh[123] on this same system explored further the concept of competition between "within phase" cross-linking and "across phase" grafting reactions touched upon in the first study. In reactively extruded 90/10 PS/PE blends, low TAIC/dcp was considered to result in predominantly PE-PE coupling. PS-TAIC-PE coupling reaction was then thought to become prevalent at higher reactive agent additions to the final extent of almost total compatibilisation of the PE phase. This was proposed to be between peroxide-generated free radicals of TAIC, PS and PE (Scheme 1.6) and anticipated to be favorable to competitive processes when efficiently mixed in the melt (ie PS-TAIC-PE > PE-TAIC-PE > PS-TAIC-PS). Impact resistance was low in all reactive

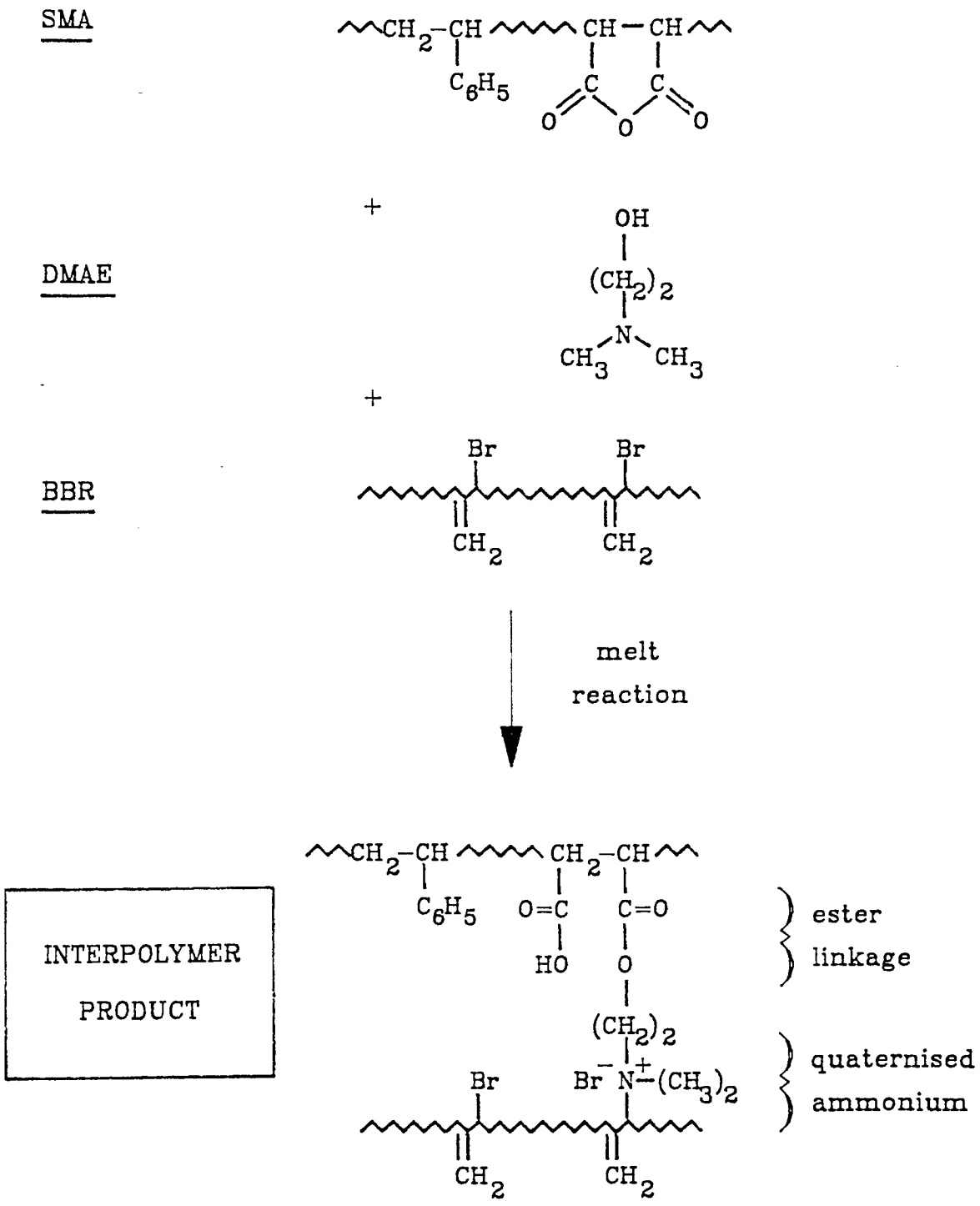
Scheme 1.6 Proposed Free Radical Coupling Reaction Between Polystyrene, Polyethylene and Triallyl Isocyanurate.



blends and deteriorated with TAIC/dcp addition level. Progressive compatibilisation was proposed as the prime cause of these effects, but data given on thermal properties, molecular weights and morphology did not entirely fit, thus a rather contrived argument was needed to reach this conclusion. The most simple explanation, supported by the data, was significant degradation of the PS phase. This was feasible considering the high level of initiator added with TAIC (1:1 by weight to a maximum 1%) and chain shortening was indeed shown by molecular weight analysis. It appears that a key principle in the use of reactive agent addition was not realised in this work, namely that inducement of reaction must not cause degradation of homopolymer or have any negative impact on component characteristics.

The use of a reactive agent with functionalised polystyrene copolymer (polystyrene-co-maleic anhydride - SMA) and modified elastomer (bromobutyl rubber - BBR) has been examined by Willis et al and was found to produce considerable compatibilisation of the blends.[124] The hydroxyalkylamine, dimethylaminoethanol (DMAE), was shown to react with each component alone and believed to react with both simultaneously in blends to produce chemical interlinking of the two polymers (Scheme 1.7). Ester formation was confirmed in the blend, as expected from reaction of SMA and DMAE, though analysis for the quaternised BBR-DMAE product was not possible due to insolubility of reactive blends, presumably due to grafting with the SMA. Morphological changes with DMAE addition were dramatic; BBR domains were reduced to almost constant sub-micron phase size, almost independent of rubber concentration (unlike unmodified blends). Promotion of good interfacial adhesion at high DMAE addition was proposed as a mechanism for the attainment of higher impact strengths than modified blends with lower DMAE content, which had similar morphologies to the high DMAE mixtures yet gave no improvement in impact strength over unmodified compositions

Scheme 1.7 Proposed Reaction Between Poly(styrene–co–maleic anhydride), Dimethylaminoethanol and Bromobutyl Rubber.



Functional polystyrene copolymers have also been used as polymeric reactive agents with polyamides to generate in-situ compatibiliser for interfacial stabilisation in otherwise fully immiscible blends between PS and polyamides. In the early work by Ide and Hasegawa[17] a polystyrene co-methacrylic and copolymer (PS-co-MAA) was shown to react with nylon 6, yielding an interpolymer product which remarkably improved dispersibility in a blend with polystyrene.

Fayt and Teyssie[125] further advanced the use of reactive copolymers with polystyrene-b-methylmethacrylate (PS-b-PMMA) in PS/nylon 6 (PS/PA6) blends. The copolymer was synthesised by well controlled anionic polymerisation methods and a variant produced by partial hydrolysis, to give fairly low levels of methacrylic acid groups randomly within the PMMA segments (ie PS-b-P(MMA-co-MAA)). Copolymer addition to PS/PA6 blends in low concentration promoted massive reduction in phases sizes (Table 1.6). The parent methacrylate copolymer was capable of a limited degree of reaction with

Table 1.6 **Morphology and grafting of polystyrene-methacrylate copolymers in 50/50 polystyrene/nylon 6 blends.[125]**

Added Copolymer (at 5% w/w blend)	Range of phase sizes (microns)	% Copolymer Grafted to Nylon 6
nil	20 - 100	-
PS - b - PMMA	5 - 50	30
PS - b - P(MMA-co-MAA) [3% MAA]	1 - 3	-
PS - b - P(MMA-co-MAA) [8.5% MAA]	0.5 - 1	98

the polyamide, but was eclipsed by almost total conversion of the carboxylic acid-containing copolymer to interpolymer product with PA6 during blending. Although the morphological action of reactive copolymer was unambiguously demonstrated, reaction pathways, compatibilising mechanisms and resulting properties were the subject of ongoing investigations and not reported. It was expected however, that the carboxylic acid and ester groups could undergo exchange reaction with the amide units as seen in other polycondensate blends.[20-23]

Polystyrene-co-maleic anhydride copolymer (SMA) is a speciality grade of PS,[82] with higher heat resistance than the homoploymer, but has also been examined as an additive for reactive compatibilisation of polystyrene and polyamide blends.[126-128] Reaction between maleanised polyolefins and amine groups in polyamides has been extensively detailed[14-16] (see 1.2.3), however the chemical action of SMA is less clear. Chen et al[126] showed considerable reduction in domain size, prevention of coalescence on re-heating and independence of phase size from blend composition for a minor addition of SMA to PS/PA6 blends. No changes in thermal properties were detected by DSC analysis of these ternary blends, leading to the conclusion that only a weak physical interaction was involved, with SMA concentrated at the interface lowering interfacial tension as an effective emulsifier. However, contradictory data was also presented in that blends of PA6/SMA above 80% PA6 were completely homogeneous and the SMA glass transition was absent in DSC traces. Furthermore, with the increased viscosity of PS/PA6/SMA blends there was sufficient evidence to feasibly suggest that a reactive process between PA6 and SMA had produced in-situ SPD for compatiblisation and even near complete miscibilisation at high PA6 content in binary SMA/PA6 blends.

A more positive presentation of the reactive compatibilisation of PS/PA66 blends by SMA was made by Chang and Hwu.[127] Reductions in phase size and viscosity increases were similar to the previous study,[126] with even low molecular weight functionalised copolymer. Changes in thermal properties of PA66/SMA blends were attributed to the presence of PA66-SMA interpolymer product, presumed to have been formed by anhydride reaction with PA66 amine ends. This was isolated by solvent extraction, showing a yield of around 12% from a 50/50 blend, and infra-red analysis was used to confirm the mixed PA-SMA functionalities. Although compatibilised blend modulus increased, toughness was significantly reduced. It was postulated that unreacted SMA caused embrittlement of the nylon phase, resulting in reduced matrix toughness which negated any rise in interfacial adhesion by interpolymer compatibiliser. This is believed to be a fundamental concept previously neglected ; there is no guarantee of toughness improvement by enhancing compatibility due to competition between advantageous changes in blend morphology and adhesion, and disadvantageous change in components. In the same work, a styrene-glycidyl methacrylate copolymer (SGMA) was also assessed and found to give a greater compatibilisation effect,[127] presumably because of higher reactivity to nucleophilic and electrophlic sites in the polyamide (see Section 1.2.3 and [43]). Morphology was too fine to favour impact strength improvement over mechanical PS/PA66 blends, but tensile strength and elongation were significantly raised. In this instance beneficial changes from compatibility enhancement by interpolymer reaction exceeded any within-phase negative factors producing net positive results.

Further work with SMA random copolymer, recently by Paul et al,[128] confirmed its suitability for reactive compatibilisation in PS/PA6 blends. SMA was compared directly with lower molecular weight anhydride-ended styrene oligomers, intended to readily diffuse between phases in the interfacial region and react to yield suitable block

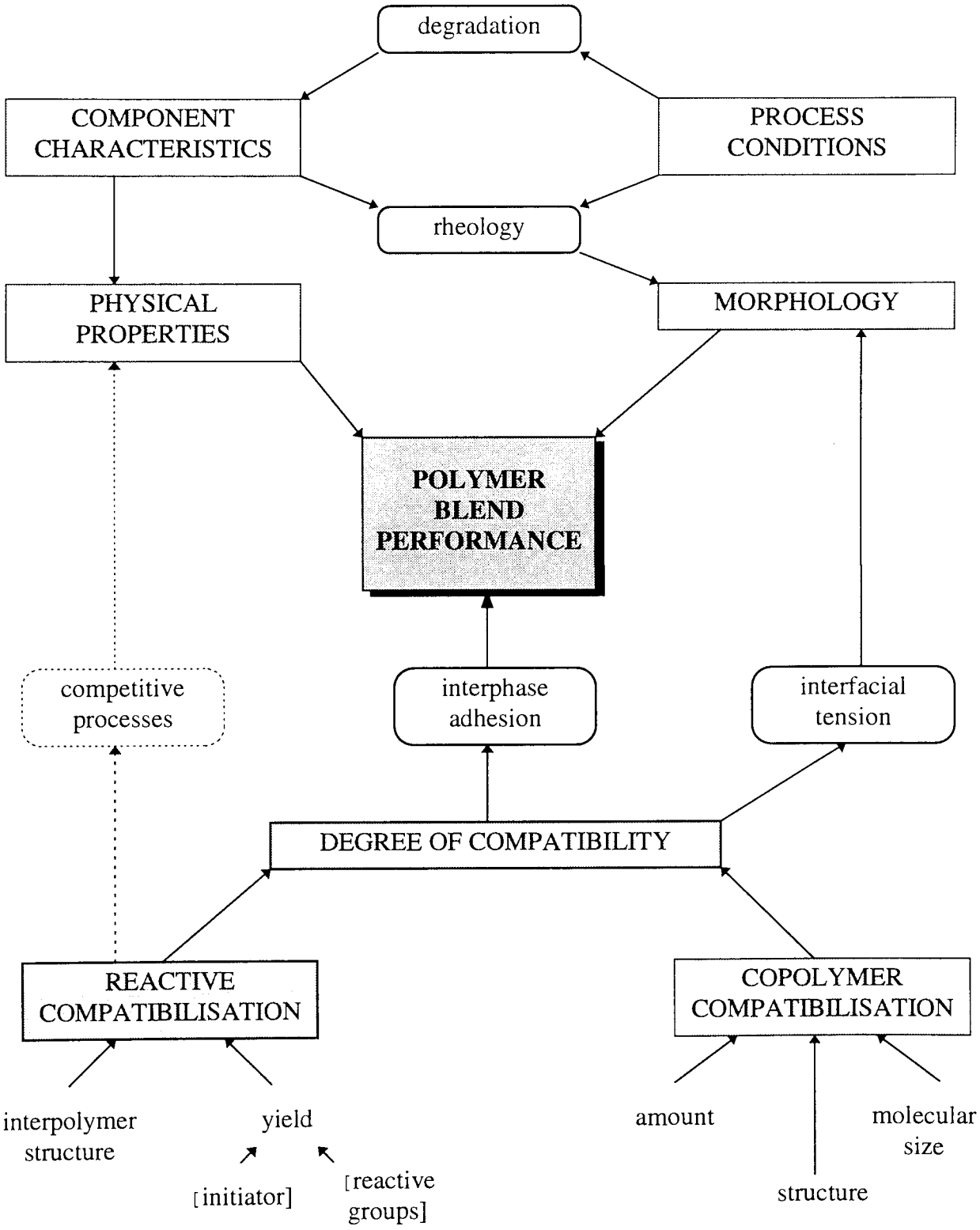
copolymers. These were not as effective as the SMA which gave higher yields of interpolymer and correspondingly greater changes in phase size and adhesion between the two dissimilar polymers. It was suggested that the SMA produced comb-like graft copolymer upon reaction due to the numerous functional sites along the chain. This form of interpolymer was believed to result in a greater anchoring effect between the phases than inadequately entangling, shorter chain, block copolymers. The mechanism of interfacial reaction was not successfully characterised ; a model study using phthalic anhydride with PA6 confirmed the occurrence of reactive events but was inconclusive as to whether terminal amine and hydrolytic chain scission, or amide linkage reaction were dominant. Anhydride functionalised styrene copolymers are thus clearly effective reactive compatibilisers in PS/PA blends. However, as with most of the reactive processes reviewed, sufficient understanding to enable complete control of these techniques has not yet been realised.

1.4.5 Overall Perspectives

From examination of the different ways in which compatibilisation has been attempted for blends incorporating polystyrene, an overall scheme of key learnings on the interrelationships between influencing factors and compatibilising effects on the performance of immiscible blends has been developed (Scheme 1.8).

The enhancement of blend performance is often achieved by a reduction in immiscibility between components rather than complete miscibilisation ; maintaining a stabilised two-phase morphology which generates advantageous behaviour. The degree of compatibility is not the only significant factor in such a system however, component characteristics contribute greatly to the ultimate blend properties and, in combination with the processing conditions, strongly influence blend morphology which is especially

Scheme 1.8 **Interrelationships between influencing factors and compatibilising effects on the performance of immiscible polymer blends.**



important. Although different approaches to compatibilisation have been attempted the mode of action is common ; reduced interfacial tension and increased interphase adhesion cause phase size to drop dramatically and improve stress transfer between phases, allowing favourable property combinations to be expressed.

Key factors for interfacial action of copolymer compatibilisers are molecular size, structure and compliance with the minimal amounts needed for optimum effect. It may be expected that interpolymer products formed in-situ by reactive agents are equivalent to copolymer compatibilisers and thus behave similarly. However, the most dominant feature in these blends is the balance between the desired across-phase reaction and within-phase competitive effects, including degradation of homopolymers. The primary controlling factor in reactive compatibilisation is thus the concentration of reactive agents, especially initiators ; "judicious" levels often give optimum results, minimising disadvantageous processes but at the expense of interpolymer yield.

It is apparent from the literature on polystyrene blends that there is not yet universal consensus on the most effective approach or even any particular agent for compatibilisation of the commonly studied systems (mostly PS/polyolefins). Many criteria can be suggested for the judgement of a best approach, such as technical effectiveness, process versatility, operational requirements, marketable value and commercial viability. Realistically however, the adoption of novel methods at production scale depends heavily upon the latter, less easily measurable techno-commercial factors even if successful compatibilisation of a useful blend is proven. As these aspects have hardly been considered in the scientific literature some pertinent comments may be appropriate.

Modern commercial blending operations are likely to be based around multi-purpose twin screw extruder systems, especially reactive processes (Section 1.2.1). The addition

and dispersion of minor amounts of solid blend components does not pose any great technical problems for such equipment. Indeed, the handling of another polymer, either a copolymer compatibiliser or functionalised polymer, may be preferable to liquid reactive agents which can be inherently more hazardous and need more involved ancillary engineering for safe use and storage (especially in the case of organic peroxide initiators). Supplies of speciality polymers, critical to the compatibilisation process would need to be assured, so if not already commercially available the installation and operation of dedicated preparation facilities could be required. Additional primary processing could adversely effect other operational factors, including environmental impact if solvent-based or energy intensive. This would be partly reflected in the cost of such speciality polymers, which if only needed in small volumes would not offer any economies of scale and be artificially expensive anyhow. Low molecular weight reactive agents may thus have some advantages in terms of costs and availability, especially if fairly common compounds can be shown to be applied effectively (eg maleic anhydride, acrylic acid, divinyl benzene). Potent reactive agent formulations may also be more readily transferable to different blends, unlike component-specific compatibilisers. The most versatile use of this approach could be with multiple extruder systems in which one or both polymers undergo controlled modification just prior to the blending step, avoiding any intermediate processing. Reactive compatibilisation thus appears to satisfy some of the prime techno-commercial factors. This is reinforced by the growing interest in this topic, focused on releasing its potential for delivering the required technical effectiveness.

The ultimate outcome of compatibilisation is obviously formation of a single phase, miscible blend from the two polymers. There are several examples of polystyrene blends that are claimed to be at least "almost fully" miscible. Most of the approaches attempted

are included in these (Table 1.7), with one notable exception - copolymer compatibilisers are not able to fully miscibilise blends and their action is purely one of interfacial stabilisation, as polymeric emulsifiers.[67-69,85] In other cases, miscibility may be approached, but only at particular compositions. However, outside of this condition there is often sufficient interaction or interpolymer yield for multiphase, compatibilised systems of favourable characteristics to result. Successful compatibilisation in practical terms is the achievement of such systems and may be gauged by the useful gains in physical properties obtained.

Table 1.7 **Examples of almost fully miscible polystyrene blends from different approaches to compatibilisation.**

Approach to Compatibilisation	Blend	Outcome	Interaction	Ref
1. Functionalised PS Copolymer	PSVP / Zn-S-EPDM	almost single phase at stoiciometric ratio	co-ordination bonding	109
2. Modified PS	SPS / amorphous PA	single phase, single Tg at high SPS	hydrogen bonding	116
3. Reactive PS Copolymer	SMA / PA6	homogeneous, single Tg at >80% PA6	reaction ?	126
4. Reactive PS Copolymer	SMA / PE-g-tBAEMA	major changes in thermal and rheological properties	polar interaction and reaction	114
5. Reactive Agent Addition	PS / PE (90/10) + TAIC/dcp	almost total disappearance of PE phase at high TAIC/dcp	coupling reaction	123

Polymer Abbrevations :

PSVP - polystyrene-co-4-vinylpyridine
Zn-S-EPDM - zinc neutralised sulphonic acid modified EPDM
SPS - sulphonic acid modified PS
SMA - styrene-co-maleic anhydride copolymer
tBAEMA - t-butylamino ethylmethacrylate (grafted to PE)
TAIC/dcp - triallyl isocyanurate / dicumyl peroxide mixture

Using the degree of improvement as a measure of compatibilisation effectiveness, the relative merits of the many approaches attempted have been assessed. The percentage difference in ultimate strength, elongation and impact strength (where given) between the compatibilised and control blends for the key results from many of the studies referred to in this chapter have been compared directly (note - positive value indicates increase over control, negative is reduction)..

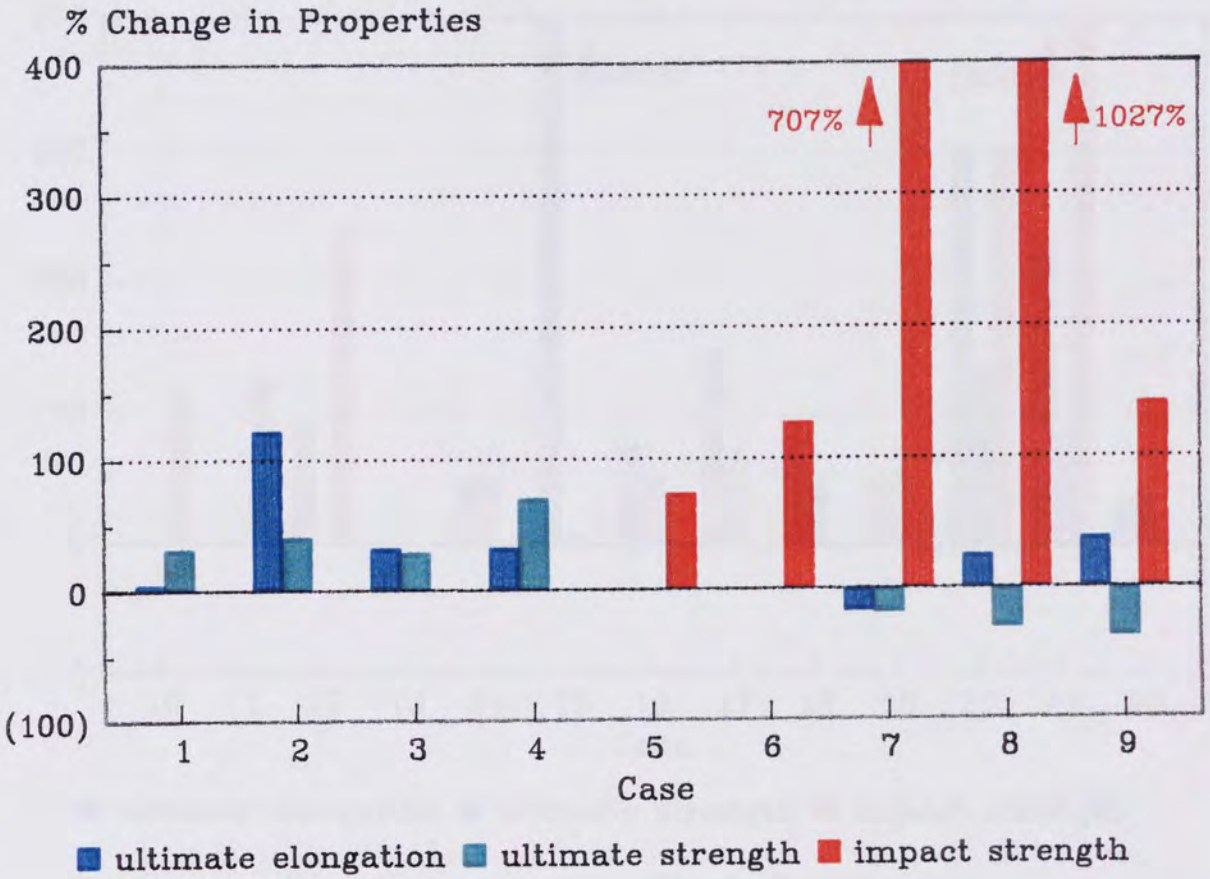
For graft copolymer compatibilisers (Figure 1.2) only modest gains in the characteristics of PS/LDPE blends have been achieved irrespective of molecular structure or amount (cases 1-6). Much greater change was found in blends with an elastomeric component (cases 7-9 : PS/EPR), in which the addition of suitable graft copolymer (PSgEP) produced orders of magnitude increases in impact strength (but with some reduction in ultimate tensile properties).[87,104]

For block copolymer additions (Figure 1.3) dramatic improvements in PS/LDPE physical properties have been obtained, depending on addition level and molecular structure. Considerable gains in impact strength have been shown with pure diblock copolymers[86] (cases 10-12), though these did not match the massive increases caused by large additions (20%) of mechanochemically synthesised SPD block copolymer[25] or SEBS triblock compatibilisers[71] which also had a large positive effect on tensile properties (cases 20 & 21). However for a lower addition (2%), SBS triblock copolymer was not as effective as diblocks, suggesting that at high compatibiliser contents, the nature of the additional phase may be more important than the compatibilising mechanism. The optimum balance of property improvements from minimal addition was found for tapered diblocks (cases 17-19) and accredited to the high interfacial activity of these agents.[87,100,103]

Reactive compatibilisation effectiveness has ranged from reduced blend performance to orders of magnitude improvements (Figure 1.4). In general blends containing high levels of functionalised polymers have been shown to give modest to large property increases (cases 23-29), especially when complete miscibility is approached (case 23 : PSVP/Zn-S-EPDM). However, the use of low molecular weight reactive agents (cases 32-36) or low levels of reactive polymers (cases 30 & 31) has been less successful ; many blends have shown little improvement and even decreased physical properties. With functionalised polymers in high concentration, reaction is more likely to occur within the interfacial regions between phases, chemically coupling dissimilar polymers together to the benefit of blend behaviour. For the more readily diffusible reagents it may be that the negative effects of competitive, within-phase reactions predominate over any positive interfacial action.

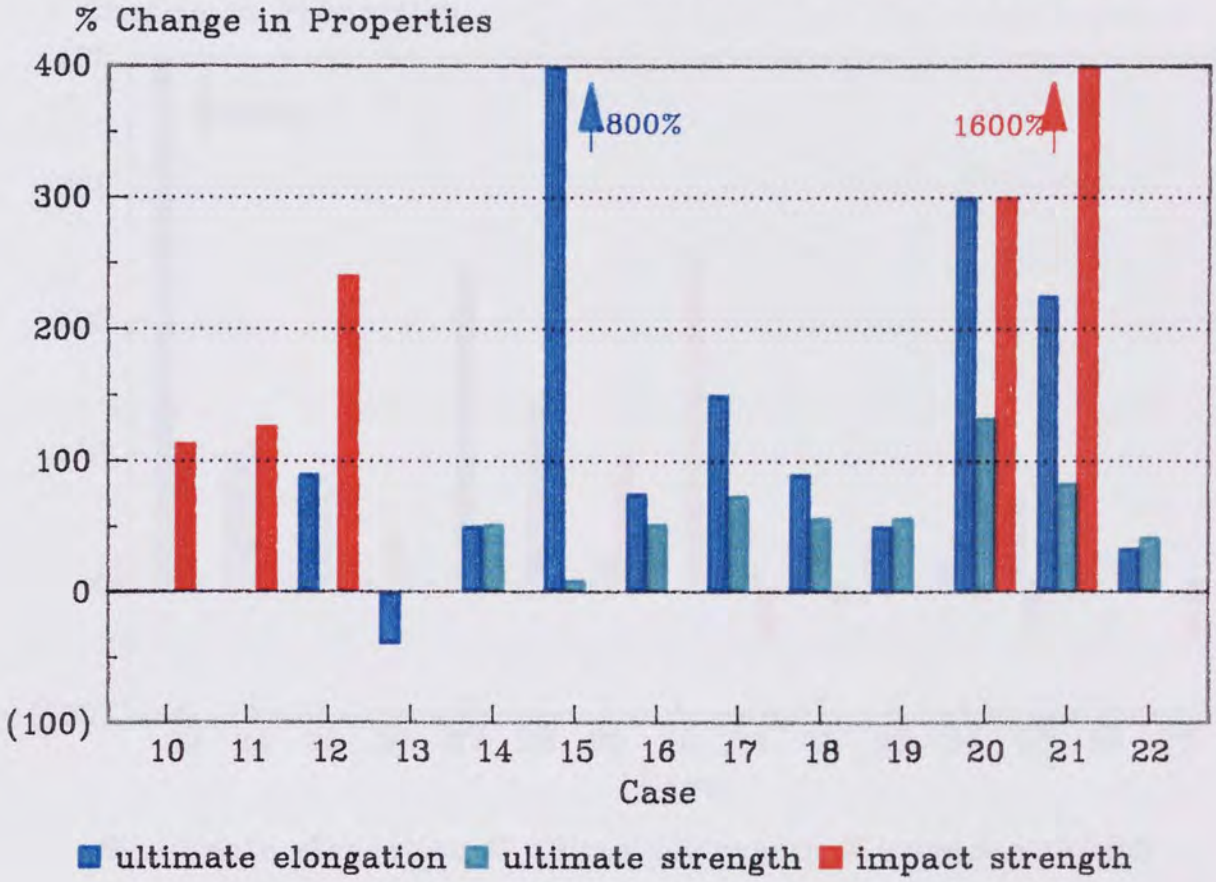
There is thus plenty of scope to unlock the potential of a reactive blending approach; however favourable this seem techno-commercially, it has not yet been fully delivered in performance terms. It is hoped that this present study will make a positive contribution to this problem and yield opportunities for the successful application of reactive processing using interlinking agents for polymer blend compatibilisation.

Figure 1.2 Measurement of the Effectiveness of Graft Copolymer Compatibilisers by Changes in Physical Properties.



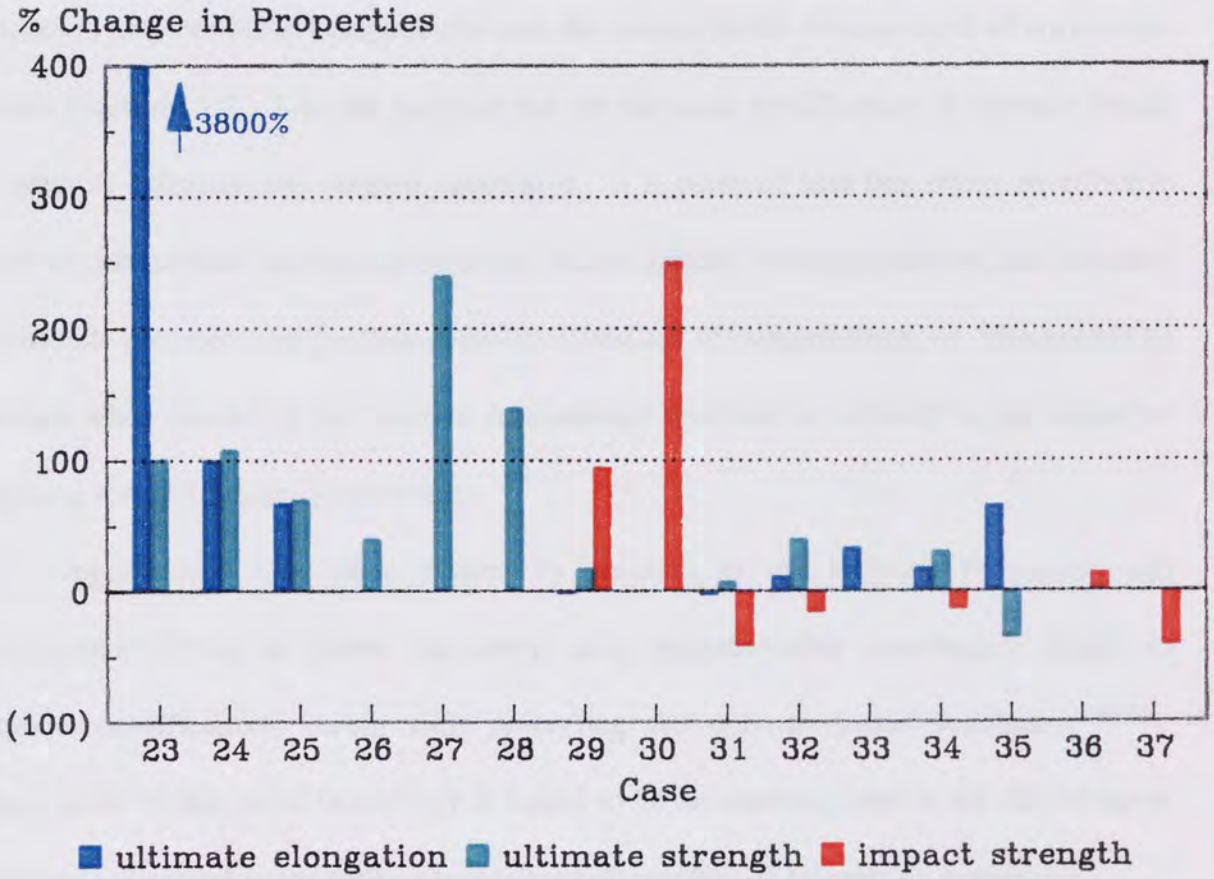
Case	Blend		Graft Copolymer		
1	PS/LDPE	50/50	PE–g–PS	+ 10%	[88]
2	PS/LDPE	50/50	PE–g–PS	+ 33%	[88]
3	PS/LDPE	75/25	PE–g–PS	5% of PE	[89]
4	PS/LDPE	75/25	PE–g–PS	30% of PE	[89]
5	PS/LDPE	85/15	PE–g–PS	5% of PE	[86]
6	PS/LDPE	85/15	PE–g–PS (partly cross–linked)	5% of PE	[86]
7	PS/EPR	75/25	PE–g–EP	30% of EPR	[87]
8	PS/EPR	75/25	PE–g–EP	100% of EPR	[87]
9	PS/EPR	80/20	PE–g–EP	100% of EPR	[104]

Figure 1.3 Measurement of the Effectiveness of Block Copolymer Compatibilisers by Changes in Physical Properties.



Case	Blend		Block Copolymer		
10	PS/LDPE	85/15	PS–b–PE	5% of PE	[86]
11	PS/LDPE	85/15	PS–(PS/PE)–PE (uneven)	5% of PE	[86]
12	PS/LDPE	85/15	PS–(PS/PE)–PE (even)	5% of PE	[86]
13	PS/LDPE	85/15	PS–(PS/PE)–PE (even)	30% of PE	[86]
14	PS/LDPE	80/20	PS–b–PE (low MW)	+ 9%	[85]
15	PS/LDPE	80/20	PS–b–PE (high MW)	+ 9%	[85]
16	PS/LDPE	80/20	PS–b–PE (mid MW)	+ 9%	[100]
17	PS/LDPE	80/20	PS–(PS/PE)–PE	+ 9%	[100]
18	PS/LDPE	80/20	PS–(PS/PE)–PE	+ 2%	[87]
19	PS/LDPE	80/20	PS–(PS/PE)–PE	+ 0.5%	[87]
20	PS/LDPE	50/50	PS–b–PE (SPD)	+ 20%	[25]
21	PS/LDPE	50/50	SEBS	+ 20%	[71]
22	PS/LDPE	85/15	SEBS	+ 2%	[97]

Figure 1.4 Measurement of the Effectiveness of Reactive Compatibilisation by Changes in Physical Properties.



Case	Blend		(Reactive Agent)		
23	PSVP/Zn–S–EPDM	50/50			[110]
24	OPS/PS/CPE	35/35/30			[111]
25	OPS/CPE	70/30			[111]
26	PST/NBR	10/90			[108]
27	PSTS/NBR	10/90			[108]
28	PSO/NBR	10/90			[108]
29	SMA/PE–g–tBAEMA	70/30			[114]
30	SMA/BBR	80/20	+5%	DMAE	[124]
31	PS/PA66	50/50	+5%	SMA	[127]
32	PS/PA66	50/50	+5%	SGA	[127]
33	PS/EPDM	60/40	+10%	$NaCl.AlCl_3$	[118]
34	PS/PE	85/15	+0.5%	BM	[97]
35	PS/PE	50/50	+2.5%	4:1 TAIC:dcp	[121]
36	PS/PE	90/10	+0.4%	1:1 TAIC:dcp	[123]
37	PS/PE	90/10	+1%	1:1 TAIC:dcp	[123]

1.5 RESEARCH OBJECTIVES AND STRATEGY.

From the comprehensive reviews of literature on the technology of reactive extrusion, polymer blend compatibility and, the compatibility enhancement of polystyrene blends (Sections 1.2 - 1.4), the potential for the chemical modification of polymer blends by reactive extrusion has seemed impressive. It is believed that this offers an effective route to systems with superior performance characteristics over physically mixed blends of immiscible polymers and possibly even other methods of compatibilisation. This should be realised when control of the reaction mechanisms involved is achieved to the extent of targeting specific advantageous effects.

Opportunities have been created by research in the Polymer Processing and Performance Group at Aston University using polymerisable interlinking agents to promote modifications during melt processing for polymer-bound stabilisers.[44,129] Application of this novel technology is hoped to be an enabling step in the delivering of effective compatibilisation for heterogeneous polymer blends by reactive processing.

The primary objective of this research project was thus to examine the concept of reactively processing immiscible polymer combinations with interlinking agents to raise the level of compatibility for improved blend performance. It was realised early on that there was a very wide scope to this research programme, different approaches to processing were numerous and investigational aspects were extensive. Hence this was intended to be a path-finding venture to position the above concept within the context of blend compatibilisation and determine the relative merits of interlinking agent technology for this application. This required identification and development of suitable experimental-scale processing and characterisation techniques to provide understanding of the chemical and physical processes involved. It was thus more appropriate to operate

within a simple process system, namely a small internal melt mixer, before considering large scale reactive processing using more complicated extrusion equipment.

The general method of reactive processing applied in this research was to target peroxide-initiated free radical reactions of both polymer components during melt blending concurrently with the addition of interlinking agents (ie trimethylolpropane triacrylate {TRIS} and divinylbenzene {DVB} - IX and XI, page 29). The intention was to synthesise interpolymer in-situ via polymer-bound interlinking agent for compatibilisation of the blend in a one-step reactive blending process. Key process parameters were to be identified and controlled to optimise interpolymer formation. Attempts to understand how reactively formed interpolymer could influence properties of the bulk were to be made.

One component of the blend was selected to be an inert hydrocarbon polymer to provide a greater challenge for modification. The scope for enhancing the reactivity of this polymer alone by reactive processing was to be sought and applied to optimise the reactive blending. Polystyrene homopolymer was chosen as an appropriately inert hydrocarbon polymer ; also being a commercially important commodity material of limited application due to its moderate physical properties,[82,83] and thus amenable to improvement.

Elastomers have been blended with PS previously,[84] but simple melt blending has not usually been found to be as effective a route to enhanced mechanical performance as copolymerisation methods. However, PS/elastomer blends could offer compounds with more balanced and even novel property profiles than the individual components. Ethylene-propylene-diene (EPDM) terpolymers are speciality elastomers having good oxidation resistance, weatherability, and physical properties.[130-131] These characteristics are in part due to a minor content of a non-conjugated diene monomer unit, providing residual unsaturation pendant to the main chain, which does not substantially disturb the polymer backbone on cross-linking or oxidation. PS and EPDM blends have been shown

to be totally immiscible, requiring modification for useful application.[132] In compatibilised blends, EPDM could complement the properties of PS, negating the inherent brittleness of the glassy polymer by the introduction of some ductility and impact resistance according to the morphology and degree of interfacial adhesion promoted.[105] Indeed in the work of Shaw and Singh,[105-107,132] using various styrene-modified EPDMs blended with PS, changes in tensile and impact strengths were linked to increasing compatibility, by partial miscibilisation through common, and thus, interacting monomer units. For the present purposes, it was expected that the minor off-chain diene units in the EPDM would be readily susceptable to reaction with interlinking agent during processing. This would facilitate interpolymer formation during reactive blending with PS and hence modification of the miscibility level in the ultimate blend. Extensive interpolymer yields in PS/EPDM blends have been obtained according to Pukansky et al[117,118] through cross-reaction of respective polymeric radicals initiated by Lewis acids, although only minor gains in mechanical properties were delivered.

Several possibilities for the behaviour of compatibilised PS/EPDM blends can be envisaged : extension of the limited physical properties of PS at low EPDM contents, particularly impact resistance ; the generation of novel thermoplastic elastomers (TPEs) at higher EPDM contents ; and compatibilising ability, as solid phase dispersants (SPDs), in other styrenic/olefinic polymer blends. Each of these areas could provide sufficient interest for detailed research in their own right, and would realistically not all be achieved in this lone project. Therefore a "pegs-in-the-ground" approach to this research was adopted to determine the general principles involved in the chemical modification of polymer blends by reactive processing with interlinking agents, for possible future translation into the reactive extrusion of suitable blends for designed polymer systems.

CHAPTER 2

EXPERIMENTAL AND ANALYTICAL TECHNIQUES.

2.1 MATERIALS.

Two different sources of polystyrene were used in this work ;

i) **Styron 634** (DOW CHEMICAL COMPANY LTD.) - general purpose PS for extrusion, MFR 3.5 g/10 minutes (ASTM D-1238 - 5kg load, 200°C).

ii) **Crystal Polystyrene 311** (HUNTSMAN CHEMICAL COMPANY) - low flow grade for extrusion, MFR 3.0 g/10 minutes (ASTM D-1238 - 5kg load, 200°C).

One grade of EPDM elastomer was used throughout ;

Vistalon 2504 (EXXON) -composed of ethylene 50%, 5-ethylidene-2-norbornene at 3.8% and the remainder propylene monomers (**XIV**).

Interlinking agents investigated were both liquids at room temperature ;

i) **trimethylolpropane triacrylate** (TRIS, **XV**) used as supplied under the trade name of ATM12 from ANCOMER LTD.

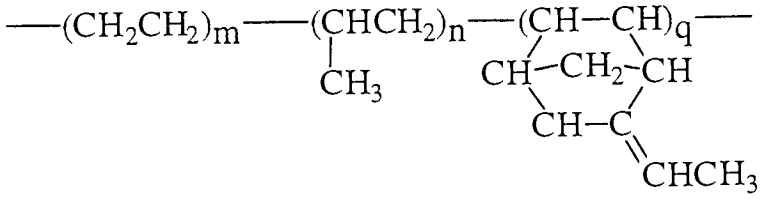
ii) **divinylbenzene** (DVB, **XVI**) technical grade from ALDRICH CHEMICALS - used as supplied, being a mixture of divinylbenzene (55%) and ethylvinyl benzene (45%), both present as meta and para-isomers.

The organic peroxide used in all work was a Noury Initiator from AKZO CHEMIE ;

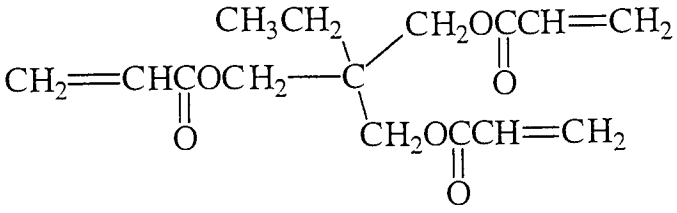
Trigonox 101 (2,5-dimethyl 2,5-bis-tertiarybutylperoxy hexane, **XVII**)

Solvents employed (methanol, dichloromethane, toluene) were laboratory reagent grades, used as supplied from FISONS or BDH CHEMICALS.

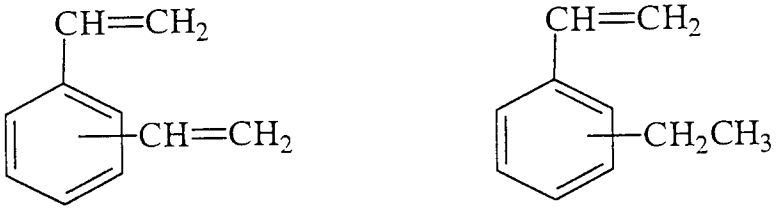
XIV EPDM (ethylene-propylene-ethylidene norbornene terpolymer)



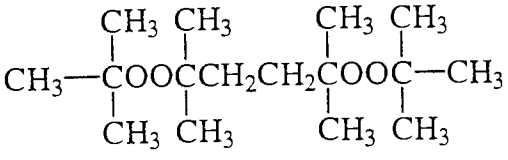
XV TRIS (trimethylolpropane triacrylate)



XVI DVB (divinylbenzene / ethylvinyl benzene mixture)



XVII Trigonox 101 (2,5-dimethyl-2,5-bis-tertiarybutylproxy hexane)



2.2 PROCESSING.

2.2.1 Preparation of Test Cells.

The EPDM elastomer was supplied as a large rubbery slab, quite unlike the hard, free-flowing pellets of the much easier to handle polystyrene. Thus, before preparing any blends the EPDM was cut into wafers, then strips and finally small granules of a similar size to the polystyrene (maximum 3mm squared).

It was found that 35g of polystyrene completely filled the mixing chamber of the HAMPDEN-RAPRA Torque Rheometer (TR), so that this quantity was chosen as a consistent charge for every test cell processed. 35g of EPDM and its blends would be expected to fill a slightly larger volume than PS alone ; this was accommodated for by the loading ram resting in a a slightly different position above the mixing chamber. There was no evidence to suggest that this had any influence on the behaviour of the test cells. Blends were prepared by pre-weighing exact amounts of PS and cut EPDM into glass bottles for tumble mixing by hand before adding the whole portion to the TR.

Blends were defined as weight of component per weight of total blend expressed as a percentage :

eg 70/30 %w/w PS/EPDM = 35g total from 24.5g PS and 10.5g EPDM.

The addition level of reactive agent (RA) was expressed by the weight of RA per 35g charge of polymer or blend as a percentage :

eg 1.75g TRIS added to 35.0g PS = 5.0% RA addition level.

The amount of free radical initiator (FRI) used in conjunction with reactive agent was expressed as the molar ratio of FRI to RA :

using TRIS (MW=296) or DVB (MW=130) and TRIGONOX 101 (MW=290)

Equivalent masses for set molar ratios ;

RA mass / g	Trigonox 101 mass / g	FRI:RA molar ratio
TRIS 296.3	290.4	1.0
296.3	2.90	0.01
296.3	0.29	0.001
DVB 130.2	290.4	1.0
130.2	2.90	0.01
130.2	0.29	0.001

Where initiator was used alone with polymer by pre-addition before processing this amount was expressed by the weight of FRI per 35g charge of polymer or blend as a percentage :

eg 0.014g Trigonox 101 added to 35.0g PS = 0.04% FRI

2.2.2 Reactive Agent Addition via Solvent.

A method of adding reactive agent and free radical initiator via a volatile solvent to polymer and blends before charging to the rheometer was investigated (Scheme 2.2). Solutions of RA and FRI in methanol were prepared, set volumes pipetted on to the polymer or blend in glass bottles and mixed by hand before solvent was evaporated off using microwave heating to leave the required amount of RA and FRI coating the polymer.

Solutions Prepared : 0.175g RA (TRIS) per cm^3 methanol

0.017g FRI (TRIGONOX 101) per cm^3 methanol

Volumes added to 35g polymer or blend :

10 cm^3 RA in methanol = 1.75g RA

1 cm^3 FRI in methanol = 0.017g FRI

Addition levels : 1.75g RA per 35.0g polymer or blend = 5.0% RA

0.017g FRI per 1.75g RA = 0.001 FRI/RA mole ratio

2.2.3 Reactive Agent Addition by Direct Injection.

For this method, mixtures of RA and FRI in the required ratio were made by weighing both liquids into the same volumetric flask and refrigerating until use :

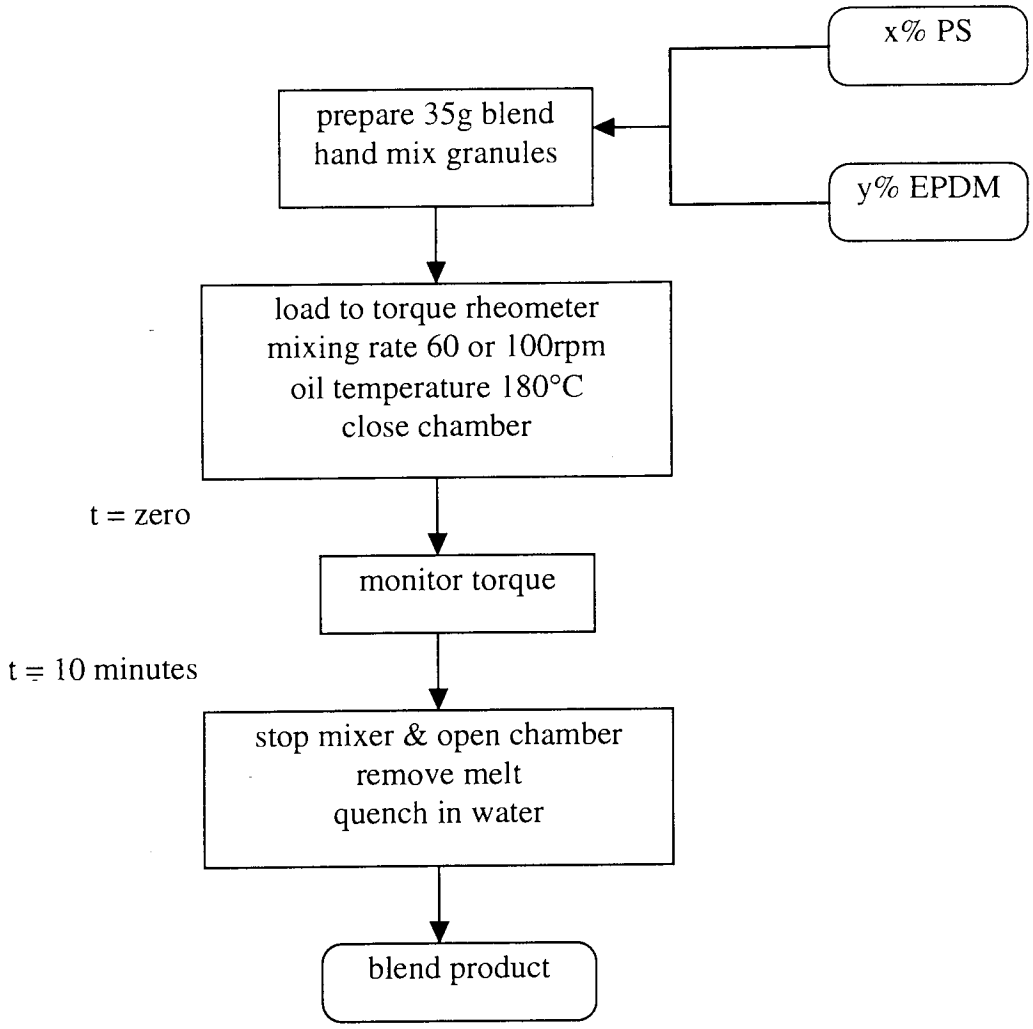
eg 22.19g TRIS with 0.22g Trigonox 101 = 0.01 FRI/RA mole ratio

Addition was made to polymer or blend in the rheometer chamber during processing by lifting the loading ram and carefully injecting a portion of RA/FRI mixture directly into the melt using a syringe with a long metal needle attached (Scheme 2.3). The exact mass of addition was found by weighing the syringe before and after this operation. Addition level of reactive agent was then expressed as a percentage by weight of polymer.

2.2.4 Process equipment and operations.

A HAMPDEN-RAPRA TORQUE RHEOMETER (TR) consisting of a pair of counter rotating rotors in a mixing chamber heated by oil and run with a BRABENDER drive and torque recording unit, was used for the batch-wise processing of polymers and blends in the melt state. The torque generated on mixing was indicated continuously on a digital readout. Before processing the torque produced by the rotors running at 60rpm in an empty chamber was adjusted to a standard value using the calibration setting. All processing was at an oil temperature of 180°C for a maximum of 10 minutes and a rotor speed of 60rpm ("the standard processing conditions"), unless otherwise stated. The 35g of polymer or blend was dropped into the loading chute of the TR with the rotors turning and timing of the processing cycle started when the loading ram was fully lowered to close the mixing chamber. Torque was monitored throughout the mixing period by manually recording the indicated torque value at appropriate time intervals. For physical blends or base polymers mixing continued uninterrupted until the end of the required time when the chamber was opened, polymer melt removed and pressed between flat brass blades before being quenched in room-temperature water (Scheme 2.1).

Scheme 2.1 Operational flowsheet for the processing of physical blends.

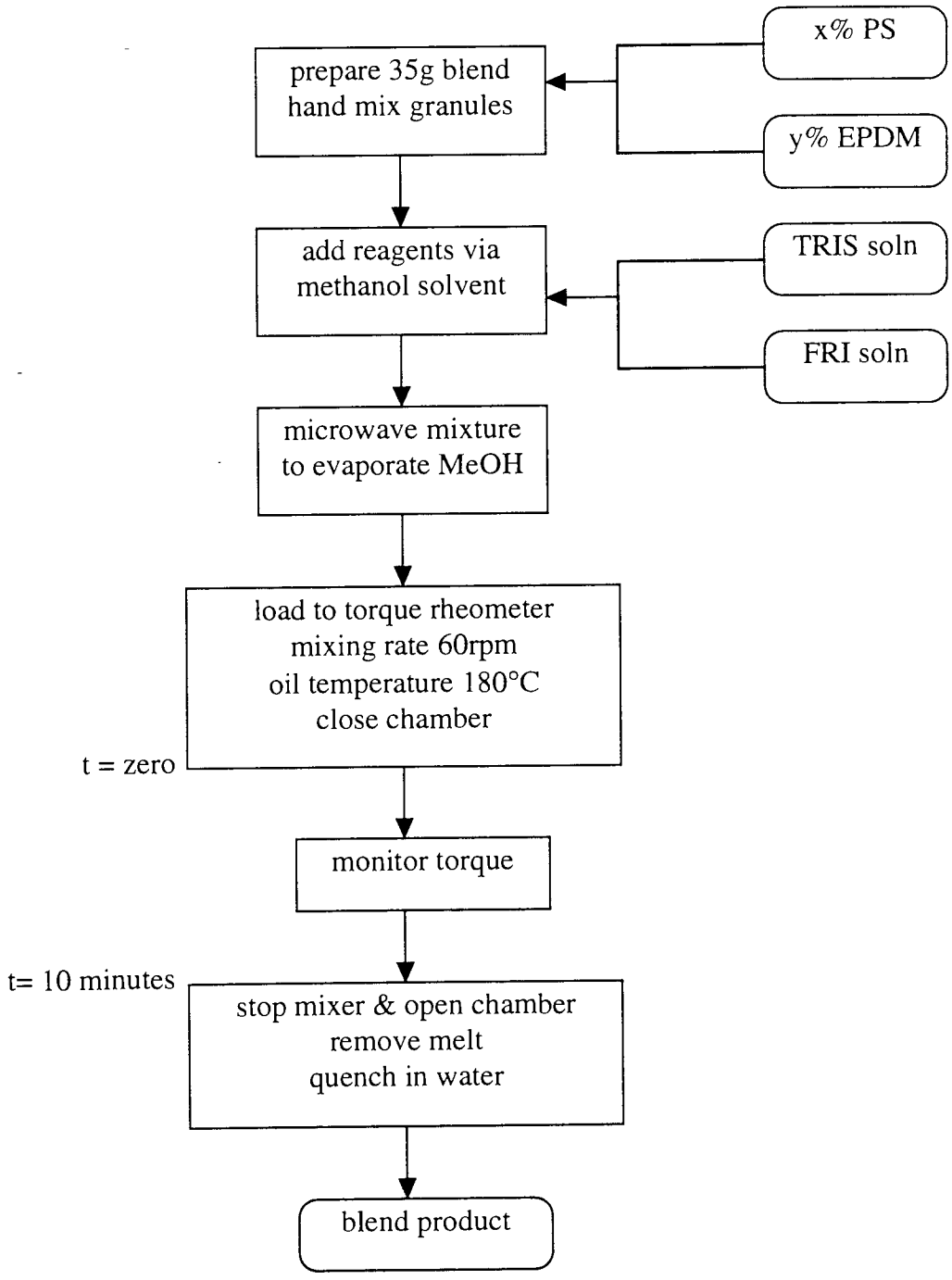


Reactive blends with RA & FRI addition via solvent were processed similarly without interruption to mixing, the reactive components having been added to the polymer before charging to the rheometer (Scheme 2.2).

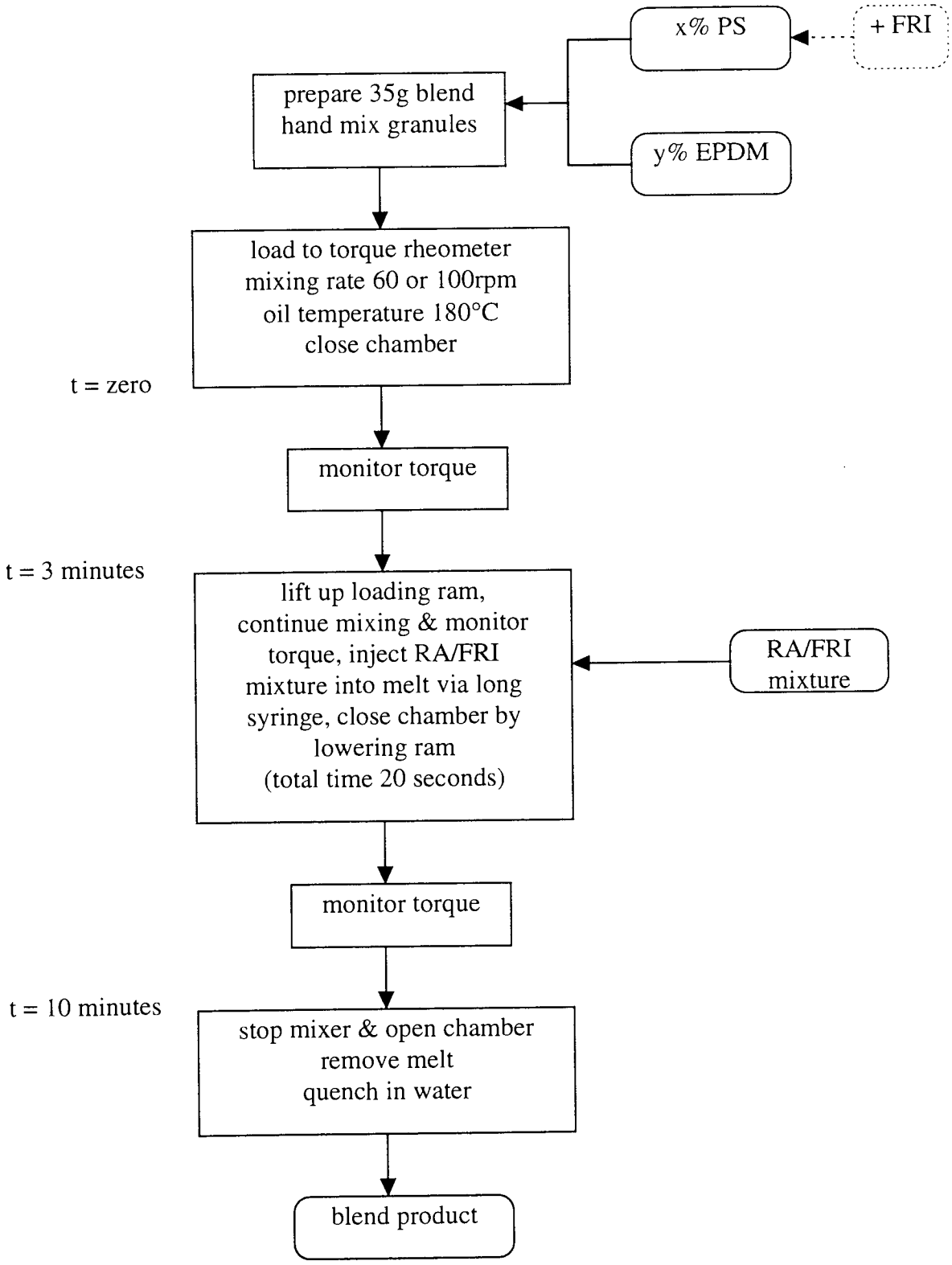
For direct addition of reactants, the polymer or blend was charged to the rheometer and mixed for an initial three minute period. The loading ram was then raised to open the chamber for insertion of the long needle and direct injection of RA & FRI mixture into the melt. The ram was then dropped to re-close the chamber. This operation took a maximum of twenty seconds during which time mixing and torque monitoring continued. Torque

readings were made at appropriate intervals following this event to fully describe the effects of reactive processing by this method (Scheme 2.3).

Scheme 2.2 Operational flowsheet for the processing of reactive blends with TRIS & FRI addition via solvent.



Scheme 2.3 **Operational flowsheet for the processing of reactive blends with reactive agent & FRI addition by direct injection.**



2.3 FILM PREPARATION.

Fairly even, thin sheeting were pressed from the processed samples using card templates between polished stainless steel plates in a DANIELS COMPRESSION MOULDING PRESS. A minimum of 8g polymer was placed in the centre of a 16 x 11cm rectangular cut-out in an A4-sized piece of card (0.18mm thickness) between the metal mould plates which were laminated across both internal surfaces with a folded sheet of Cellophane. This was placed directly between the electrically heated platens of the press, set at 180°C, and held for 90 seconds under minimum load. The 12" ram was then lowered to apply 150 kg/cm^2 pressure, heating was isolated and cold water circulated through the platens, whilst maintaining pressure. Mould plates were taken out after approximately 3 minutes, once below 150°C, and left until cooled to ambient temperature before removing the film sample. Film thickness was found to be around 0.6mm in the centre to about 0.5mm at the edges. Sheets with obvious flaws (creases, unfilled template) were discarded and fresh samples prepared.

2.4 TENSILE TESTING.

2.4.1 Preparation of Tensile Test Specimens.

A device incorporating a series of razor blades, held apart by spacer plates and clamped along the length, was used to cut several strips with straight, clean edges and approximately uniform width from the sheets of pressed film identified for tensile testing. Specimen length was 150mm minimum and width approximately 6mm to satisfy the requirements of the appropriate standard test method (ASTM D882-83[133]). For each specimen thickness was measured using a dead-weight dial micrometer to 0.01mm and the width to 0.1mm using a NIKON PROFILE PROJECTOR at x10 magnification in four positions along the length. Mean values for each dimension were used for the calculation of measured tensile properties.

2.4.2 Tensile Test Procedures.

Tensile testing was carried out almost wholly in accordance with ASTM D882-83 Method A for "Tensile Properties of Thin Plastic Sheeting" which was considered to be appropriate for films of < 1.0mm thickness.[133] A MODEL 4301 COMPUTER CONTROLLED INSTRON SERIES IX TESTING STATION was used for this work, with a dedicated routine programmed to collect the data and report a statistical analysis of the important tensile parameters from five replicates per film sample. A constant rate of grip separation was used, this also giving specimen elongation in the absence of any other extension indicating device. Flat grips were used, with 4 bar compressed air clamp pressure, in a 0.1 kN test cell. The load measurement system was calibrated and zeroed prior to use. For the specified strain rate of 0.1 min^{-1} (materials with < 20% elongation at break ; Table 1 ASTM D882), with a gauge length of 100mm, grip separation rate was set at 10 mm/min. Conditioning of samples was considered not to be necessary for the PS/EPDM blends, though all testing was carried out under standard laboratory conditions of 21-25°C and 45-55% RH. Individual specimen dimensions were entered into the testing routine once clamped in the Instron grips and the test started through the computer station. Any specimens which failed at obvious flaws were discounted from the rest ; jaw breaks (at the grips) were not omitted.

2.4.3 Tensile Properties Measured.

The tensile properties measured were as follows, and explained with reference to the idealised stress-strain curves shown in Figure 2.1 ;

Extension (%) - the gain in length caused by a tensile load expressed as a percentage of original length, to both yield (ε_y) and break (ε_b) points. The yield point was detected as the point at which an increase in strain first occurred without an increase in stress (position B -

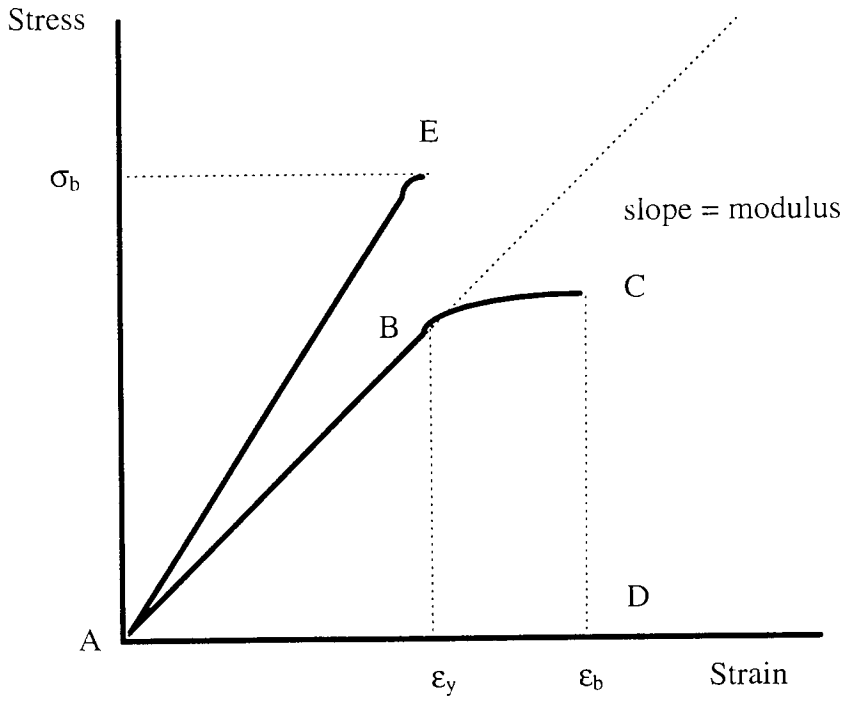
Figure 2.1). Some of the cells tested broke without yielding (line AE), for these brittle failures only extensions to break were thus reported.

Tensile Strength (MPa) - the maximum stress (tensile load per unit cross- sectional area) sustained by the sample during test ; typically occurred at the point of rupture due to the characteristics of the blends tested.

Modulus (MPa) - the Elastic or Young's Modulus is the ratio of stress to corresponding strain below the yield or break point, shown by the slope of the initial straight line of the tensile curve (Figure 2.1), and was used to give an index of the stiffness of the material.

Toughness Factor (MPa) - this was obtained by normalising the energy to break under the tensile curve (area ABCD - Figure 2.1) to specimen volume (cross-section area x gage length) and is termed the tensile energy to break (TEB) in the ASTM.[133] This is quite different to any measure of toughness from impact testing (Charpy or Izod), but was useful to provide an integrated measure of tensile characteristics.

Figure 2.1 **Idealised Tensile Stress-Strain Curves.**



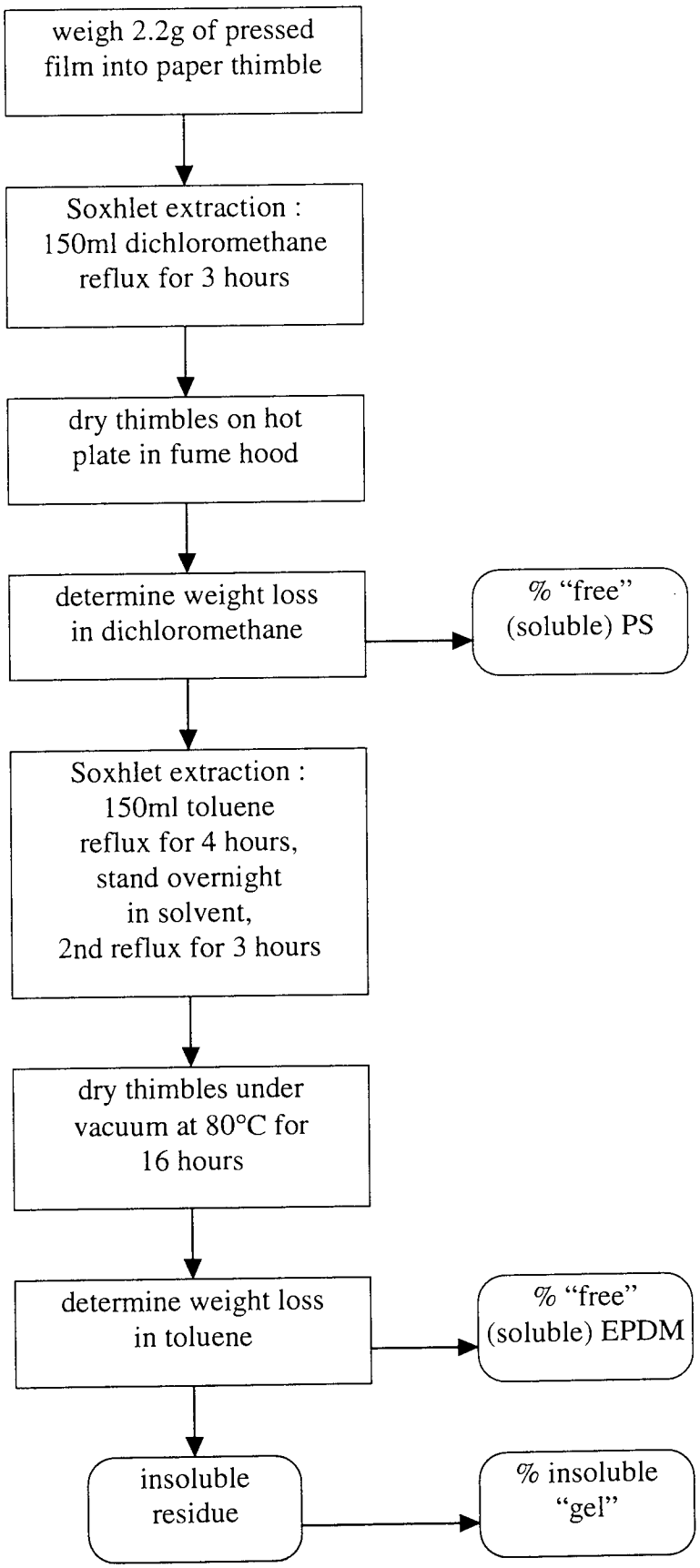
2.5 SCANNING ELECTRON MICROSCOPY.

Scanning electron microscopy (SEM) was used to view fracture surfaces from tensile testing for comparitive assessment of blend morphology. For each cell a specimen with tensile properties closest to the sample mean was selected for microscopy. One of the broken ends of the film test piece was attached to a metal stub using a double sided sticky carbon pad, with the fractured face over the edge of the stub. Before viewing, samples were coated with a conducting layer of gold using an EMSCOPE SM300 COATER set at 20mA for 2 minutes. Fractures were then viewed end-on at appropriate magnification in a CAMBRIDGE INSTRUMENTS STEREOSCAN 90 SCANNING ELECTRON MICROSCOPE.

2.6 SOLVENT EXTRACTION OF PS/EPDM BLENDS.

Polystyrene and EPDM were extracted sequentially from samples of key reactive and control blends to determine the relative content of "free" (soluble) components and insoluble, possibly PS-EPDM interpolymer, gel. Dichloromethane was shown to be a good solvent for PS and a non-solvent for EPDM over several hours refluxing and was thus chosen to determine the soluble PS fraction. Several more solvents were assessed for selective EPDM solubility (hexane, decalin & tetrahydrofuran), but even if PS was insoluble (hexane & decalin) then EPDM only partially dissolved, giving gels rather than proper solutions in all three. Eventually toluene was found to be suitable ; after refluxing for one hour and leaving overnight a fluid EPDM solution resulted. However, toluene was also a solvent for PS under the same conditions, but did serve the purpose of removing the remaining soluble portion from a blend sample, leaving entirely insoluble matter at the end of the extraction sequence. Thus pressed film samples of blends were first extracted in dichloromethane and secondly in toluene using standard Soxhlet extraction assemblies (QUICKFIT E5/53) on electric isomantles under a vented enclosure according to the detail in Scheme 2.4.

Scheme 2.4 **Sequential extraction of PS and EPDM from blends.**



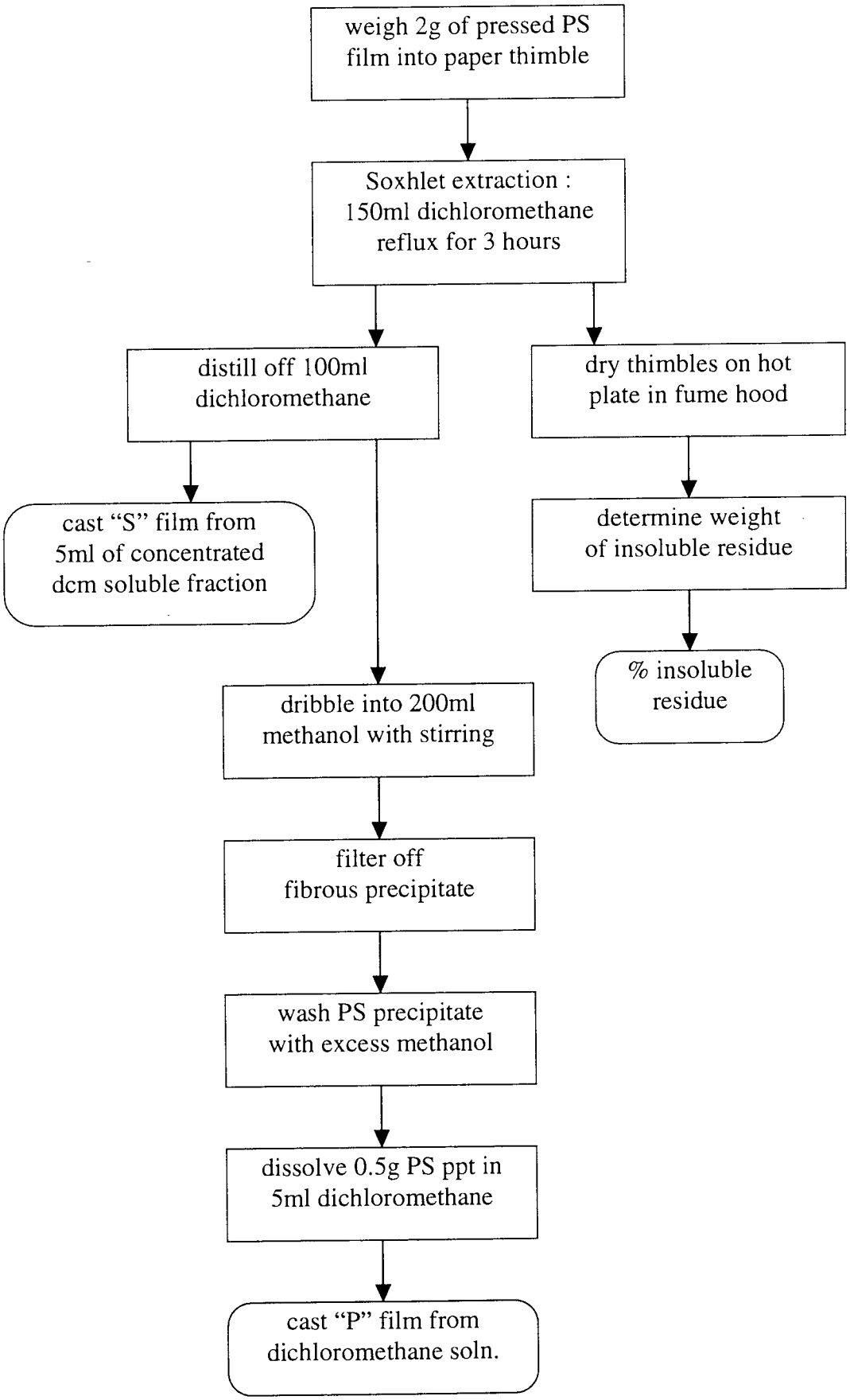
2.7 EXTRACTION AND FRACTIONATION OF PS COMPOSITIONS.

Samples of thin films (around 0.2mm thick) from key PS reactive and control cells were subjected to Soxhlet extraction using dichloromethane solvent according to the detail in Scheme 2.5. Complete dissolution of a 4g sample of unprocessed PS (as a thin film) was shown within 2 hours for Soxhlet extraction using refluxing dichloromethane (bp 40°C). On cooling the resulting solution was stable, unless the dichloromethane was allowed to evaporate (having high volatility even at room temperature), which gave a route to acceptable quality cast films. The amount of insoluble residue remaining after dichloromethane extraction was measured and assumed to be self-polymerised (cross-linked, and thus insoluble) interlinking agent. The soluble portion from each sample was concentrated by distilling off and discarding 100ml of dichloromethane into each Soxhlet, to cast films directly for analysis (soluble : "S" series) and allow separation of incompletely reacted modifier and PS fractions. Modifier that was not chemically bound to the polymer was removed by precipitating PS from the dichloromethane concentrate on dribbling into excess methanol and further alcoholic washing after filtration of the fibrous polymer fraction. Cast films for FT-IR analysis ("P" series) were made from fresh dichloromethane solutions of precipitates (Scheme 2.5).

2.8 FOURIER TRANSFORM INFRA-RED (FT-IR) SPECTROSCOPY.

All infra-red spectroscopy was carried out on a PERKIN ELMER MODEL 1710 FOURIER TRANSFORM INFRA-RED SPECTROPHOTOMETER. Film specimens were clamped by a magnetic ring onto a metal plate having a 25x14mm aperture and presented to the sample beam in the usual position. Both reactive agents were as neat liquid films between KBr discs. Spectra were obtained over a range 4000-600cm^{-1} from 5 scans at a resolution of 4cm^{-1} and saved to individual files using PERKIN ELMER DATA STATION APPLICATIONS SOFTWARE (M1700) for subsequent analysis and manipulation.

Scheme 2.5 **Extraction and fractionation of polystyrene compositions.**



2.9 NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY OF PS COMPOSITIONS.

In Nuclear Magnetic Resonance (NMR) spectroscopy the absorption of radio-frequency electromagnetic radiation is governed by the local electronic environment and hence the magnetic properties of atomic nuclei. Charge associated with certain nuclei may "spin" resulting in a magnetic dipole which within an applied magnetic field will align either in a low energy condition with the applied field or a high energy states opposing it. Absorption of an appropriate quantum of energy causes transition between spin states and hence nuclear magnetic resonance. Particular magnetic nuclei come into resonance at slightly different field strengths due to the neighbouring electronic (ie chemical) environment of other nuclei. This provides a means for analysing chemical structure. For organic materials proton and carbon-13 nuclei are the particular species examined under different instrumental set-ups.

Proton NMR of precipitate fractions ("P" Scheme 4.1) was attempted to assess differentiation of styrenic hydrogens in selective reactively processed PS cells from unmodified control PS. It was hoped that such changes could be identified by a) the presence of new peaks or shifts in existing resonances due to incorporation of interlinking agent and b) peak area measurements to proportion the concentration of different types of protons in samples. 10-20mg of sample was dissolved in 5ml of deuterated chloroform and run at room temperature in a BRUKER AC300 HIGH RESOLUTION NMR SPECTROMETER AT 300 MHz. Peak chemical shift positions and integral values were recorded by the operating software and hard-copy reports of spectra obtained.

^{13}C NMR was also carried out on samples dissolved in deuterated chloroform on the same instrument using a multipulsed Fourier Transform technique developed at Aston University ; ^{13}C PENDANT NMR.[158] This method displays ^{13}C resonances at the

characteristic chemical shift positions in a positive or negative manner according to the hybridisation state of the carbon nuclei (methyl and tertiary carbons as positive, methylene and quarternary carbons as positive). Peak positions and intensities were recorded by operating software and listed with spectra when printed.

2.10 DIFFERENTIAL SCANNING CALORIMETRY.

Many different thermal techniques can be applied in the study of the thermal behaviour of polymers and blends,[154, 155, 157] according to the nature of the materials and specific information required. In this study, both PS and EPDM were fully amorphous materials so that the important thermal parameter of both components would be their glass transitions (ie the temperature above which large-scale chain segments develop mobility that permits conformational rearrangements of chain backbone with resultant changes in specific heat capacity and other free volume effects). Glass transitions were expected to be easily discernible individually, without any crystalline phase interferences, and in blends, due to the large difference between the two Tg's (for PS ; 92-112°C[82] and EPDM; -55 to -60°C[132]). A suitable method for the measurement of accurate glass transition temperatures of amorphous polymers is Differential Scanning Calorimetry (DSC), by determination of the inflexion point of the heat capacity curve where this changes from a low level in the glassy temperature region to a higher level when in the liquid phase.[154]

All analyses were made using a PERKIN-ELMER DSC7 on small sample discs (7-10mg) cut from pressed films of PS/EPDM compositions and crimped in aluminium pans. Temperature scans were made from 30 to 150°C at 10°C per minute for PS and from -100 to 150°C at 10°C per minute for EPDM and blends (after cooling from 30 to -100°C at 130°C per minute). Glass transitions were determined from heat capacity curves normalised for weight using operating software analysis functions.

CHAPTER 3

DETERMINATION OF AN EXPERIMENTAL METHOD AND INVESTIGATION OF THE PRINCIPAL CONCEPTS OF THE REACTIVE PROCESSING OF POLYSTYRENE / EPDM BLENDS.

3.1 OBJECTIVES AND METHODOLOGY.

As this was an initial investigation into the assessment of reactive processing using interlinking agent technology for the compatibilisation of the challenging polystyrene / EPDM blend, a primary objective was to determine a suitable experimental method for examination of the underlying principles involved. This was to be achieved using a laboratory-scale internal mixer, rather than larger and more complex extrusion equipment, to provide a practical and versatile technique for the simultaneous melt blending and attempted reaction of both polymers with interlinking agents for in-situ interpolymer formation and blend compatibilisation. It was recognised that for an experimental-scale reactive blending method a major difficulty would be the accurate addition and even distribution of minor quantities of reactive agents without the introduction of any interfering factors, hence the evaluation of two different routes. Once a successful method was developed, it was intended to determine the principal concepts of reactive processing using interlinking agents for polymer blend modification by examining the influence of key process parameters.

Initial experimental work involved processing a series of PS/EPDM physical blends in the internal mixer of a HAMPDEN-RAPRA TORQUE RHEOMETER (TR) to assess baseline torque behaviour and blend characteristics. Two possible routes to a practical reactive blending method were then examined to meet the main criteria of accurate addition and even distribution of minor quantities of reactive agent (RA) and free-radical

initiator (FRI) to the 35g total blend charged to the torque rheometer per run. Firstly, pre-addition of RA (TRIS) and FRI to blends via solvent was attempted (Scheme 2.2) with the aim of spreading RA & FRI evenly throughout PS/EPDM blends once solvent had been removed by forced evaporation using microwave heating prior to processing. The second method was to mimic an approach used in extruder- based reactive processing,[1] that of direct injection of reactive agent into the blend during melt mixing (Scheme 2.3). The merits of the two techniques were compared in terms of process complexity and flexibility, metering of reactive agent addition and interfering factors.

Determination of the principal concepts involved in this feasibility study of PS/EPDM reactive blending, using a triacrylate interlinking agent (TRIS), was achieved by variation of key process parameters; namely, blend composition, reactive agent addition and mixing speed. Torque behaviour during processing was monitored in all cases to provide some insight into reaction progress and outcome. Only preliminary product assessment was thought to be appropriate at this stage considering the initial results of attempted reactive blending. The general experimental procedure for these investigations, using the most suitable process route, was as shown in Scheme 3.1, and all samples processed as given in Table 3.1 for ready reference. Nevertheless, this preliminary investigation was important in finding the most suitable operating windows for subsequent optimisation of reactive blending (Chapter 5) and to indicate the necessary direction of specific effort required to unlock the application and understanding of this novel technique (Chapter 4 - PS reactive modification and analysis).

Scheme 3.1 **General experimental procedure for the initial investigation of PS/EPDM reactive processing with TRIS interlinking agent.**

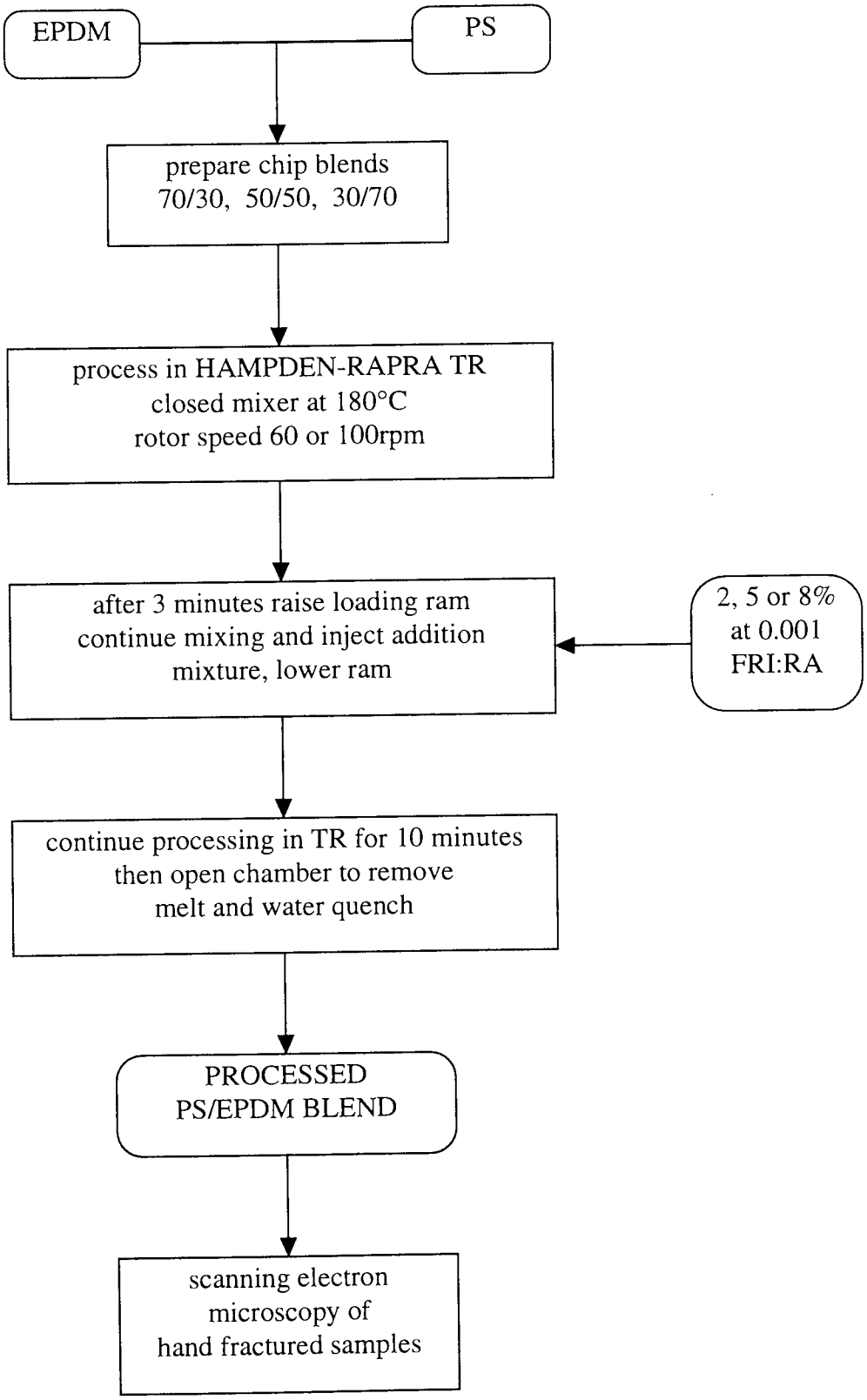


Table 3.1 **Reference list of samples for the initial investigation of PS/EPDM reactive processing using TRIS interlinking agent with organic peroxide free radical initiator (Trigonox 101).**

Sample Cell	Method[1]	Rotor speed (rpm)	PS grade[2]	PS % w/w	EPDM[3] % w/w	RA type	RA Level % w/w	FRI:RA molar ratio	+ FRI % w/w
2KA2	PB	60	S634	100	nil	none	nil	nil	nil
3KA2	PB	60	S634	nil	100	none	nil	nil	nil
5KA2	PB	60	S634	70	30	none	nil	nil	nil
6KA2	PB	60	S634	50	50	none	nil	nil	nil
7KA2	PB	60	S634	30	70	none	nil	nil	nil
8KA2	PB	60	S634	10	90	none	nil	nil	nil
4KA3	SA	60	S634	70	30	TRIS	5.0	0.001	nil
5KA3	SA	60	S634	50	50	TRIS	5.0	0.001	nil
6KA3	SA	60	S634	30	70	TRIS	5.0	0.001	nil
7KA3	SA	60	S634	10	90	TRIS	5.0	0.001	nil
8KA3	SA	60	S634	nil	100	TRIS	5.0	0.001	nil
9KA3	SA	60	S634	100	nil	TRIS	5.0	0.001	nil
1KA4	DA	60	S634	100	nil	TRIS	5.0	0.001	nil
4KA4	DA	60	S634	nil	100	TRIS	5.0	0.001	nil
7KA4	DA	60	S634	70	30	TRIS	5.0	0.001	nil
8KA4	DA	60	S634	70	30	TRIS	2.0	0.001	nil
9KA4	DA	60	S634	70	30	TRIS	8.0	0.001	nil
11KA4	C	60	S634	70	30	none	(opened)	none	nil
12KA4	DA	60	S634	30	70	TRIS	5.0	0.001	nil
13KA4	DA	60	S634	30	70	TRIS	2.0	0.001	nil
14KA4	DA	60	S634	30	70	TRIS	8.0	0.001	nil
16KA4	DA	60	S634	50	50	TRIS	5.0	0.001	nil
17KA4	DA	100	S634	30	70	TRIS	5.0	0.001	nil
18KA4	DA	100	S634	50	50	TRIS	5.0	0.001	nil
19KA4	DA	100	S634	70	30	TRIS	5.0	0.001	nil
20KA4	PB	100	S634	50	50	none	nil	none	nil
24KA4	C	60	S634	30	70	none	(opened)	none	nil

Notes :

1 : PB = physical blend (Scheme 2.1 - page 82)
SA = RA via solvent (Scheme 2.2 - page 83)
DA = RA direct addition (Scheme 2.3 - page 84)
C = control

2 : PS Grade ; S634 = Styron 634

3 : EPDM Grade ; Vistalon 2504

3.2 RESULTS.

3.2.1 Polystyrene/EPDM Physical Blends.

Constituent polymers and a series of blends were melt mixed in a HAMPDEN-RAPRA TORQUE RHEOMETER to determine baseline torque characteristics and blend behaviour prior to attempting reactive blending (in accordance with the operations and standard conditions detailed in Scheme 2.1).

Both constituent polymers and all blends exhibited the same pattern of torque changes over the 10 minute mixing period (Figure 3.1). Initial torque was very high, but decreased rapidly in the first three minutes, as polymer melted. Torque then dropped slowly or remained almost level as the polymer or blend was further homogenised, with little change to the end of the processing cycle.

EPDM elastomer alone gave the highest torque viscosity throughout the mixing period. Styron 634 polystyrene (MFR 3.5 g/10 minutes) had much lower torque viscosity than the EPDM at all times. A lower flow grade of PS (Styron 648, MFR 1.3 g/10 minutes) was processed separately but did not give particularly higher torque than the Styron 634 (final values 14 vs 12 Nm) and was more difficult to remove from the Brabender after mixing. The slightly more fluid Styron 634 PS was thus selected for use in the EPDM blends. The torque behaviour of blends was intermediate to that of the PS and EPDM alone. Blended compositions were all opaque, white or off-white and free from any gross inhomogeneities. Processed PS retained its high transparency and EPDM, although slightly darkened, was translucent. Blend opacity was a key indicator of immiscibility between PS and EPDM at all compositions examined. The multiphase nature of blends was confirmed by scanning electron microscopy of internal structure from hand-fractured samples (Figure 3.2). Within an almost continuous matrix of the major component, many

Figure 3.1 **Torque behaviour of PS (Styron 634), EPDM (Vistalon 2504) and physical blends processed under standard conditions.**

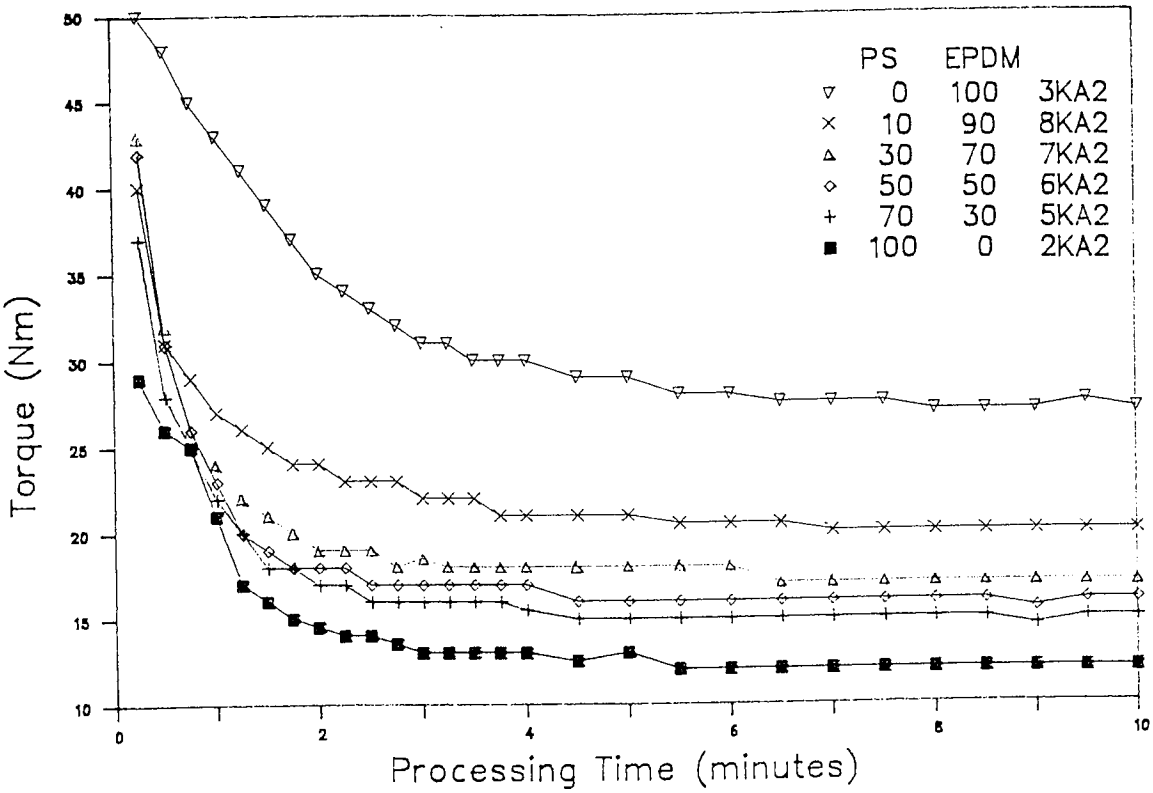
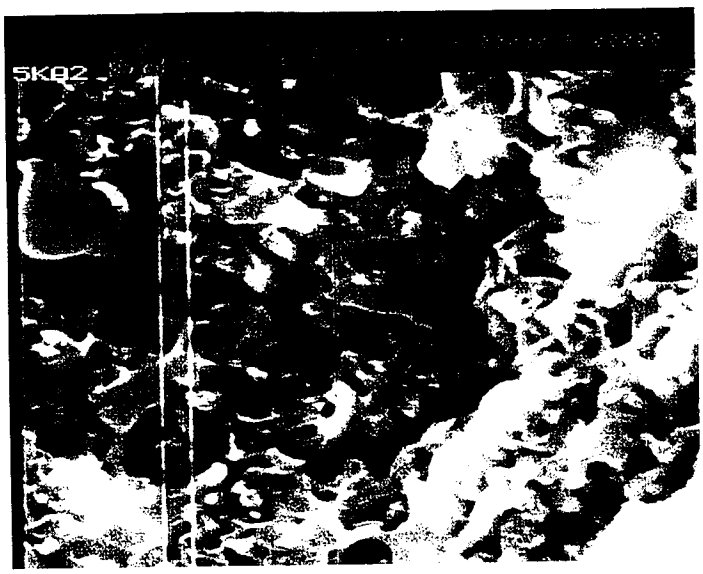


Figure 3.2 **Scanning electron micrograph of hand fractured sample of 70/30 PS (Styron 634)/ EPDM (Vistalon 2504) physical blend.**



irregular open voids (2 to 10 microns across) could be seen, with no apparant adhesion between phases. The physical nature of blends varied with composition between the slightly tacky, rubbery EPDM and the hard, rigid PS. All blends were quite weak and could be easily fractured by hand.

3.2.2 Methods of Addition of Reactive Agents.

Two routes were assessed to meet the objective of a controllable experimental-scale process ; addition of reactive agent and free radical initiator (RA & FRI) via a volatile solvent removed from polymer by forced evaporation using microwave heating prior to processing, and direct injection of RA &FRI mixture into the TR chamber during blending.

3.2.2.1 Reactive Agent Pre-addition via Solvent.

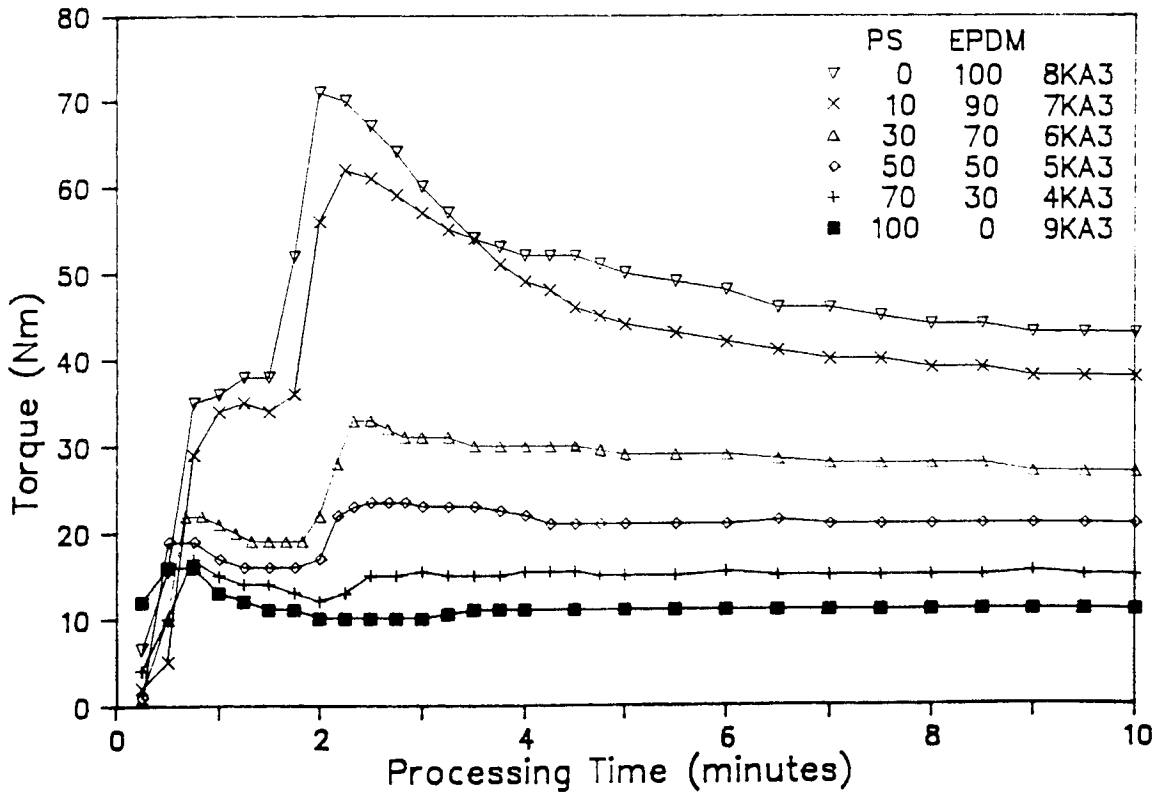
A set of blends were prepared by the method of RA addition via solvent (methanol) with nominally 5% TRIS and a FRI:RA molar ratio of 0.001 (Table 3.2). These were then processed under standard conditions (Scheme 2.2) to determine effectiveness of this route. A major discrepancy was that a portion of the RA & FRI mixture coated the inside of the glass bottle during preparation of the blend and was not completely transferred to the TR. Estimates of the actual addition were made by finding the mass left behind in the glass bottle (Table 3.2). Large and indeterminate errors were expected this way so that little confidence could be placed on the absolute level of TRIS addition and FRI:RA ratio. Some losses were also suspected during microwaving, such was the vigor of solvent evaporation.

Torque changes on processing blends with TRIS and FRI (Figure 3.3) were very different to inert blends (cf Figure 3.1). Torque rose within the first minute from low initial levels to different peak values according to blend composition. A second, higher torque rise was then given, with subsequent decay on continued mixing, depending on the amount of EPDM in the blend. The final torques of reactive blends containing 50% or more EPDM were higher than for the physical blends.

Table 3.2 **Compositions of PS/EPDM blends and component polymers with TRIS and FRI pre addition via solvent (methanol) evaporated by microwave heating prior to reactive processing under standard conditions (nominally 5% TRIS and 0.001 molar ratio FRI:RA additions).**

Sample	Composition (% w/w)			
	PS (Styron 634)	EPDM (Vistalon 2504)	TRIS target	TRIS estimate
4KA3	70	30	5.0	3.9
5KA3	50	50	5.0	3.7
6KA3	30	30	5.0	4.1
7KA3	10	90	5.0	4.5
8KA3	nil	100	5.0	4.3
9KA3	100	nil	5.0	4.2

Figure 3.3 **Torque behaviour of PS, EPDM and blends with TRIS & FRI addition via methanol evaporated by microwave heating prior to reactive processing under standard conditions (nominally 5% TRIS additions at 0.001 FRI:RA molar ratio).**



3.2.2.2 Reactive Agent Direct Addition via Injection.

Test cells and controls for this method were compared at two blend compositions (Table 3.3) according to the operations detailed earlier in Scheme 2.3. RA & FRI formulation was readily controlled by careful preparation of mixtures prior to processing and accurate addition levels at or near to target values were achieved. Torque curves for reactive blends were again found to be different to physical blends, the magnitude of increased torque depending on EPDM content (Figures 3.4a & 3.4b). Torque peak, decay pattern, final torque (T_{10}) and a reference point (at 3 minutes - T_3) could all be readily quantified from the torque curves of blends processed by this method (Table 3.3).

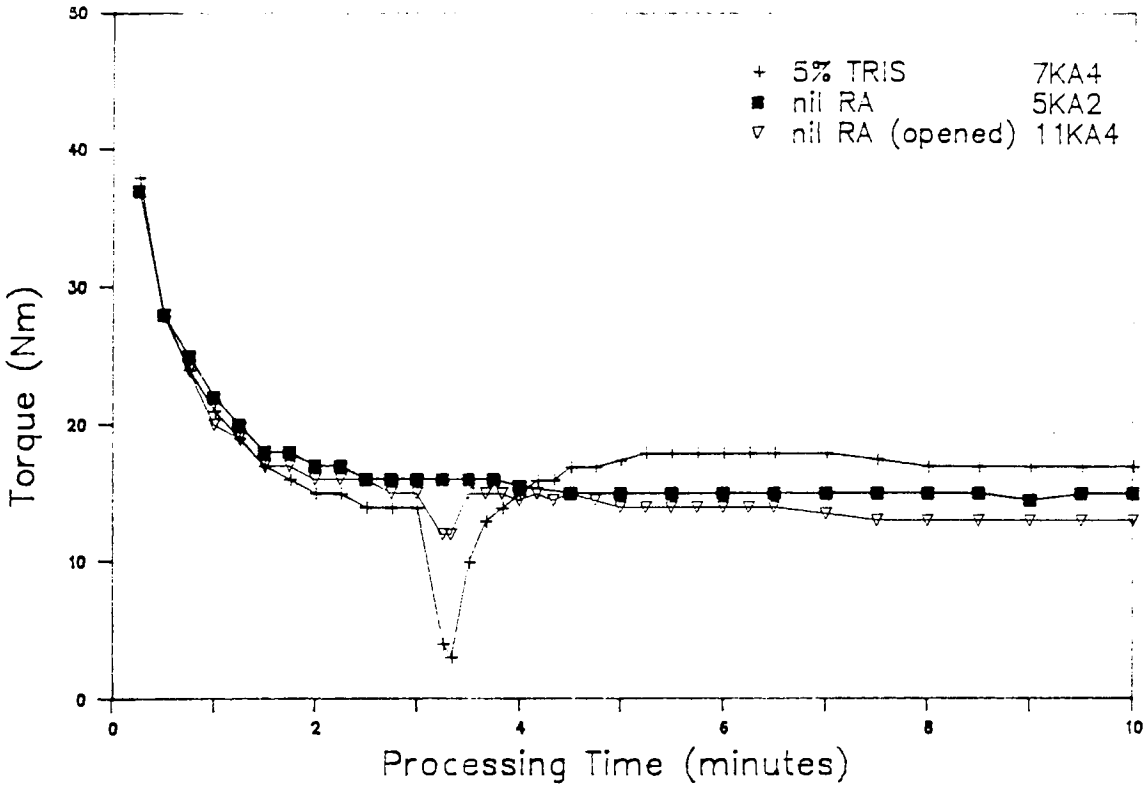
For the control blends, without any addition (11KA4 & 24KA4), opening the chamber at 3 minutes caused a drop in torque which recovered on closing, but to a marginally lower level than for an undisturbed physical blend. This was no bigger than the

Table 3.3 **Compositions and torque behaviour for 70/30 and 30/70 PS/EPDM blends reactively processed with direct addition of TRIS & FRI by injection into the melt during mixing (nominally 5% TRIS and 0.001 molar ratio FRI:RA) and controls processed under standard conditions.**

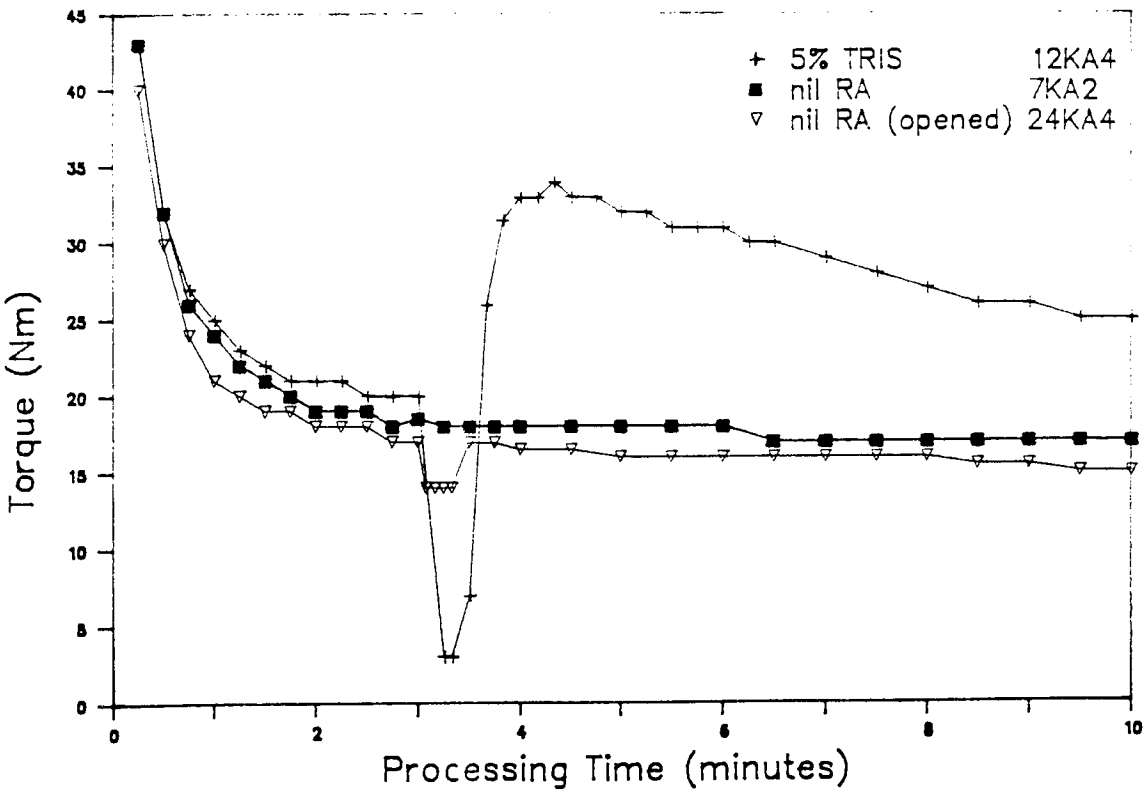
	Composition (% w/w)				Torque Behaviour			
Sample Cell	PS Styron 634	EPDM Vistalon 2504	TRIS & FRI target	TRIS & FRI actual	T_3 (Nm)	Peak (Nm)	Peak (min)	T_{10} (Nm)
7KA4	70	30	5.0	5.0	14	18	5.25	17
11KA4	70	30	nil (opened)		15	15	3.5	13
5KA2	70	30	nil		16	none		15
12KA4	30	70	5.0	4.9	20	34	4.33	25
7KA2	30	70	nil		18.5	none		17
24KA4	30	70	nil (opened)		17	17	3.5	15

Figure 3.4 **Torque behaviour of PS/EPDM blends reactively processed with direct addition of TRIS & FRI by injection into the melt during mixing (nominally 5% RA at 0.001 FRI:RA molar ratio) and controls processed under standard conditions.**

a) 70/30 PS (Styron 634)/ EPDM (Vistalon 2504).



b) 30/70 PS (Styron 634)/ EPDM (Vistalon 2504).



variation between torque curves during the initial mixing prior to opening. The transitional torque drop was considerably sharper when the liquid RA & FRI mixtures were injected, but did recover on further mixing in the re-closed chamber. Torque increases above control levels were given later in the mixing period, particularly for the high EPDM content blend (12KA4). For this blend (12KA4) torque rose rapidly after RA & FRI addition, reaching a high peak value before subsequent decay to a final torque considerably greater than the controls. At high PS (7KA4), torque increased slowly to a point just higher than the control blends, remaining close to this level to the end of mixing.

3.2.3 Principle Concepts of PS/EPDM Reactive Blending using a Triacrylate Interlinking Agent (TRIS).

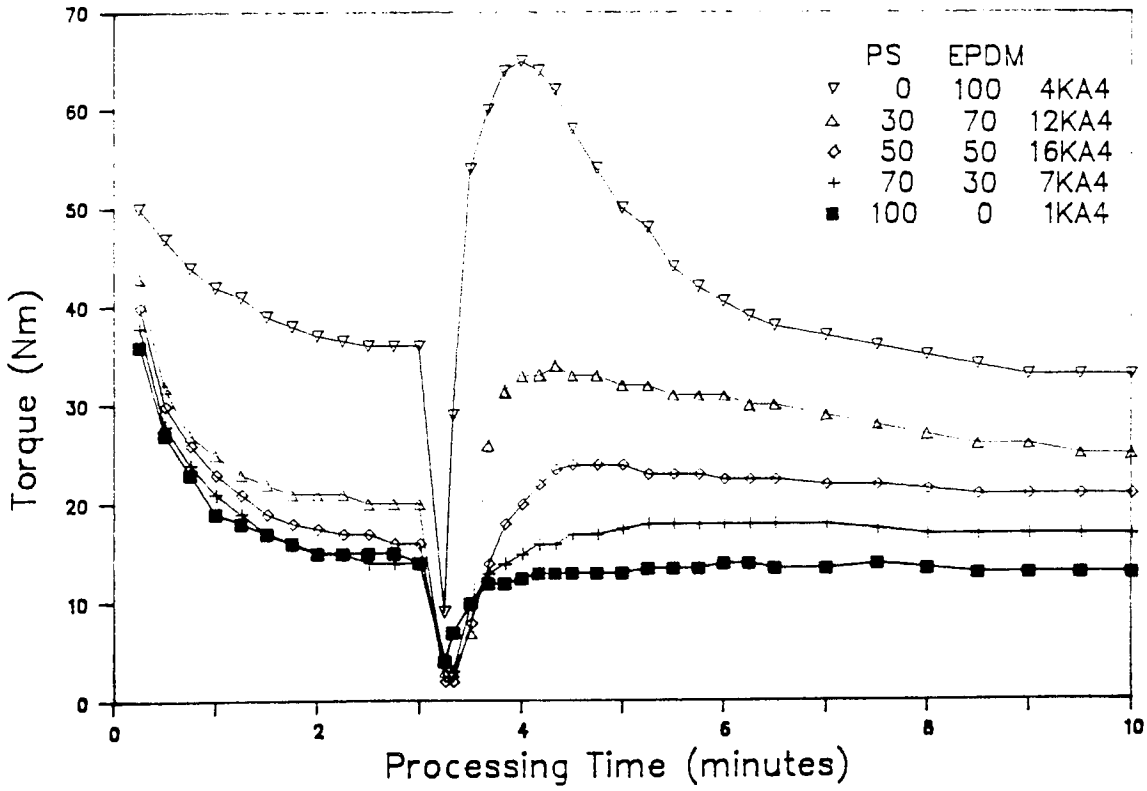
3.2.3.1 Effect of Blend Composition.

Component polymers and a series of blends with different compositions were processed in the Brabender TR under standard conditions with a direct addition after 3 minutes of nominally 5% TRIS and FRI at 0.001 FRI:RA molar ratio (Scheme 2.3). Torque behaviour was different for all blends (Table 3.4 and Figure 3.5). In PS alone (1KA4) torque recovered after the sharp drop on addition of the fluid reagents and maintained a fairly steady level until the end of processing. EPDM alone (4KA4) exhibited much greater change : a large torque peak was given directly on addition of TRIS & FRI and decayed substantially with further processing to a final steady torque level still higher than any of the blends. In blends, peak height and final torque increased with EPDM content. There was no adverse effect on appearance or form of any of the blends. Reactively processed PS was slightly cloudy, but essentially no different to inert PS . The EPDM was still rubbery, a little darker and less tacky than unprocessed material.

Table 3.4 **Compositions and torque behaviour for a series of PS/EPDM blends and component polymers reactively processed under standard conditions with direct addition of TRIS & FRI (nominally 5% TRIS and 0.001 molar ratio FRI:RA).**

	Composition (% w/w)				Torque Behaviour			
Sample Cell	PS Styron 634	EPDM Vistalon 2504	TRIS & FRI target	TRIS & FRI actual	T_3 (Nm)	Peak (Nm)	Peak (min)	T_{10} (Nm)
1KA4	100	nil	5.0	4.92	14	14	6.0	13
7KA4	70	30	5.0	5.0	14	18	5.25	17
16KA4	50	50	5.0	5.06	16	24	4.5	21
12KA4	30	70	5.0	4.9	20	34	4.33	25
4KA4	nil	100	5.0	5.0	36	65	4.0	33

Figure 3.5 **Torque behaviour for PS/EPDM blends reactively processed under standard conditions with direct addition of TRIS and FRI (nominally 5% TRIS at 0.001 FRI:RA molar ratio).**



3.2.3.2 Effect of TRIS Addition Level.

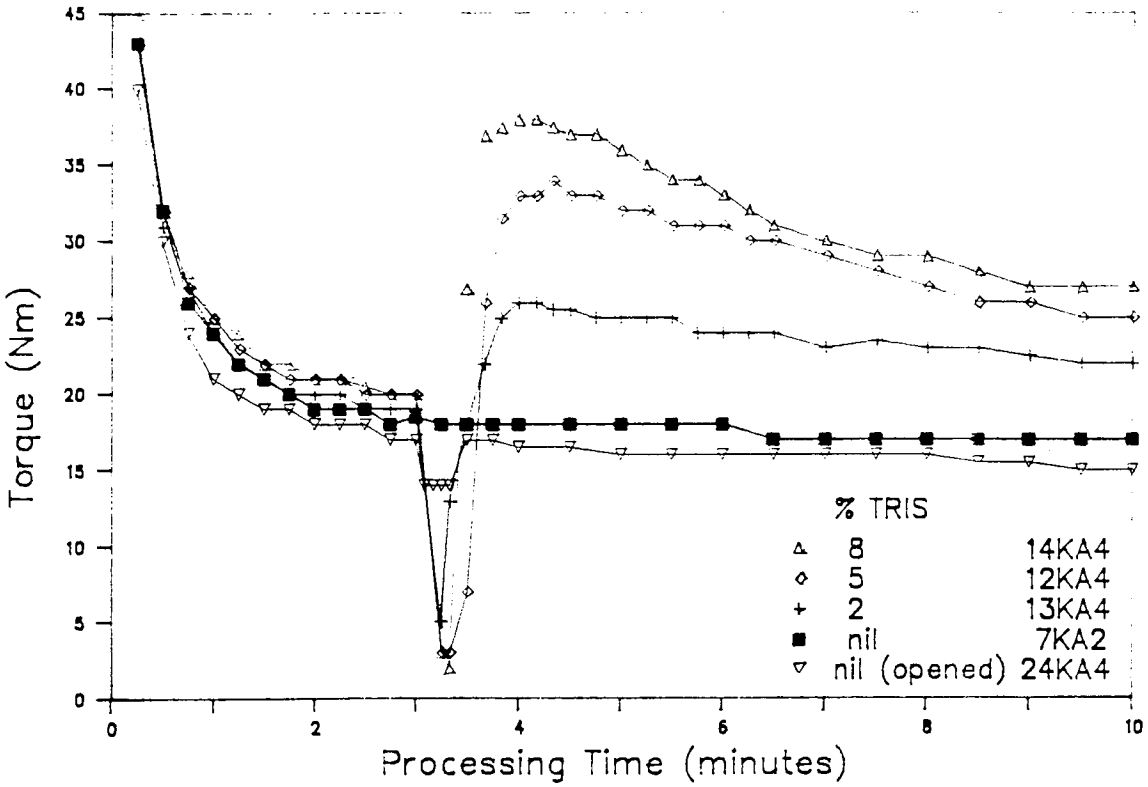
A series of TRIS additions with FRI:RA constant at 0.001 molar ratio were made to both 70/30 and 30/70 PS/EPDM blends during melt blending under standard conditions (Scheme 2.3). Major torque peaks were evident in high EPDM blends at all additions (Table 3.5 and Figure 3.6a) ; maximum torque increased with TRIS addition level. This was also seen in the 70/30 PS/EPDM blends (Figure 3.6b) although torque peaks were much less distinct. Final torque (T_{10}) was raised above control levels with higher TRIS additions, more so with EPDM as the major component. In the 30/70 PS/EPDM blends a minor addition of 2% TRIS (13KA4) had a definite effect whereas for 70/30 PS/EPDM (8KA4) torque was only slightly higher than the controls. At 8% TRIS in both blends (9KA4 & 14KA4) a heavy loading of particulate solids was obvious in the final material. This was absent with lower TRIS additions.

Table 3.5 **Compositions and torque behaviour for 70/30 and 30/70 PS/EPDM blends reactively processed with different TRIS additions at constant FRI:RA (0.001 molar ratio) and controls processed under standard conditions.**

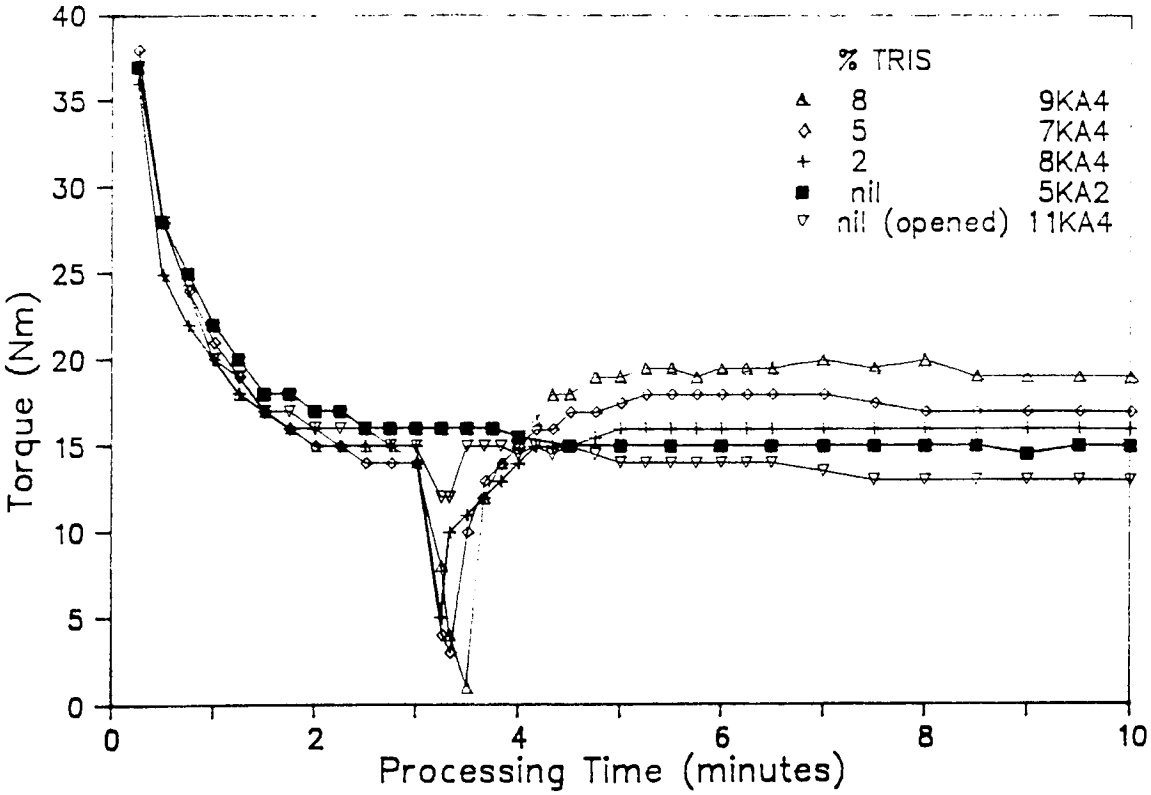
Sample Cell	Composition (% w/w)				Torque Behaviour			
	PS Styron 634	EPDM Vistalon 2504	TRIS & FRI target	TRIS & FRI actual	T_3 (Nm)	Peak (Nm)	Peak (min)	T_{10} (Nm)
8KA4	70	30	2.0	2.15	15	16	5.0	16
7KA4	70	30	5.0	5.0	14	18	5.25	17
9KA4	70	30	8.0	8.21	14	20	7.0	19
5KA2	70	30	nil		16	none		15
11KA4	70	30	nil (opened)		15	15	3.5	13
13KA4	30	70	2.0	2.26	19	26	4.0	22
12KA4	30	70	5.0	4.9	20	34	4.33	25
14KA4	30	70	8.0	8.40	20	38	4.0	27
7KA2	30	70	nil		18.5	none		17
24KA4	30	70	nil (opened)		17	17	3.5	15

Figure 3.6 **Torque behaviour of PS/EPDM blends reactively processed with different TRIS additions at 0.001 FRI:RA molar ratio and controls processed under standard conditions.**

a) **30/70 PS (Styron 634)/ EPDM (Vistalon 2504).**



b) **70/30 PS (Styron 634)/ EPDM (Vistalon 2504).**



3.2.3.3 Effect of Mixing Speed.

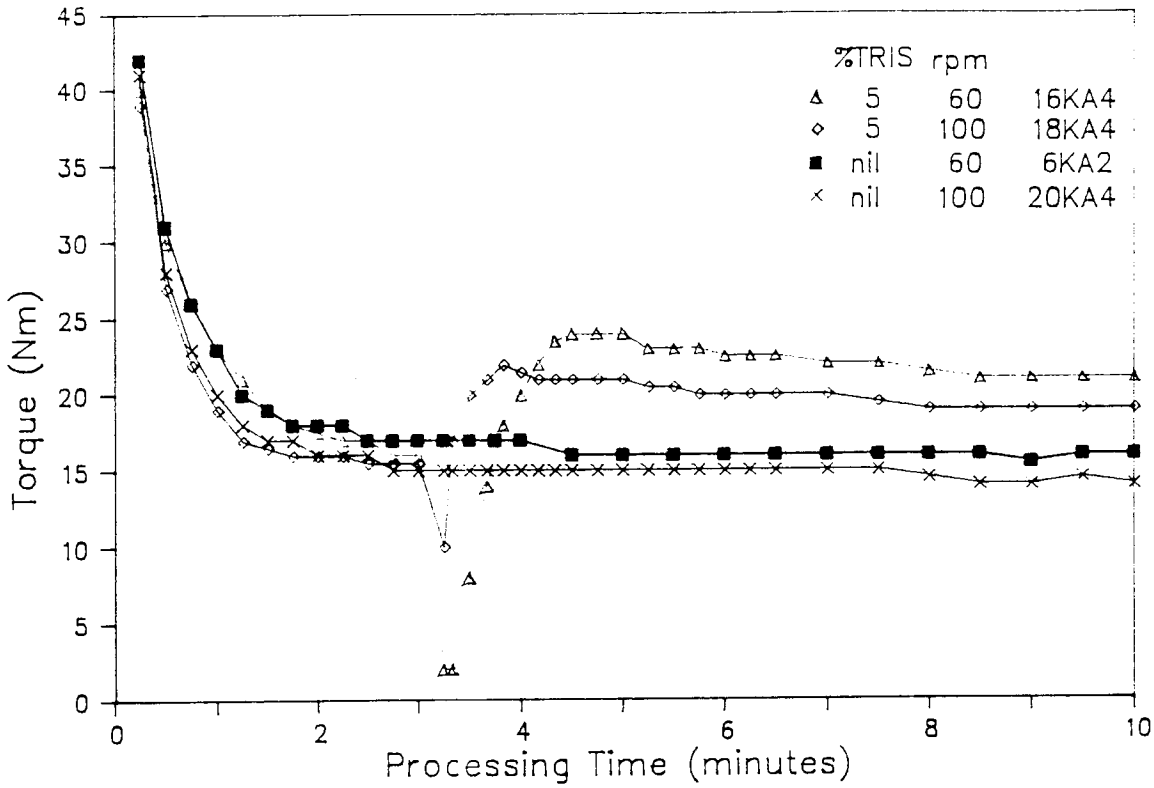
A series of physical and reactive blends using direct addition of TRIS & FRI were processed at a mixing speed of 100 rpm and compared to controls mixed at the lower speed of 60 rpm (Table 3.6). The pattern of torque changes at the higher speed was generally similar to standard conditions (Figure 3.7a and 3.7b). A common feature at the higher speed was that torque peak maximum was reached earlier, especially in the high EPDM content blend (17KA4) which gave no transitional drop in torque on addition of fluid reagents. Peak heights and final torques were not significantly different to values from equivalent blends at 60 rpm, being within 2 Nm and not consistently higher or lower. The final form and appearance of products was no different at higher blending speed.

Table 3.6 **Compositions and torque behaviour for physical and reactive PS/EPDM blends at different compositions processed at two mixing speeds. Reactive blends with nominally 5% TRIS addition at constant FRI:RA (0.001 molar ratio).**

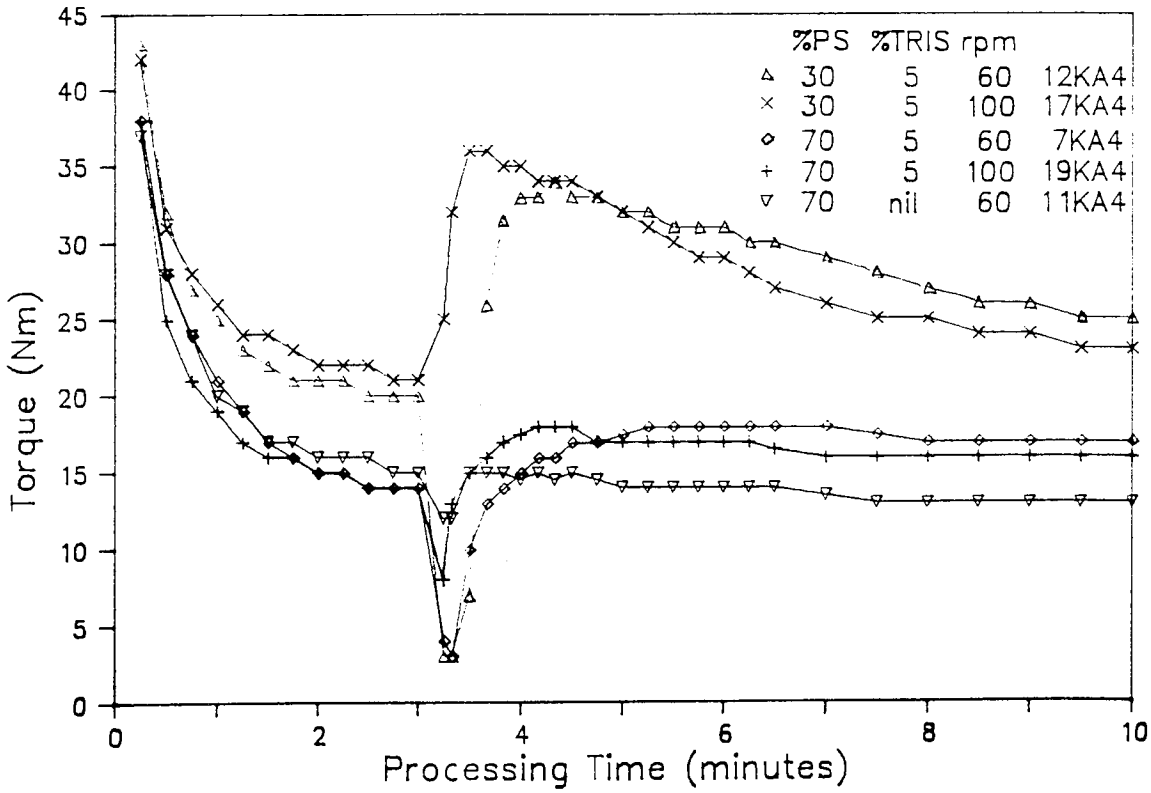
	Composition (% w/w)				Torque Behaviour				
Sample Cell	PS Styron 634	EPDM Vistalon 2504	TRIS & FRI target	TRIS & FRI actual	T_3 (Nm)	Peak (Nm)	Peak (min)	T_{10} (Nm)	Mixing speed (rpm)
18KA4	50	50	5.0	5.51	15.5	22	3.83	19	100
20KA4	50	50	nil		15	none		14	100
16KA4	50	50	5.0	5.06	16	24	4.5	21	60
6KA2	50	50	nil		17	none		16	60
17KA4	30	70	5.0	5.26	21	36	3.5	23	100
12KA4	30	70	5.0	4.9	20	34	4.33	25	60
19KA4	70	30	5.0	4.77	14	18	4.17	16	100
7KA4	70	30	5.0	5.0	14	18	5.25	17	60

Figure 3.7 **Torque behaviour for control and reactively processed PS/EPDM blends at two mixing speeds (with 5% TRIS additions at 0.001 FRI:RA molar ratio).**

a) 50/50 PS (Styron 634)/ EPDM (Vistalon 2504).



b) 30/70 and 70/30 PS (Styron 634)/ EPDM (Vistalon 2504) blends.

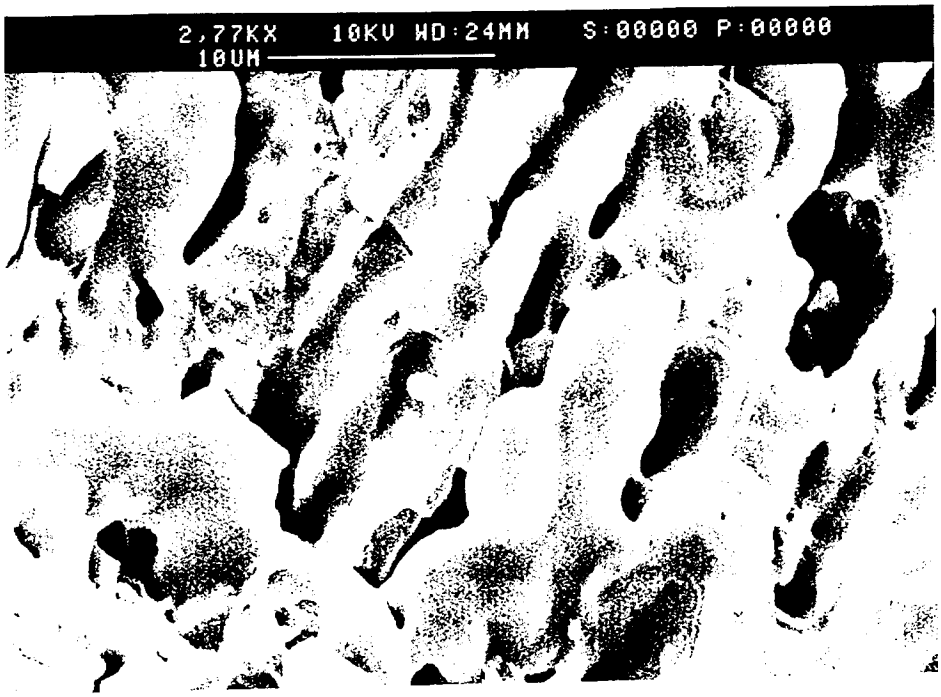


3.2.3.4 Preliminary Product Assessment.

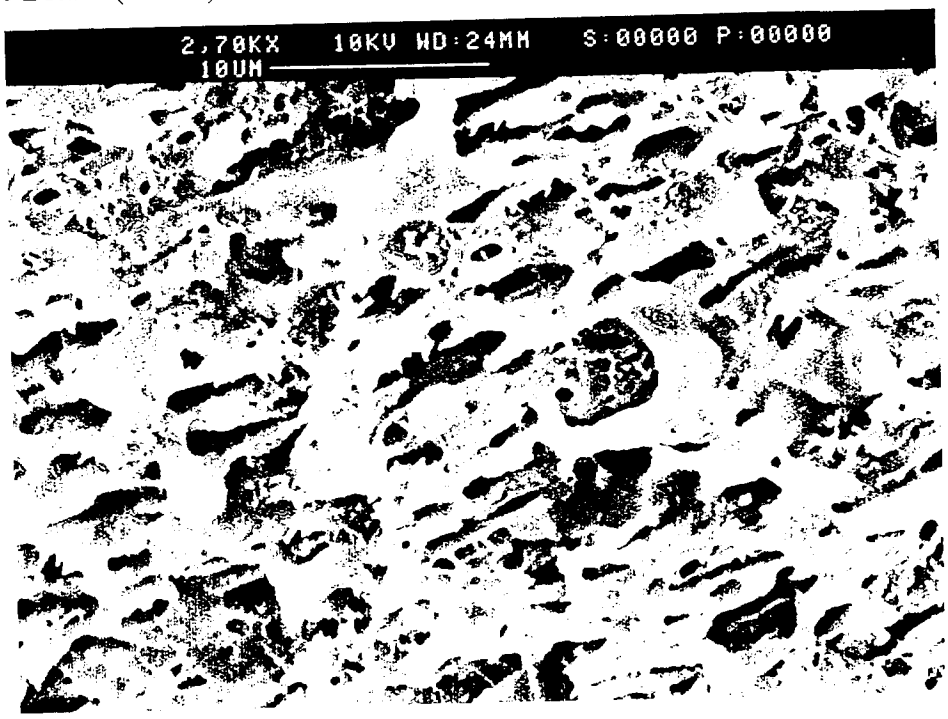
Scanning electron microscopy was used to examine for morphological differences between physical and reactively processed 70/30 PS/EPDM blends. Internal surfaces from samples fractured by hand were viewed at appropriate magnification (Figures 3.8a and 3.8b). The inert blend (5KA2) had a generally smooth surface texture where phases, with domain sizes typically above 5 microns, had been pulled apart quite easily. The corresponding reactive blend (7KA4) had much more even morphology and phase domains well below 2 microns. The surface was very much rougher and showed fracture by matrix failure rather than de-bonding of phases.

Figure 3.8 **Scanning electron micrographs of hand-fractured samples of 70/30 PS (H311)/ EPDM (V2504) physical blend (1KA7) and blend reactively processed with 5% TRIS addition at 0.001 FRI:RA molar ratio (2KA7) under standard conditions.**

a) Physical Blend (1KA7)



b) Reactive Blend (2KA7)



3.3 DISCUSSIONS.

In the following sections learnings from the initial investigations into the feasibility of PS/EPDM reactive blending using interlinking agent technology are discussed. The suitability of the experimental processing technique adopted and explanation of the torque behaviour displayed by application of this method were important foundations upon which the following studies were based. This also allowed realisation of some important principle concepts for the reactive blending of PS and EPDM, from determination of the influence of key process parameters, and clearly defined the direction of effort for subsequent investigations.

3.3.1 Suitability of the Experimental Processing Technique.

Determination of an experimental technique equivalent to larger scale reactive extrusion processing was a main objective for this research. By using the Hampden-RAPRA Torque Rheometer (TR), a laboratory-scale internal mixer, it was believed that a suitable method of reactive blending could be developed. It was expected that this experimental process would enable rapid and reproducible assessment of the reactive effects of interlinking agent and initiator mixtures in PS/EPDM blends without the imposition of any significant interfering factors. However, due to the small scale (35g of polymer per run), it was recognised that direct application of reactive agents to polymer chip blends prior to processing would not provide the required degree of accuracy, nor ensure even distribution throughout the blends. A solution addition route (Scheme 2.2) was intended to overcome this. However, losses prior to loading the TR, from pre-mixing in glass bottles and due to vigorous solvent evaporation on microwaving, were too large, variable and imprecise to control RA addition and thus would not allow quantitative assessment of reactive effects with any confidence.

Torque changes upon addition of TRIS & FRI were considerable (Figure 3.1), but probably not entirely resulting from reactive effects. It was thought that the low initial torque in all cases was due to lubrication of solid polymer by the fluid RA/FRI mixture. As polymer was heated up and melted this effect was overcome by the viscosity of the molten mass, with a corresponding torque rise. The second torque peak was assumed to be due to reaction of polymer, forming high viscosity polymeric networks or cross -links through the polyfunctional TRIS. Shear from continued mixing would then break a portion of these linkages, to yield modified polymer products rather than highly cross-linked material, reducing torque. This behaviour further complicated qualitative analysis. Thus this method was considered to be unsatisfactory and not used for any further work.

Injection of RA/FRI mixture into polymer within the mixing chamber during processing (Scheme 2.3) offered a direct, versatile approach that could meet the requirements for a controllable experimental-scale process. Accurate addition could be achieved for precise RA/FRI compositions with minimal complexity. A further advantage was addition after initial mixing to homogenised melt blends, which was hoped to improve the probability of interfacial reaction. Since RA & FRI was injected over a 20 second period during continuous mixing, good distribution throughout molten polymer was expected (at 60rpm over 20s = 20 revolutions of mixing blades). In some cases white powdery deposits were found in the feeding zone of the mixing chamber at the end of processing. This could have been self-polymerised TRIS arising from contact with hot metal surfaces, initiator and the absence of any polymer substrate in this region, all providing suitable conditions for self-reaction. It was thus important that injection was directly into polymer melt to avoid this effect.

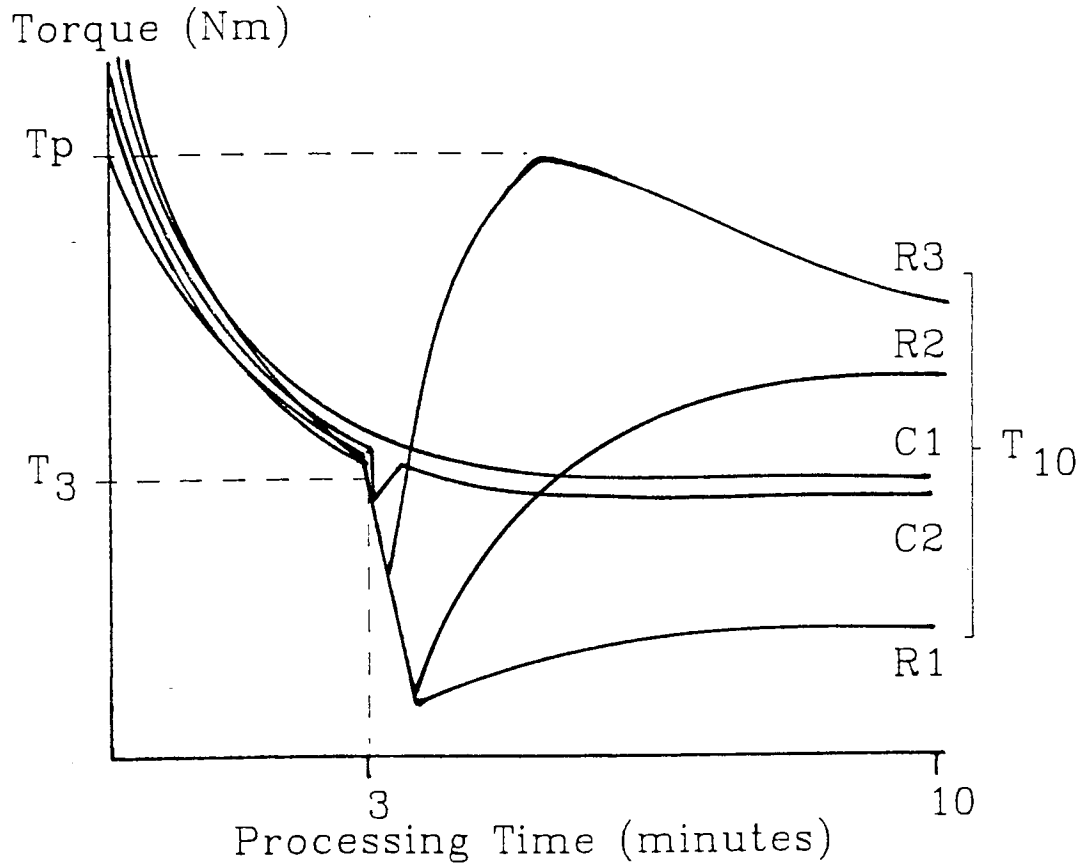
The torque changes on addition of RA & FRI were distinct (Figure 3.4) and quantifiable (Table 3.3), allowing clear differentiation of process effects (eg composition-dependence). The torque drop on opening the loading chute during processing and minor differences in torque levels afterwards for control blends (11KA4 and 24KA4) could have been due to both physical position of melt within the mixing chamber and the promotion of thermo-oxidative degradation on contact with air. As changes were no greater than variation between torque curves, any oxidative effect was not thought to be significant. Thus considering how this practical method of direct addition allowed precise control of RA/FRI ratio, provided a means of monitoring the dynamics of reactive blending and had potential for using similar principles in extruder-based processing, it was adopted for all subsequent work.

3.3.2 Explanation of General Torque Behaviours.

Although the detailed torque curves for both polymers and blends with TRIS and DVB were found to vary according to test cell conditions, some general patterns of torque behaviour during processing were found (Figure 3.9) ; possible mechanisms to explain these features can be proposed.

For both inert polymers or physical blends (Figure 3.1) the resulting torque curves followed a smooth decay from very high initial torque to a steady, lower level after about four minutes (C1 - Figure 3.9). This was most probably due to the physical action of melting and homogenisation. Later torque viscosity was constant as fully molten polymer experienced steady mixing conditions. Raising the loading ram caused torque to drop slightly, and without RA addition torque returned to the original curve on closing (C2 - Figure 3.9 ; eg 24KA4 30/70 PS/EPDM control - Figure 3.4b). This was from the physical constraints imposed in the closed mixer being released, allowing melt to escape into the feeding chute, thus reducing torque. On closing the loading chute, all melt would be

Figure 3.9 General Patterns of Torque Behaviour During Reactive Processing of PS/EPDM With Interlinking Agent Addition.



forced back into the mixing chamber, restraining polymer so that torque returned to the natural level. There was only a slight difference between torque levels for physical blends from closed mixing and momentarily opened controls (eg 7KA2 vs 24KA4 - Figure 3.4b), suggesting the influence of thermo-oxidative degradation to be minimal. For EPDM alone the difference was larger (3KA2 closed T_{10} = 27 Nm vs 9KA5 opened T_{10} = 23 Nm - Figure 4.6 Section 4.2.3), possibly indicating a greater oxidative effect in the melt, which was practically absent for PS alone (1KA5 vs 4KA5 - Figure 4.1 Section 4.2.1).

On reactive processing, a dramatic feature was the very sharp drop in torque on addition of every TRIS and DVB reactive agent formulation. This was believed to be due to the lubricating action of fluid RA between the interface of molten polymer and metal surfaces in the mixing chamber, reducing friction and thus lowering torque.[134,135] The

possibility of torque being lowered by degradation causing large reductions in molecular weight was discounted after considering the timescale for these events and the commonality across all RA formulations and blend compositions. This lubrication effect was highly likely for PS/TRIS, with the triacrylate reagent expected to have low compatibility with the styrenic polymer, but having an affinity for metal surfaces due to its polar functional groups. Subsequent torque rise could initially have been due to reduction in this lubricating effect by chemical change or loss of the fluid reactive agent. As processing was in a closed mixer, loss of RA by volatilisation would have been difficult. Considering the influence of initiator content on the rate and extent of torque rise, reaction of the interlinking agent was believed to be favoured, with polymer modification or self-reaction both capable of consuming the lubricating component (Section 4.3.1).

Directly following the sharp drop after RA addition, torque began to increase ; the rate, extent and final outcome all depending on the type of reactive agent used, addition level, initiator concentration and blend composition. The most extreme cases were ;

i. - curve R1 Figure 3.9 (realised in later work ; 9KA8 - 70/30 PS/EPDM +5% DVB with no FRI, Figure 5.5) : torque rise after RA addition was limited, remaining well below control levels for the whole cycle.

ii. - curve R3 Figure 3.9 (eg 12KA4 30/70 PS/EPDM +5% TRIS 0.001 FRI:RA, Figure 3.4b) : torque increase was rapid to a distinct peak with high maximum torque above control and reference points, the peak then decayed on further mixing, but remained at a high final level.

Maintained low torque could arise from continued lubrication or even a plasticising effect, when reaction of the interlinking agent was limited or not favoured. In most cases however, torque rise was fairly sharp until a steady torque was reached at or above control

levels (Curve R2 - Figure 3.9). Torque gains significantly higher than control levels could be accounted for by major molecular changes from reactive processes entirely within each component or by the targeted interpolymer reaction between interlinking agent and both polymers. Viscosity would stabilise according to the characteristics of the new molecular arrangements once equilibrium between competitive processes was reached. Several possible reactive processes were envisaged and their implications on torque viscosity considered ;

i. - **polymer cross-linking** could occur exclusively within each (or both) of the PS and EPDM phases, directly through degradation of polymer or via a coupling reaction incorporating the multifunctional modifier. Torque would be significantly raised due to increased molecular weight (x2 increase in MW = x10 viscosity) and enhanced chain entanglements producing orders of magnitude higher melt viscosity.[135,136]

ii. - **modification of either polymer** by grafting of the polymerisable reactive agent could raise component viscosities (assuming there was no reduction in the average molecular chain length of the host polymer) and hence increase the overall torque of blends. The magnitude of change would depend on modified product structure ; branch length, geometrical arrangement and distribution would all influence various aspects of the rheology.[135,136] An important point, however, is that if graft size was below a critical entanglement length then there would be little change in shear viscosity.

ii. - **interlinking agent polymerisation** could also cause considerable resistance to flow and raise viscosity, by extended network formation due to the multi-functionality of these reagents (Section 4.3.1). If discrete micro-gels or larger solid particles were produced then torque could be significantly increased, similarly to the reinforcing action of fillers, where just minor concentrations (<2%) can cause more than a 10% increase in melt

viscosity.[135,137] This process may have contributed to the high torque level given by the heavily solid-loaded PS cell at 10% TRIS with high initiator concentration (6KA5 - Section 4.2.1).

iv. - **interpolymer formation**, the targeted process to enable blend compatibilisation, was expected to result in higher torque if interpolymer yield was significant. Such torque rises during reactive blending have previously been linked to graft and interpolymer alloy formation in other PS blends. In the work of Ballegooie and Rudin[121,122] using a reactive agent (TAIC) in PS/PE blends, the greatest torque increases correlated with high grafting levels, especially in blends with high molecular weight grades of polymer and with reactive, copolymer-modified PS (containing ortho-vinylbenzaldehyde units). Similarly Baker and Saleem[8,9] found the most substantial torque increases in OPS/CPE blends to occur in conditions favouring almost total conversion to OPS-g-CPE alloy.

Torque rise and decay as a definite peak could also be rationalised by changes at a molecular level. This behaviour was uncommon in PS alone (except 6KA5, 10% TRIS at 0.01 FRI:RA molar ratio - Section 4.2.1), but dominant in EPDM with TRIS addition (Section 4.2.3) and high EPDM content blends (Section 3.2.3.1). The origin of this behaviour has been proposed to be restructurisation of polymer-bound, partially cross-linked networks of the interlinking agent under the action of shear (reported for PP/TRIS by Al-Malaika et al[138]). At the peak torque, grafted RA networks would be extensive, yielding high viscosity. Then with a depletion of radicals, from consumption of initiator, combined with high shear and entanglement stresses, mechanochemical scission of network cross-links results. Reduction of network molecular weight is thus effected, reducing melt viscosity until an equilibrium position is maintained, resulting in steady torque.

Torque rise, peak height and final level may thus indicate ongoing reactive processes and products formed by interlinking agent addition to PS, EPDM and blends. Critical analysis of these features, combined with an understanding of the most probable reactions of components and product characterisation should thus give a good measure of polymer and blend modification effectiveness by the approaches investigated.

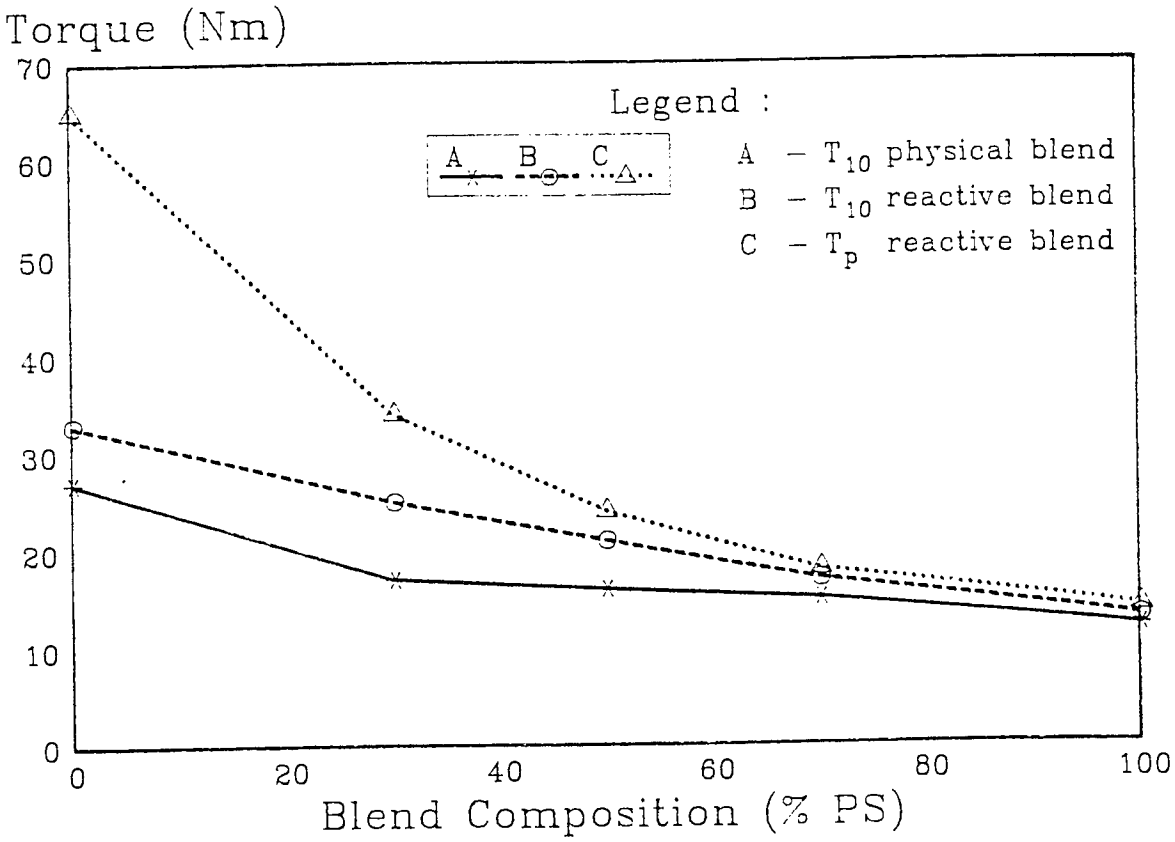
3.3.3 Principal Concepts of PS/EPDM Reactive Blending using TRIS Interlinking Agent by Determination of the Influence of Key Process Parameters.

The starting point for studying PS/EPDM reactive blending with the triacrylate interlinking agent (TRIS) was to determine baseline behaviour, key process parameters and reasonable operating windows from the wide range of variables possible.

Blend composition was recognised from the outset as being of prime importance in determining the nature of final products from the physically different, brittle PS and elastic EPDM. However, it soon became apparent that the torque response of each component to TRIS addition was also very different, with blend behaviour intermediate to the two extremes (Figure 3.5). The final torque (T_{10}) / blend composition curve for the physical blends gave a negative deviation to additivity (Figure 3.10) ; a typical outcome for the rheology of fully immiscible polymers possessing different viscosities (as for PS/PE[139]). In the current study EPDM was the higher viscosity component, presumably due to its high molecular weight, random copolymer structure and irregular distribution of bulky termonomer. Blend incompatibility was obvious from the resulting characteristics typical of an immiscible combination - opacity, general lack of physical strength and distinct two phase morphology lacking adhesion between the phases (as seen by SEM - Figure 3.2). This incompatibility was consistent with a previous study of PS/EPDM and as predicted by polymer solubility parameters mismatch (EPDM vs PS ; 7.7 vs 9.2 $cal^{1/2}cm^{3/2}$).[132]

The final torque of reactive blends was significantly greater than physical blends only at high EPDM content (Figure 3.10), though the full torque / compostition curve was again below the contribution expected from the proportion of each individual component, suggesting little interaction between the two polymers on reactive blending with TRIS. For EPDM alone, TRIS addition produced huge torque changes ; a large peak was given, with considerable decay to a still significantly higher final level (Figure 3.5 - 4KA4). As PS content was raised the effect of this peak was appreciably diluted (T_{peak} curve Figure 3.10), becoming insignificant at 70% PS (7KA4 - Figure 3.5). Thus there was little indication of any reaction between TRIS and PS, but large torque changes in high EPDM compositions suggested dominant reactive processes between TRIS and the elastomer.

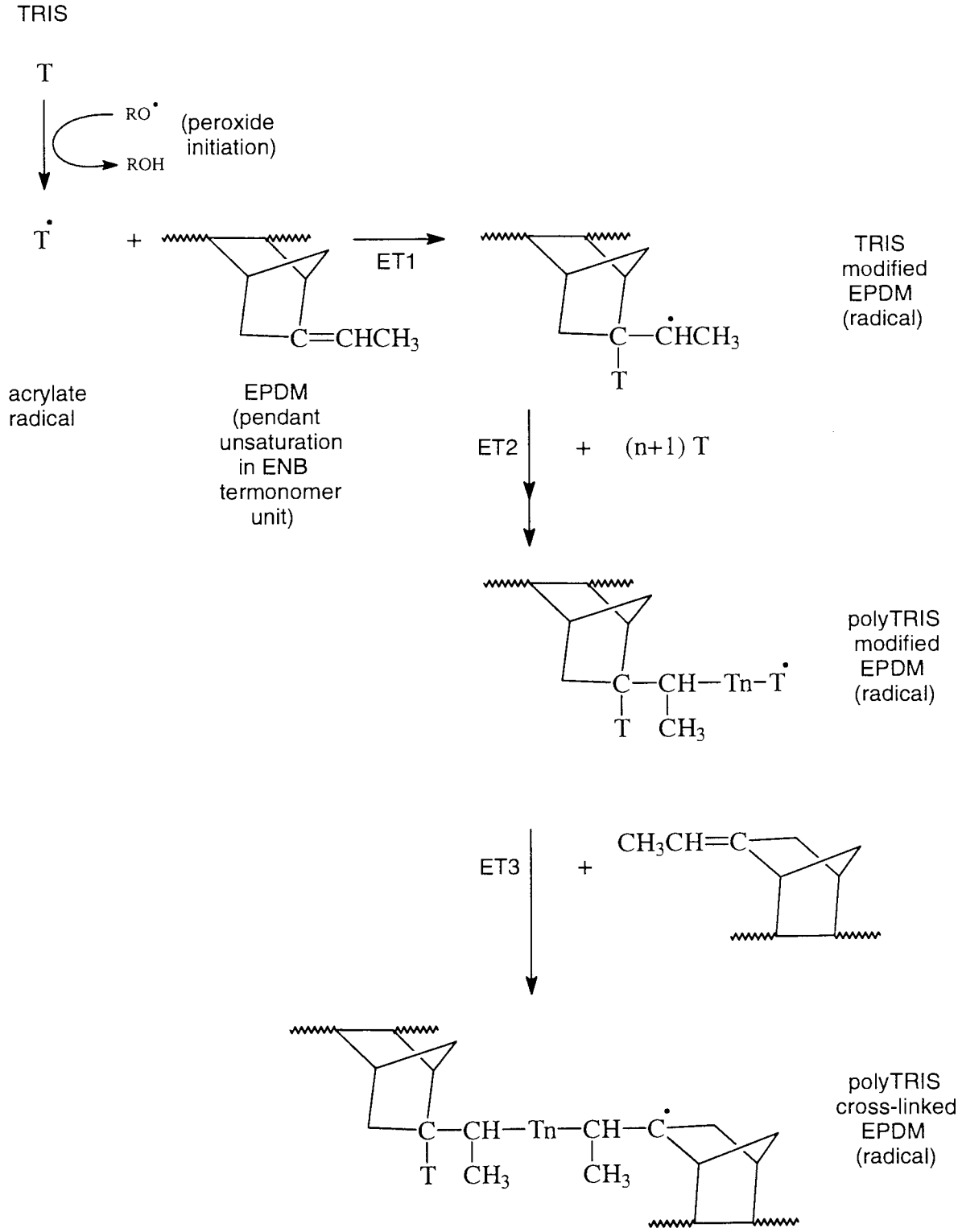
Figure 3.10 Torque/composition curves for physical PS/EPDM and reactive blends (with 5% TRIS at 0.001 FRI:RA molar ratio).



Unsaturation in the diene units of EPDM was acknowledged as the likely reactive centre for such events to occur, presumably via a free radical mechanism. One possible route is given in Scheme 3.2, where an initiated acrylate radical (T^*) reacts with pendant unsaturation in the EPDM (ET1), giving a radical centre from which further reactive agent may continue to be added (ET2), until cross-linking with another EPDM chain occurs (ET3). Comparison of this scheme with models developed later in the programme for triacrylate polymerisation and possible reactions with polystyrene (Section 4.3.1), suggests that this proposed route for EPDM is feasible. Opportunities for network formation and cross-linking would have been extensive due to the multifunctionality of the reactive agent, and were indeed supported by the large viscosity increase. However neither the torque decay behaviour nor the flexibity of reactively processed EPDM suggested cross-linking to be as dense as in a thermosetting material, probably due to the relatively minor amount of diene monomer in the elastomer (believed to be 3.8 mol% ENB). Further EPDM reaction may also have occurred by radical-initiated hydrogen abstraction from main chain ethylene and/or propylene sites. If considered similar to the degradation of polyethylene and polypropylene, the former may lead to cross-linking and also raise viscosity,[140] whereas the latter would result in chain scission and reduce viscosity[141] (perhaps evident during torque decay).

As the reactivity of PS was considered to be more limited than that of EPDM or TRIS, it was proposed that TRIS reaction occured predominantly within the EPDM phase, resulting in considerable cross-linking via a network of polymerised interlinking agent to produce the large torque gains found in high EPDM blends. To reduce this interference of essentially EPDM reaction and encourage formation of PS-EPDM interpolymer, it was decided that further studies of this system should be limited to high PS compositions (ie

Scheme 3.2 **Possible reaction of EPDM and triacrylate interlinking agent (TRIS) during reactive processing.**



70/30 PS/EPDM) until a suitable route for in-situ PS modification could be targetted and employed in the optimisation of PS/EPDM reactive blending.

Variation of TRIS addition level in 30% & 70% PS blends (Figure 3.6) affected the extent of torque changes, though in high PS blends this was more limited, presumably due to the composition factor. At a 5% addition in the 30/70 PS/EPDM blend (12KA4) significant torque gains were produced. Torque increased slightly further at an 8% addition, but the predominant feature at this level in both blends (14KA4 & 9KA4) was a heavy loading of coarse particles in the resulting products. This was believed to arise from greater reactive agent self polymerisation at high addition. It was thus decided that a 5% addition level would be appropriate to identify and measure reactive events, whilst limiting interlinking agent self reaction.

A higher mixing speed was found to produce consistently earlier torque peaks and lower final torques over all compositions (Figure 3.7). This suggested that mass transfer, rather than kinetics of the chemical processes involved, determined reaction rate, though not necessarily the outcome. This was not surprising since the macro-radicals involved would be expected to be highly reactive, with short life-times, but have limited mobility due to their high viscosity. Lower control torque was also shown at higher mixing speed (20KA4 - Table 3.6) and could be accounted for by decreased blend viscosity at higher shear rate. Thus on first assessment there appeared to be no advantage in operating at the higher mixing rate ; indeed since lower torques were given the significance between different levels may have been more difficult to evaluate and torque peaks less distinct, so that 60rpm was accepted as the "standard processing conditions" for all further experimentation.

A fundamental principle throughout this initial work was the lack of any indication of PS modification by the triacrylate reagent, contrasted by apparent facile reaction with EPDM. Indeed the PS component had been selected as a challenge, being an inert hydrocarbon polymer (Section 1.5). However, the morphology of reactively processed 70/30 PS/EPDM (7KA4) was so different to the corresponding physical blend (5KA2 - Figure 3.8) that it was felt that some degree of miscibilisation had been achieved. From studies using copolymer compatibilisers it has been found that only very low levels of these interfacial agents (2-5%) are required to produce such effects.[87,102] Thus even a low yield of interpolymer formed in-situ between the PS and EPDM phases would probably improve blend compatibility. The key to exploiting this effect must be in unlocking the modification of the polystyrene component and targetting this in the presence of EPDM - hence the vitally important extended study of PS modification (Chapter 4), the learning from which was then applied in a final optimisation phase of PS/EPDM reactive blending (Chapter 5).

CHAPTER 4

MODIFICATION OF POLYSTYRENE AND EPDM BY REACTIVE PROCESSING AND ANALYSIS OF POLYSTYRENE COMPOSITIONS.

4.1 OBJECTIVES AND METHODOLOGY.

From the early studies of PS/EPDM reactive blending (Chapter 3), it was found that PS and high PS blends exhibited little changes in torque behaviour during processing with the triacrylate reactive agent (TRIS). This was accepted as an indication of the recognised "inertness" of PS. The key to unlocking effective reactive modification of the blends thus appeared to lie in enhancing interlinking agent reaction with the PS in the presence of facile EPDM reaction. The investigations presented in this chapter were undertaken on each of the component polymers from the PS/EPDM blend system, carried out with the objective of determining the most effective approach to modification. This learning was subsequently used to raise the effectiveness of reactive blending between these two polymers and the same modifiers (Chapter 5).

Targeted functionalisation of the polystyrene alone was thus studied more completely to determine the key process parameters ; such as TRIS addition level and initiator concentration (free radical initiator : reactive agent molar ratio - FRI:RA). A further approach was to separate TRIS and FRI additions by pre-mixing initiator with the PS chip prior to processing. This was to target the generation of PS macro-radicals for direct reaction with TRIS on addition in the standard way, in preference to initiation and self-reaction of the polymerisable interlinking agent.

Since modification of the polystyrene appeared to be problematic with TRIS, an alternative interlinking agent was assessed. Divinylbenzene (DVB) has been used as a minor co-monomer in styrene polymerisation to introduce a degree of cross-linking and affect specific properties.[82] Considering this and its probable miscibility with

polystyrene, it was deemed suitable for evaluation. Initiator concentration and FRI pre-addition were also examined as control parameters for modification of PS by DVB, and compared to the behaviour of TRIS. Another major objective for this phase of the work was to develop a scheme of analysis to quantify the outcome of PS reactive modification. Thus key test cells and controls from TRIS and DVB reactive processing with PS were selected for a common scheme of chemical analysis by solvent extraction and fraction separation in conjunction with FT-IR spectroscopy to measure interlinking agent grafting (binding level) at various process formulations (Scheme 4.1).

The behaviour of an ethylene-propylene-diene (EPDM) elastomer alone (Vistalon 2504 from EXXON, believed to be composed of 50% ethylene, 3.8% ethylidene norbornene [ENB] and the remainder as propylene monomer) was also examined over a range of addition and FRI:RA levels with the triacrylate interlinking agent (TRIS). This data was then used to determine if torque changes during the reactive processing of blends were in proportion with the contribution of this component, expected to arise from the reactive unsaturation pendant to the main chain in the ENB tri-monomer units. EPDM was also reactively processed with DVB to assess the suitability of this alternative interlinking agent compared to TRIS.

The general experimental procedure (Scheme 4.1) was as follows : reactive interlinking agent (RA - TRIS or DVB) and peroxide free radical initiator (FRI - Trigonox 101) mixtures were accurately prepared to give a range of FRI concentrations (nil to 0.01 FRI:RA molar ratio). 35.0g of polymer (PS or EPDM) was processed in a HAMPDEN-RAPRA TORQUE RHEOMETER (TR) at 180°C with a rotor speed of 60rpm under closed mixer conditions ("the standard processing conditions") and after three minutes an accurate addition of RA & FRI mixture (from 2-10%) injected directly into the melt. Mixing was continued with a closed chamber for a total of ten minutes ; torque was

monitored throughout the whole mixing period to characterise the behaviour and to indicate any changes due to physical or chemical processes. In some of the PS test cells an accurate mass of peroxide initiator (< 0.1%) was added directly to the PS chip and tumble mixed prior to processing. Relevant control cells of both polymers were also processed. All samples processed are detailed in Table 4.1 for reference.

Samples of the key PS test cells and controls were moulded into thin films (around 0.2mm thick) and subjected to dichloromethane extraction in Soxhlets for four hours to determine the content of insoluble residue, most likely to be self-polymerised interlinking agent. Thin films were cast directly by evaporation of solvent from portions of the soluble fractions, and the remainder run into methanol to precipitate a purified PS fraction, from which any free or insoluble interlinking agent had been extracted. Samples of these precipitate fractions were analysed by proton and ^{13}C NMR to assess if any structural or compositional data could be derived from this technique. Thin films of these precipitate samples were also cast from fresh dichloromethane and analysed by FT-IR spectroscopy. The initial PS film samples, and films from the soluble fractions, were similarly analysed by FT-IR to measure the relative interlinking agent contents and identify any chemical changes between different test cells, controls and extracted fractions. Measurements of the PS glass transition behaviour were also made on entire and precipitate fractions by DSC.

It was realised that this analysis would not completely characterise the resulting modifications of reactively processed polymer and further analytical studies could be proposed to interrogate the extent and nature of the considerable polymer modifications achieved. However, as an assessment of the effectiveness of different approaches for application in blend modification, valuable insight on the mechanisms involved was provided and optimum process conditions for PS modification could be recommended.

Scheme 4.1 **General Experimental Procedure for the Investigation of PS or EPDM Reactive Processing with TRIS and DVB Interlinking Agents and Analysis of PS Compositions.**

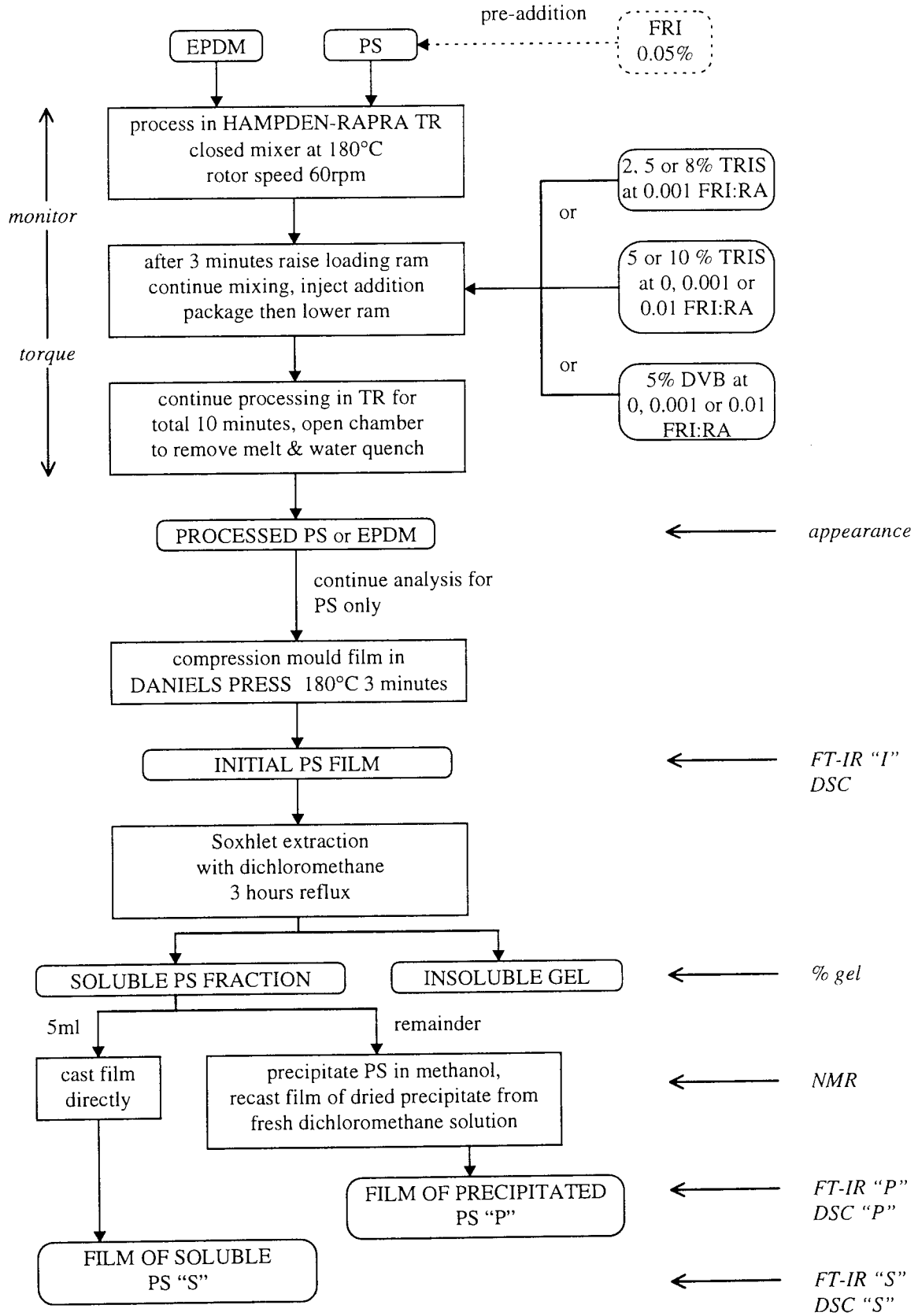


Table 4.1 **Reference List of Samples for the Investigation of PS and EPDM Modification Using TRIS or DVB Interlinking Agents With Organic Peroxide Free Radical Initiator (Trigonox 101) by Reactive Processing Under Standard Conditions[1].**

Sample Cell	Method[2]	Polymer grade[3]	RA type	RA Level % w/w	FRI:RA molar ratio	+ FRI % w/w
2KA2	C	PS S634	none	nil	nil	nil
2KA4	DA	PS S634	TRIS	2.0	0.001	nil
1KA4	DA	PS S634	TRIS	5.0	0.001	nil
3KA4	DA	PS S634	TRIS	8.0	0.001	nil
1KA5	C	PS H311	none	nil	nil	nil
4KA5	C	PS H311	none	nil	(opened)	nil
4KA6	DA	PS H311	TRIS	5.0	nil	nil
2KA5	DA	PS H311	TRIS	5.0	0.001	nil
3KA5	DA	PS H311	TRIS	5.0	0.01	nil
8KA6	DA	PS H311	TRIS	10.0	nil	nil
5KA5	DA	PS H311	TRIS	10.0	0.001	nil
6KA5	DA	PS H311	TRIS	10.0	0.01	nil
6KA6	CC	PS H311	none	nil	nil	0.04
7KA6	DA	PS H311	none	nil	(opened)	0.05
3KA6	DA	PS H311	TRIS	5.0	nil	0.03
5KA6	DA	PS H311	TRIS	5.0	0.001	0.04
3KA8	DA	PS H311	DVB	5.0	nil	nil
4KA8	DA	PS H311	DVB	5.0	0.001	nil
1KA8	DA	PS H311	DVB	5.0	0.01	nil
7KA8	DA	PS H311	DVB	5.0	nil	0.07
8KA8	DA	PS H311	DVB	5.0	0.01	0.05
3KA2	C	EPDM V2504	none	nil	nil	nil
9KA5	C	EPDM V2504	none	nil	(opened)	nil
5KA4	DA	EPDM V2504	TRIS	2.0	0.001	nil
8KA5	DA	EPDM V2504	TRIS	5.0	nil	nil
4KA4	DA	EPDM V2504	TRIS	5.0	0.001	nil
7KA5	DA	EPDM V2504	TRIS	5.0	0.01	nil
6KA4	DA	EPDM V2504	TRIS	8.0	0.001	nil
6KA8	DA	EPDM V2504	DVB	5.0	0.001	nil

Notes :

1 - Standard processing conditions ; 180°C, 60rpm, 10 minutes.

2 - C = control (Scheme 2.1 [PS or EPDM only], page 82)

- DA = RA direct addition (Scheme 2.3 [PS or EPDM only], page 84)

3 - PS grades ; S634 = Dow Styron 634

H311 = Huntsman Crystal PS 311

- EPDM grade ; V2504 = EXXON Vistalon 2504

4.2 RESULTS.

4.2.1 Polystyrene Reactive Processing With Triacrylate Interlinking Agent (TRIS).

In the first part of this study, to assess the effect of TRIS addition level, Dow Styron 634 was employed as the PS feedstock. However, only a limited quantity of this grade was available. For the remainder of the work, an equivalent grade from a different supplier was used (Huntsman Crystal PS 311, Huntsman Chemical Company Limited, Manchester, UK). Similarity of behaviour was confirmed and key process cells were repeated with the Huntsman polymer to allow direct comparison of control and test cells.

4.2.1.1 Effect of TRIS Addition Level.

With the Dow Styron 634 it was found that although higher final torque (T_{10}) was obtained with increasing TRIS addition at constant FRI:RA molar ratio (0.001), intermediate torque peaks were practically absent and the overall behaviour was not much different to inert material (Table 4.2 and Figure 4.1). The torque drop on injection of fluid TRIS & FRI mixture was deeper at higher additions. Recovery was at a similar rate for all cells, with only 8% TRIS (3KA4) exceeding the three minute torque (T_3). Polymer with this high RA content was heavily loaded with many coarse particulate solids after processing.

4.2.1.2 Effect of Initiator Concentration.

For the Huntsman PS it was found that the degree of torque rise after TRIS & FRI addition, peak height and final torque were all substantially increased by raising the concentration of initiator at both 5% and 10% TRIS additions (Table 4.3). At the 5% addition, torque recovery to control levels was managed by both the low FRI:RA ratio (2KA5 - 0.001 molar ratio) and addition of TRIS without any initiator (4KA6). Immediate

Table 4.2 **Torque behaviour of polystyrene (Dow Styron 634) and rective compositions with different TRIS additions at constant FRI:RA molar ratio (0.001) processed under standard conditions.**

Sample Cell	Composition (% w/w) TRIS & FRI target	actual	Torque Behaviour T_3 (Nm)	Peak (Nm)	(min)	T_{10} (Nm)
2KA2	nil		13	none		12
2KA4	2.0	2.20	13	12	3.67	11
1KA4	5.0	4.92	14	14	6.0	13
3KA4	8.0	8.03	13	15	5.75	15

Figure 4.1 **Torque behaviour of polystyrene (Dow Styron 634) inert and reactively processed with different TRIS additions at 0.001 FRI:RA molar ratio under standard conditions.**

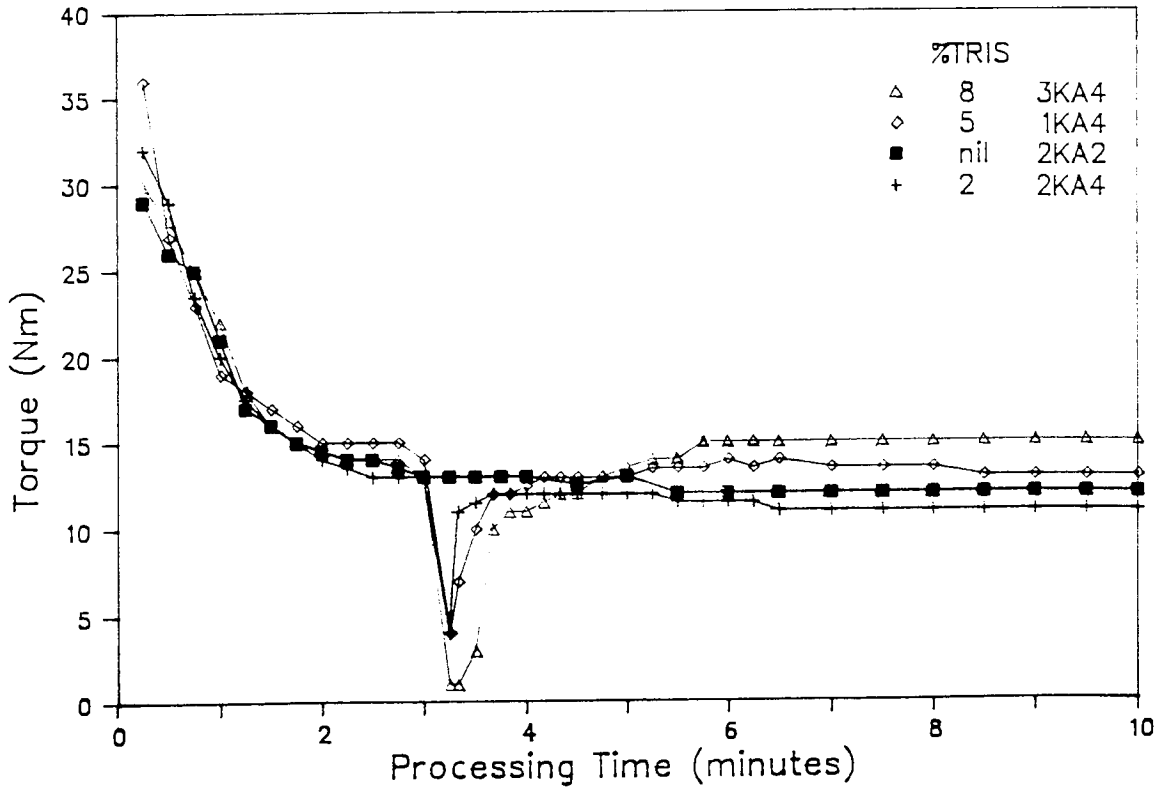


Table 4.3 **Torque behaviour of polystyrene (Huntsman 311) reactively processed with different TRIS additions & FRI:RA molar ratios and controls processed under standard conditions.**

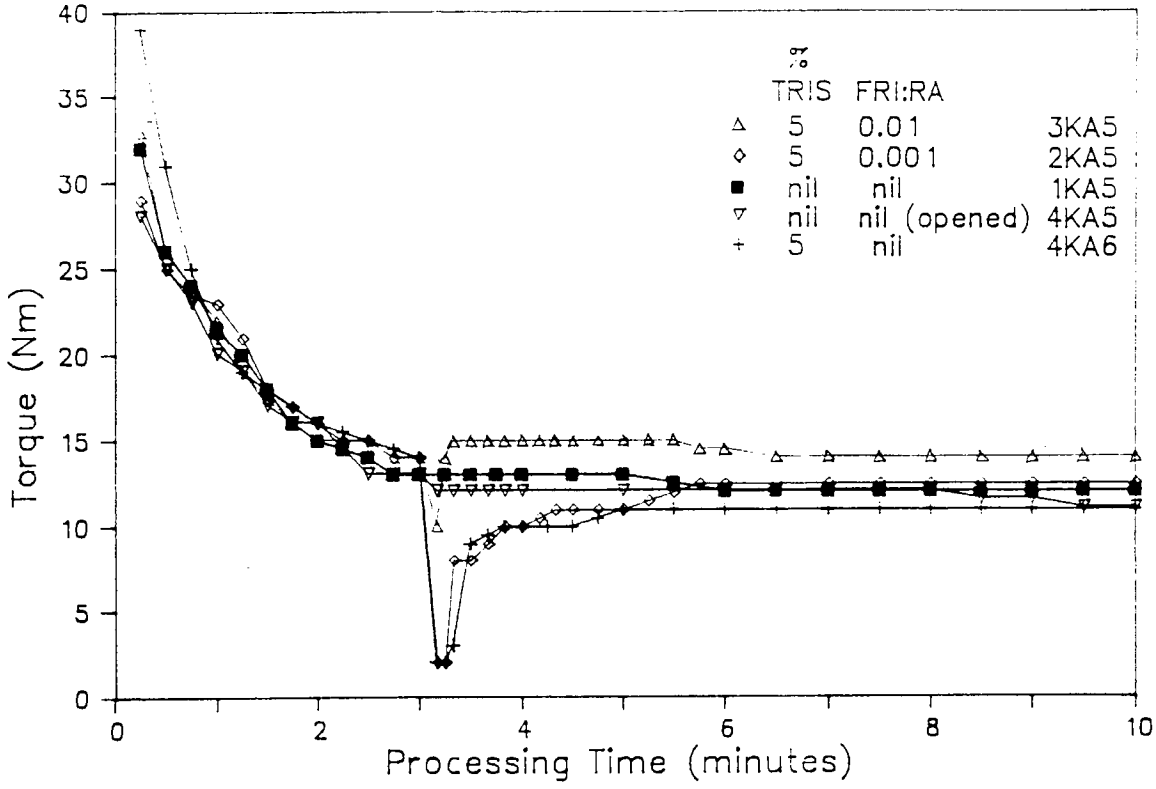
Sample Cell	Composition (% w/w) TRIS & FRI target	actual	FRI:RA molar ratio	Torque Behaviour T_3 (Nm)	Peak (Nm)	(min)	T_{10} (Nm)
1KA5	nil		nil	13	none		12
4KA5	nil	(opened)	nil	13	none		11
4KA6	5.0	5.13	nil	14	11	5.0	11
2KA5	5.0	5.52	0.001	14	12.5	5.75	12.5
3KA5	5.0	5.26	0.01	14	15	3.3	14
8KA6	10.0	10.14	nil	13	11	10.0	11
5KA5	10.0	9.89	0.001	13	14	5.0	13
6KA5	10.0	10.37	0.01	13.5	19	3.3	16

torque rise to the highest maximum of this series occurred at the highest initiator concentration (3KA5 - 0.01 FRI:RA molar ratio). This increase was just above the T_3 reference torque and the controls, and remained just higher even with a slight decay on further mixing (Figure 4.2a).

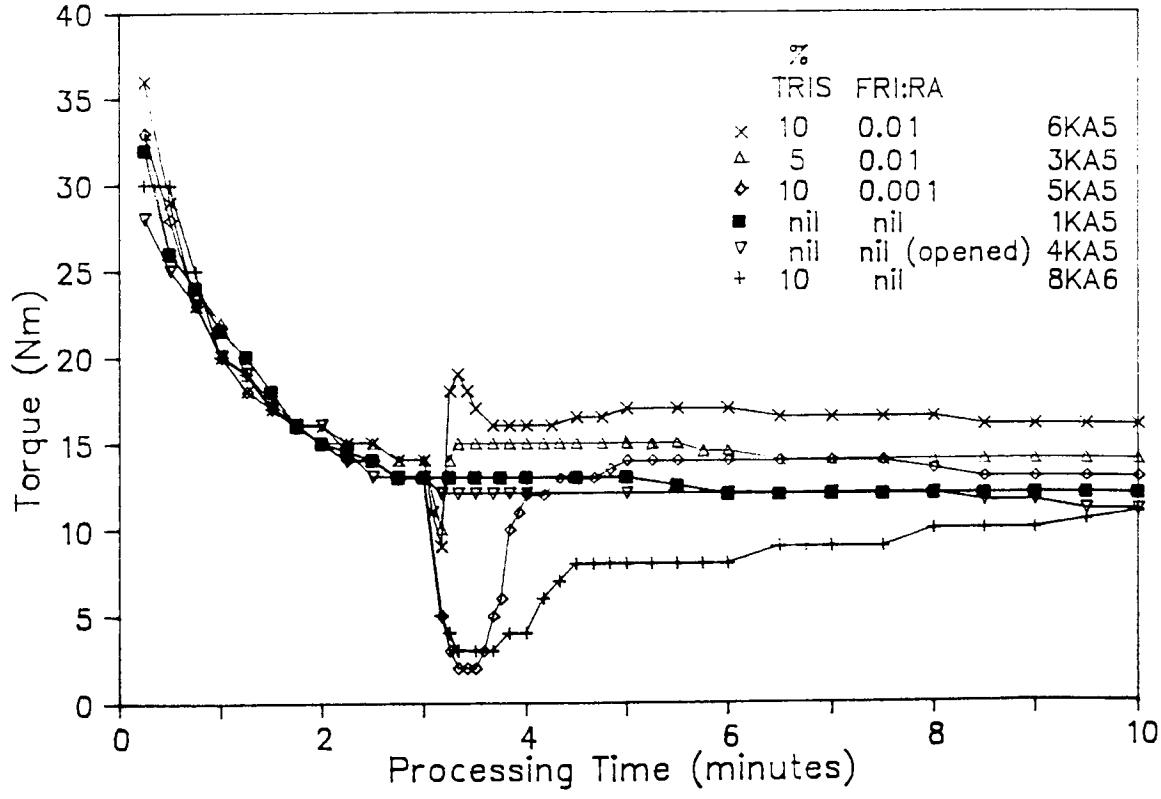
The pattern at 10% TRIS addition was found to be fairly similar, though slightly more distinct (Figure 4.2b). Neat TRIS (8KA6 - nil FRI) gave a slow torque rise for most of the mixing time, only regaining the control level at 10 minutes. With low initiator concentration (5KA5), torque rise just exceeded the reference and was maintained above control values. The most dramatic torque peak seen for PS was achieved under the most extreme conditions ; high FRI:RA ratio at high addition level (6KA5). Torque rose immediately after injection, to a distinct peak with decay at an almost equal rate, before levelling off well above control levels to yield the most significant final torque.

Figure 4.2 **Torque behaviour of polystyrene (Huntsman 311) reactively processed with 5 and 10% TRIS additions at variable FRI:RA molar ratios and controls under standard process conditions.**

a) 5% TRIS additions.



b) 10% TRIS additions.



It was observed that in some of the reactively processed compositions product appearance was adversely affected in comparison with processed PS controls (Table 4.4). Loss of transparency and increased solids loading resulted from high TRIS addition or high FRI:RA ratio. For 10% TRIS without FRI (6KA5) the final material also had a noticeable acrylate odour.

Table 4.4 **Appearance of polystyrene (Huntsman 311) reactively processed with different TRIS additions & FRI:RA molar ratios and controls processed under standard conditions.**

Sample Cell	TRIS addition actual (w/w)	FRI:RA molar ratio	Appearance after processing
1KA5	nil	nil	clear, a few bubbles & dirty specks
4KA5	nil	(opened)	clear, a few bubbles & dirty specks
4KA6	5.13	nil	translucent, some bubbles & dirty specks
2KA5	5.52	0.001	translucent, a few small whiteparticles
3KA5	5.26	0.01	opaque, many coarse white particles
8KA6	10.14	nil	translucent, almost opaque, pale yellow tinge
5KA5	9.89	0.001	opaque, many coarse white particles
6KA5	10.37	0.01	opaque, pale grey, many coarse white particles

4.2.1.3 Effect of Initiator Pre-Addition.

Polystyrene controls were processed under standard conditions having had a minor amount of the Trigonox 101 free radical initiator mixed in with the PS chip prior to melt fluxing in the Brabender TR (Table 4.5). No differences in torques for these controls were seen (Figure 4.3a). There was however, substantial change in the appearance of both controls with FRI pre-addition, which became slightly off-white and almost opaque.

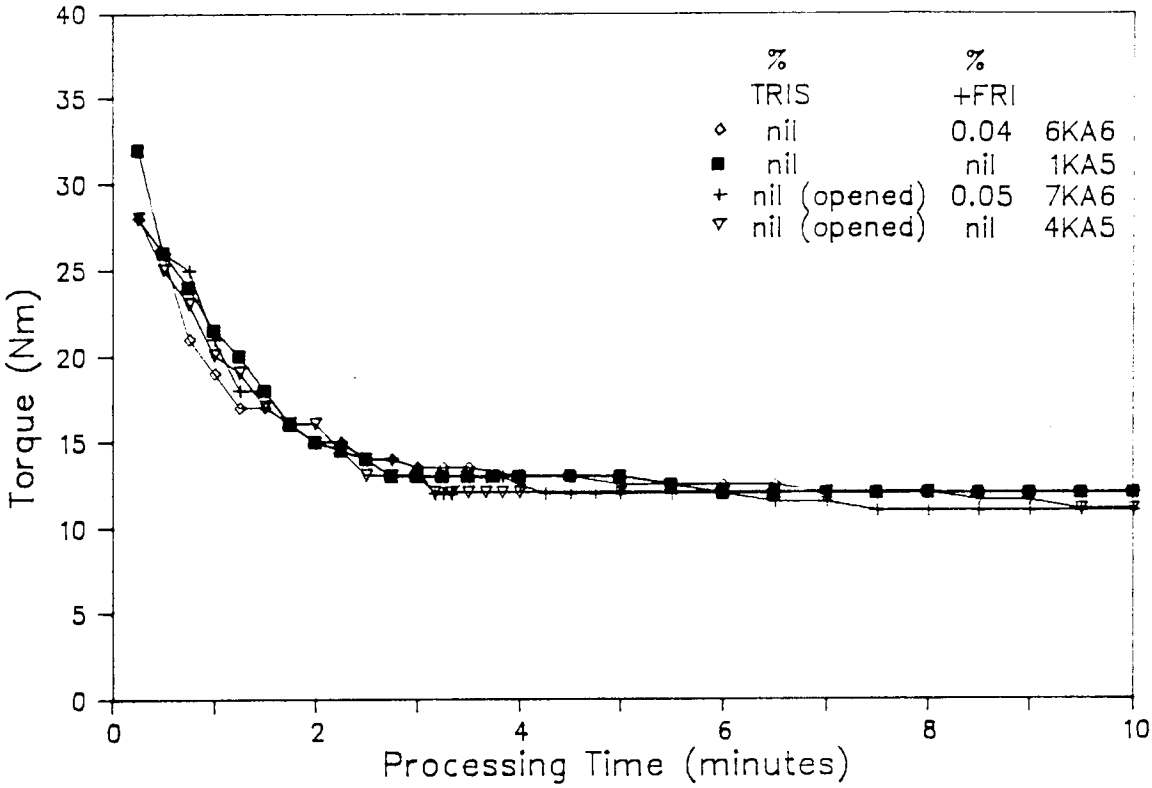
Substantial torque rise above control levels was achieved when TRIS and FRI were injected into the melt of PS with pre-addition of initiator (Table 4.5 and Figure 4.3b). Torque gains were to maxima above control levels, maintained to the end of processing, irrespective of FRI content of the TRIS at addition. For FRI pre-treatment followed by addition of TRIS alone (3KA6) torque peak matched the T_3 reference point, whereas for TRIS & FRI combined with initiator pre-addition (5KA6) the torque maximum exceeded the T_3 reference value. The rate of increase to these distinctly higher torques was similar for both cells. Previously such torque gains had only been found with extreme FRI:RA ratio or high RA addition. Unlike in these cases, there was less detrimental effect on product appearance with FRI pre-addition (Table 4.6) ; solids contamination was no worse than the corresponding cell without the initial FRI (2KA5), although the bulk was slightly more opaque (as found for controls without RA - 6KA6 & 7KA6).

Table 4.5 **Torque behaviour of polystyrene (Huntsman 311) reactively processed with nominally 5% TRIS at different FRI:RA molar ratios, incorporating pre-addition of peroxide initiator (Trigonox 101) and controls processed under standard conditions.**

Sample Cell	Composition				Torque Behaviour			
	TRIS & FRI (% w/w) target	TRIS & FRI (% w/w) actual	FRI:RA molar ratio	+ FRI (% w/w)	T_3 (Nm)	Peak (Nm)	Peak (min)	T_{10} (Nm)
1KA5	nil		nil	nil	13	none		12
4KA5	nil	(opened)	nil	nil	13	none		11
6KA6	nil		nil	0.04	13.5	none		12
7KA6	nil	(opened)	nil	0.05	13.5	none		11
4KA6	5.0	5.13	nil	nil	14	11	5.0	11
2KA5	5.0	5.52	0.001	nil	14	12.5	5.75	12.5
3KA6	5.0	5.39	nil	0.03	15	15	5.8	14.5
5KA6	5.0	5.12	0.001	0.04	13	15	5.3	14

Figure 4.3 **Torque behaviour of polystyrene (Huntsman 311) reactively processed with 5% TRIS additions at different FRI:RA molar ratios incorporating pre-addition of peroxide initiator and controls under standard process conditions.**

a) PS controls.



b) 5% TRIS additions.

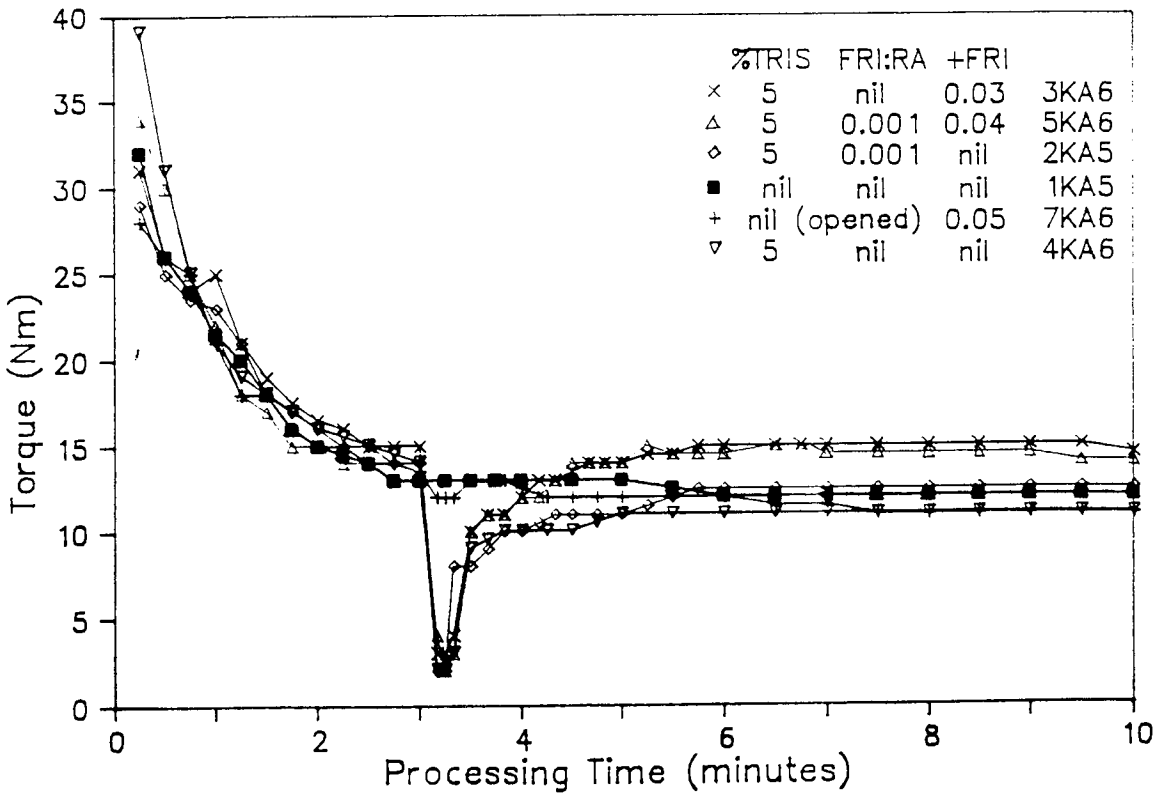


Table 4.6 **Appearance of polystyrene (Huntsman 311) reactively processed with nominally 5% TRIS at different FRI:RA molar ratios, incorporating pre-addition of peroxide initiator (Trigonox 101) and controls processed under standard conditions.**

Sample Cell	TRIS addition actual (w/w)	FRI:RA molar ratio	+ FRI (% w/w)	Appearance after processing
1KA5	nil	nil	nil	clear, a few bubbles & dirty specks
4KA5	nil	(opened)	nil	clear, a few bubbles & dirty specks
6KA6	nil	nil	0.04	opaque, off-white
7KA6	nil	(opened)	0.05	almost opaque, slightly off-white
4KA6	5.13	nil	nil	translucent, some bubbles & dirty specks
2KA5	5.52	0.001	nil	translucent, a few small white particles
3KA6	5.39	nil	0.03	almost opaque, no particles
5KA6	5.12	0.001	0.04	almost opaque, a few small white particles

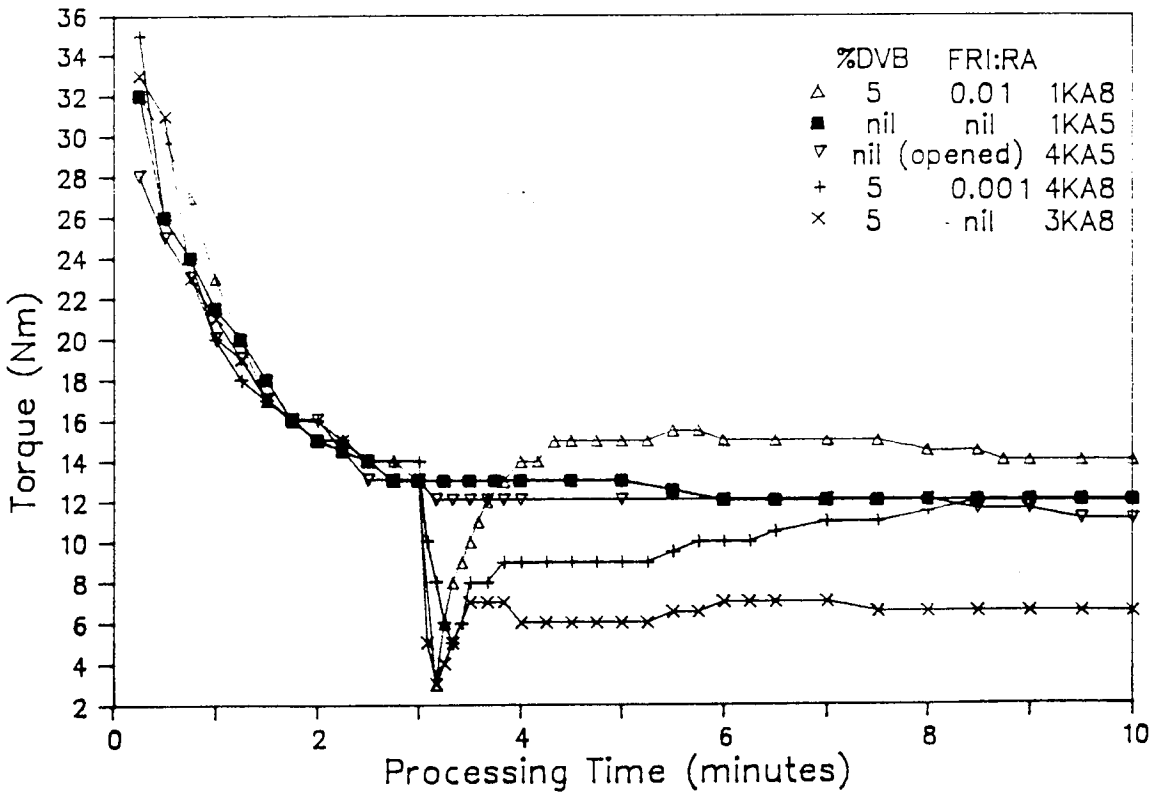
4.2.2 Reactive Processing of Polystrene With Divinylbenzene (DVB) Interlinking Agent.

Both factors believed to have the most influence in controlling the effects of reactive processing with interlinking agents, namely initiator concentration and FRI pre-addition, were examined in polystyrene using divinylbenzene (Table 4.7). With increasing initiator concentration the rate of torque rise after DVB addition, peak value and final torque level were all raised (Figure 4.4). DVB alone without any initiator (3KA8) gave only fractional recovery of torque, after the usual drop on addition, to about half the control level. The low FRI:RA ratio (4KA8) produced a slow torque rise to a maximum around 5 minutes after addition, holding steady in this position, equivalent to the controls, for the remainder

Table 4.7 **Torque behaviour of polystyrene (Huntsman 311) reactively processed with nominally 5% DVB at different FRI:RA molar ratios, incorporating pre-addition of peroxide initiator (Trigonox 101) and controls under standard conditions.**

Sample Cell	Composition				Torque Behaviour			
	DVB & FRI (% w/w) target	DVB & FRI (% w/w) actual	FRI:RA molar ratio	+ FRI (% w/w)	T_3 (Nm)	Peak (Nm)	Peak (min)	T_{10} (Nm)
1KA5	nil		nil	nil	13	none		12
4KA5	nil	(opened)	nil	nil	13	none		11
7KA6	nil	(opened)	nil	0.05	13.5	none		11
3KA8	5.0	5.29	nil	nil	13	7	3.5	6.5
4KA8	5.0	5.54	0.001	nil	12	12	8.5	12
1KA8	5.0	5.06	0.01	nil	13	15.5	5.5	14
7KA8	5.0	5.45	nil	0.07	13	13	8.5	12.5
8KA8	5.0	5.20	0.01	0.05	13	13	5.0	12.5

Figure 4.4 **Torque behaviour of polystyrene (Huntsman 311) reactively processed with 5% DVB additions at variable FRI:RA molar ratios and controls under standard process conditions.**



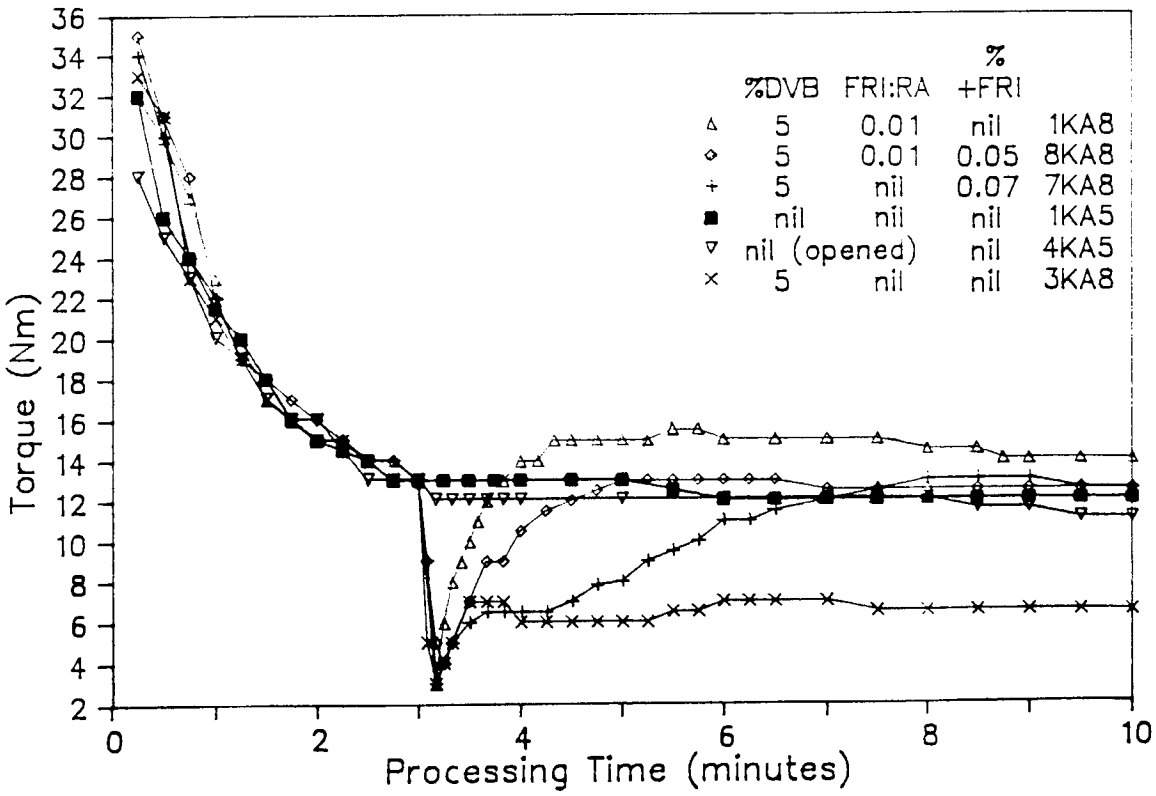
of mixing. Higher initiator content (1KA8) gave increased torque growth to a greater maximum torque, which decayed slightly during further mixing, but still exceeded the reference point and controls. Such large torque changes for PS with 5% DVB at high FRI:RA were at least equal to the highest obtained for 5% TRIS with optimised FRI:RA and FRI pre-addition (5KA6 - see 4.2.1). However, whereas TRIS gave severe solids contamination (especially at high FRI:RA), only minor reductions in clarity were found with DVB (Table 4.8).

The effect of initiator pre-addition varied according to the presence of FRI in the DVB at the point of addition (Figure 4.5). For DVB without FRI, initiator pre-addition significantly improved torque recovery (7KA8). The initial rate of torque rise was similar for DVB only additions to PS with and without initiator pre-treatment (7KA8 vs 3KA8), but torque subsequently continued to rise when pre-addition was used, to reach the control level about five minutes later, where it remained through to the end of processing. However when initiator pre-addition was followed by the introduction of the best-effort DVB & FRI formulation (8KA8), rate of torque rise and ultimate level were lower than without pre-treatment (1KA8). Appearance was not adversely affected (Table 4.8). This behaviour was surprisingly different to the TRIS system in which a minor initiator pre-addition had been found to promote significant torque increases (Section 4.2.1).

Table 4.8 **Appearance of polystyrene (Huntsman 311) reactively processed with nominally 5% DVB at different FRI:RA molar ratios, incorporating pre-addition of peroxide initiator (Trigonox 101) and controls under standard conditions.**

Sample Cell	DVB addition actual (w/w)	FRI:RA molar ratio	+ FRI (% w/w)	Appearance after processing
1KA5	nil	nil	nil	clear, a few bubbles & dirty specks
4KA5	nil	(opened)	nil	clear, a few bubbles & dirty specks
7KA6	nil	(opened)	0.05	almost opaque, slightly off-white
3KA8	5.29	nil	nil	clear, particle-free
4KA8	5.54	0.001	nil	translucent, particle-free
1KA8	5.06	0.01	nil	translucent, slightly darkened, particle-free
7KA8	5.45	nil	0.07	translucent, particle-free
8KA8	5.20	0.01	0.05	translucent, particle-free

Figure 4.5 **Torque behaviour of polystyrene (Huntsman 311) reactively processed with 5% DVB additions at different FRI:RA molar ratios incorporating pre-addition of peroxide initiator (Trigonox 101) and controls under standard conditions.**



4.2.3 Reactive Processing of EPDM With A Triacrylate Interlinking Agent (TRIS).

Using the standard method for reactive processing in the rheometer, both the effect of TRIS addition level and FRI:RA molar ratio at a 5% TRIS addition were investigated in the Vistalon 2504 ethylene-propylene-diene elastomer (Table 4.9). Difficulties were found in loading the TR with cut pieces of EPDM ; they tended to stick in the feeding chute rather than fall directly into the mixing chamber, needing the ram to be lowered and raised several times during the loading operation. Once the 35g batch had been fully charged and torque measurements started, perhaps because of the loading difficulties, the initial torque decline was not consistent for all samples and the T_3 reference torques extended over a range of 7Nm.

TRIS addition level at 0.001 molar FRI:RA ratio had a dramatic impact upon the torque behaviour of EPDM during melt mixing (Figure 4.6). Torque rise was at the same high rate for all reactive cells, increasing to peak maxima substantially higher than control levels within a minute after TRIS & FRI addition. The greatest peak was at the intermediate 5% TRIS content (4KA4), about double the torque of the controls at the corresponding time. More TRIS (8% - 6KA4) produced a lower peak maximum, closer to that of the lowest RA addition (2% - 5KA4). Decay was extreme at both 2% and 5% TRIS, but less so for the higher level such that the resulting final torque was found to increase with TRIS addition level ; all were still above control T_{10} values however. The opened-chamber control for EPDM (9KA5) gave a sharp torque drop on opening which was not completely recovered, showing lower torque for the remainder of mixing than when fully closed (3KA2). All samples were similar in form and appearance, except at high TRIS which was considerably darker and cloudy.

The effects of initiator concentration at 5% TRIS addition were also quite dramatic (Figure 4.7). The greatest changes were again found at the intermediate, rather than the highest level ; the 0.001 FRI:RA molar ratio (4KA4) produced the largest torque peak, most considerable decay as mixing continued and yet still the highest final torque. Rate of torque rise did appear to be raised at higher FRI concentration (7KA5), though the maximum torque from this was slightly lower than when TRIS without FRI was added (8KA5). Product from high FRI:RA ratio (7KA5) was darker, cloudy and much stiffer than any of the other samples.

Table 4.9 **Torque behaviour of reactively processed EPDM (Vistalon 2504) for TRIS and DVB additions at different FRI:RA molar ratios and controls processed under standard conditions.**

Sample Cell	RA type	Composition (% w/w) RA & FRI target	actual	FRI:RA molar ratio	Torque Behaviour T_3 (Nm)	Peak (Nm)	(min)	T_{10} (Nm)
3KA2	nil	nil		nil	31	none		27
9KA5	nil	nil	(opened)	nil	30	none		23
5KA4	TRIS	2.0	2.26	0.001	36	53	4.0	30
8KA5	TRIS	5.0	5.16	nil	30	41	4.5	29
4KA4	TRIS	5.0	5.00	0.001	36	65	4.0	33
7KA5	TRIS	5.0	5.20	0.01	29	39	3.67	28
6KA4	TRIS	8.0	8.26	0.001	34	56	3.67	43
6KA8	DVB	5.0	5.57	0.001	29	31	4.25	22

Figure 4.6 **Reactively processed EPDM (Vistalon 2504) torque behaviour with different TRIS additions at 0.001 FRI:RA molar ratio and controls processed under standard conditions.**

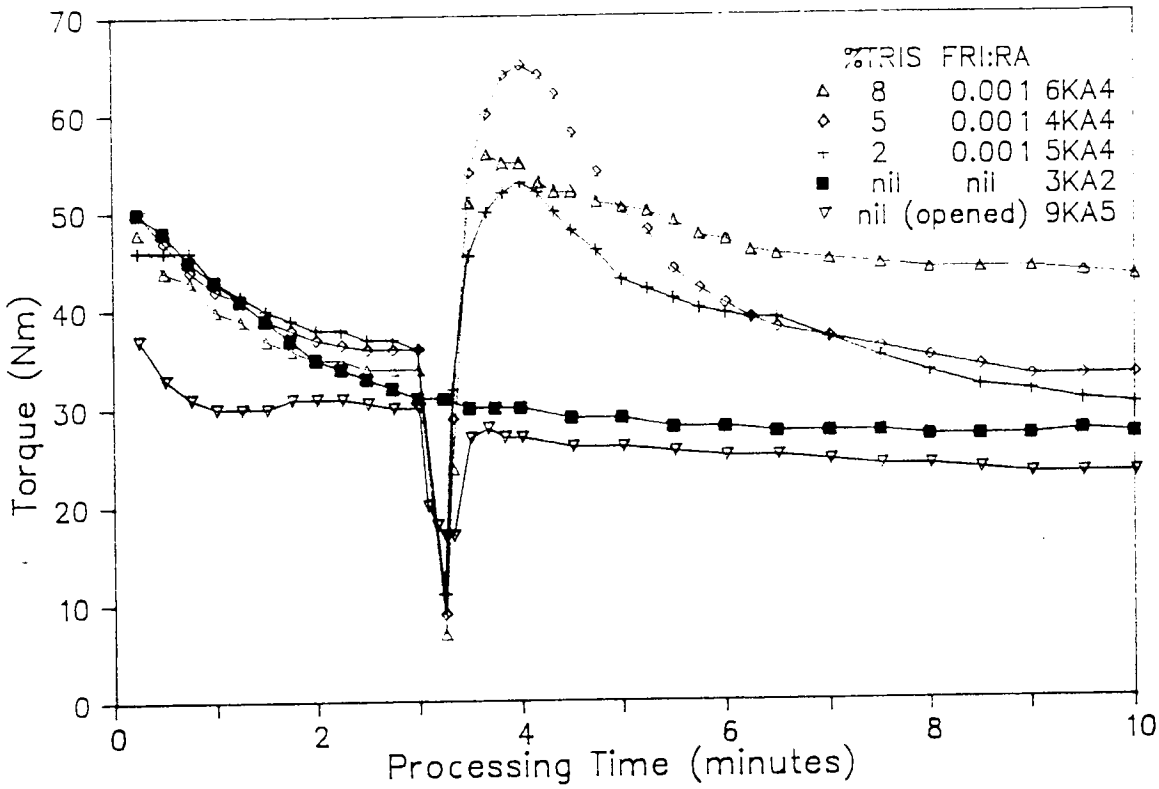
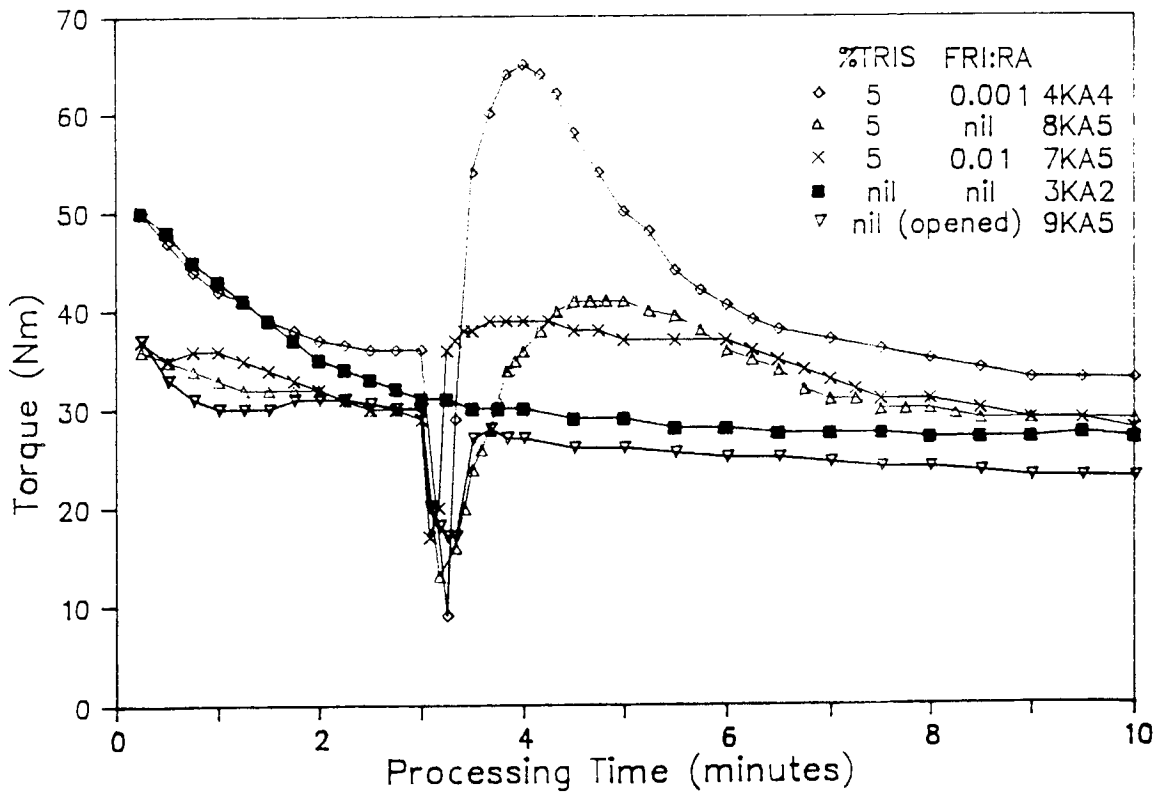


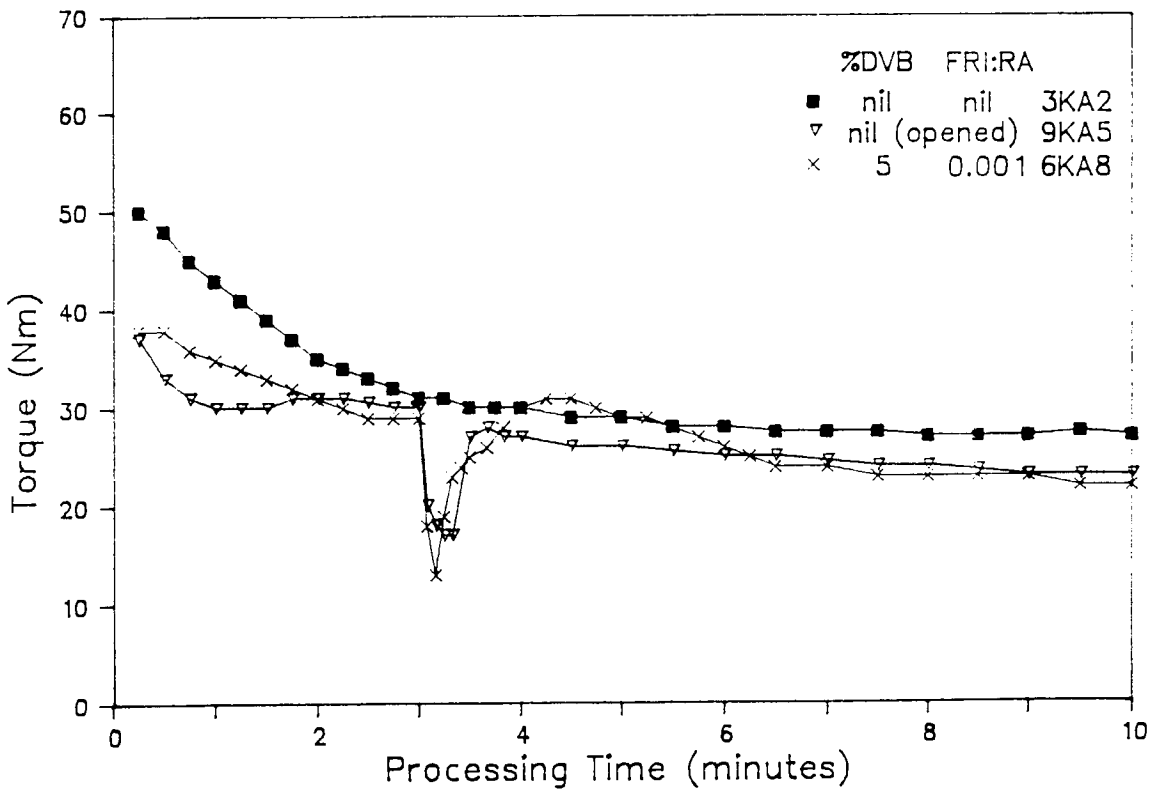
Figure 4.7 **Reactively processed EPDM (Vistalon 2504) torque behaviour with 5% TRIS additions at variable FRI:RA molar ratios and controls processed under standard conditions.**



4.2.4 Reactive Processing of EPDM With Divinylbenzene Interlinking Agent.

For a 5% addition of DVB at 0.001 FRI:RA molar ratio to EPDM (6KA8) only a very slight torque rise was experienced (Table 4.9 and Figure 4.8). The low peak was just above T_3 reference and control torques, but decay brought the final torque to a similar level as the opened-chamber control (9KA5). This was significantly different to the behaviour of EPDM with TRIS, which had caused the most substantial torque gains at the same addition and FRI:RA levels (4KA4, Section 4.2.3).

Figure 4.8 **Reactively processed EPDM (Vistalon 2504) torque behaviour with 5% DVB addition at 0.001 FRI:RA molar ratio and controls processed under standard conditions.**



4.2.5 Solvent Extraction of Reactively Processed Polystyrene Compositions (With TRIS and DVB Interlinking Agents).

A series of key polystyrene test cells from reactive processing with TRIS or DVB interlinking agents and controls were selected for analysis, along with a sample of unprocessed Huntsman 311 PS (Table 4.10). Pressed films from each material were analysed by solvent extraction, fraction separation and infra-red spectroscopy (as detailed in Sections 2.7 & 2.8) to determine the chemical effects upon polystyrene of reactive processing using the two different interlinking agents at various reactive agent & free radical initiator formulations.

Table 4.10 Compositions and torque behaviour of key polystyrene test cells reactively processed with nominally 5% TRIS or DVB additions at various FRI:RA ratios, incorporating pre-addition of peroxide initiator (Trigonox 101) and controls processed under standard conditions.

	Composition					Torque Behaviour			
Cell	RA type	TRIS & FRI (% w/w) target	TRIS & FRI (% w/w) actual	FRI:RA molar ratio	+ FRI (% w/w)	T_3 (Nm)	Peak (Nm)	Peak (min)	T_{10} (Nm)
H311	none	nil		nil	nil	unprocessed Huntsman 311 PS			
4KA5	nil	nil	(opened)	nil	nil	13	none		11
7KA6	nil	nil	(opened)	nil	0.05	13.5	none		11
4KA6	TRIS	5.0	5.13	nil	nil	14	11	5.0	11
2KA5	TRIS	5.0	5.52	0.001	nil	14	12.5	5.75	12.5
3KA5	TRIS	5.0	5.26	0.01	nil	14	15	3.3	14
3KA6	TRIS	5.0	5.39	nil	0.03	15	15	5.8	14.5
5KA6	TRIS	5.0	5.12	0.001	0.04	13	15	5.3	14
3KA8	DVB	5.0	5.29	nil	nil	13	7	3.5	6.5
1KA8	DVB	5.0	5.06	0.01	nil	13	15.5	5.5	14
8KA8	DVB	5.0	5.20	0.01	0.05	13	13	5.0	12.5

The amount and nature of any insoluble material in the PS reactive compositions and controls was determined by exhaustive Soxhlet extraction with boiling dichloromethane. This was shown to be a particularly good solvent for PS at both room temperature and on boling (40 °C) ; 100ml dissolving 5g of PS film completely within 2 hours in a soxhlet extractor and the solution remaining fully stable on standing at room temperature. Some problems were encountered in use due to its susceptability to bumping under reflex when first boiling and after draining a full Soxhlet of cool solvent back into the flask. Even careful control of heating and the use of anti-bumping granules could not totally prevent random "bumping" events in some extractions.

The behaviour of different samples during the course of extraction with dichloromethane was in itself interesting. Virgin and control PS (H311 & 4KA5) readily dissolved, giving a clear solution which drained freely through the paper extraction thimbles. Some other cells were more peculiar in that the PS become swollen before dissolving (3KA6 & 5KA6) and in extreme cases rose to the top of the thimble, with some of the swollen mass lost to the solution on draining (4KA6 & 2KA5). Most of the cells with interlinking agent yielded cloudy solutions after concentrating and cooling, an exception being from DVB without FRI (3KA8). None of the samples left any great quantities of residue on completion of extraction, though in cases where an amount was measureable and visible, white particulate solids were evident. The behaviour and final outcome of extraction for each key cell and controls are given in Table 4.11.

After observations of cloudiness in some of the extraction soluble fractions, solutions of both reactive agents in dichloromethane were prepared for visual assessment of appearance. With DVB, concentrations well in excess of those possible from the amount present, even if freely available on extraction (5% of 2g = 0.1g in 150 ml), gave

clear and colourless solutions solutions even on standing overnight. A high concentration of TRIS in dichloromethane, well above that possible, was also needed before any slight haziness developed.

Films cast directly from portions of the concentrated solutions were typically very thin and thus clear, though some particulates were still present in most of the cells from the TRIS processing (2KA5, 3KA5 & 5KA6). Precipitated PS (by running the remaining concentrate into methanol) was similar in form to cotton wool. This readily dissolved in a small volume of fresh dichloromethane to allow the casting of fairly thick films of the purified PS fraction. All of these films were fully transparent, with just 2KA5 and 5KA6 having any particulates, at a much reduced loading to the original and previous fractions.

Table 4.11 **Behaviour and residue content of polystyrene (Huntsman 311) controls and compositions reactively processed with TRIS or DVB from exhaustive dichloromethane extraction (according to Scheme 2.5 Section 2.7).**

Film Sample	Behaviour during Extraction	Resulting Solution	Insoluble Residue Appearance	% w/w
H311	PS readily dissolved	crystal clear	-	nil
4KA5	PS readily dissolved	crystal clear	-	nil
7KA6	PS readily dissolved	crystal clear	-	nil
4KA6	swollen out of thimble (some lost)	slightly cloudy	not visible	< 0.5
2KA5	swollen out of thimble (some lost)	cloudy, some gel	white particles	0.5
3KA5	PS readily dissolved	slightly cloudy	white particles	3.6
3KA6	swollen inside thimble	very cloudy	-	nil
5KA6	swollen inside thimble	very cloudy,some fine solids	not visible	< 0.5
3KA8	PS readily dissolved	crystal clear	-	nil
1KA8	PS readily dissolved	milky	white particles	0.5
8KA8	PS readily dissolved	milky	white particles	0.5

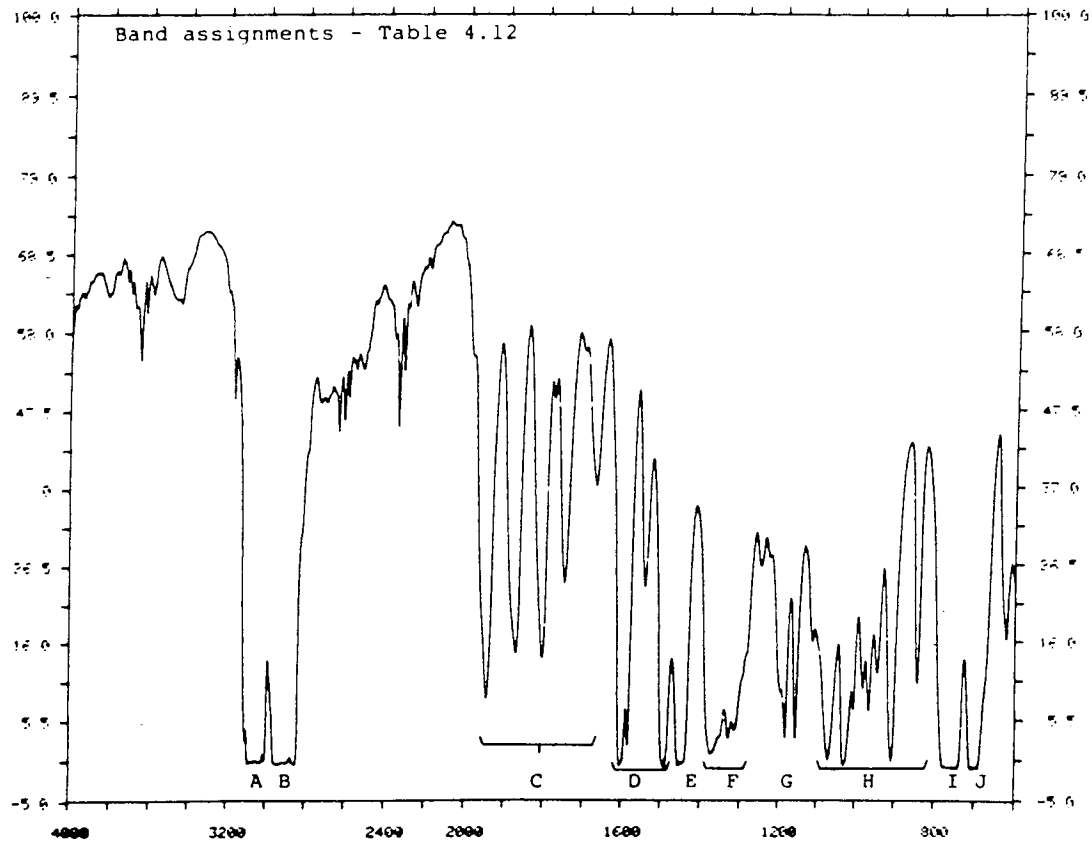
4.2.6 FT-IR Analysis of Polystyrene, Controls and Extracted Fractions.

For the first series of films analysed by FT-IR, namely unprocessed and control PS cells, it was found that the intensity of absorption was strongly related to film thickness. Most of the films examined were 0.15 to 0.25mm thick, giving intense absorption by the majority of vibrations. Resolution of inherently strong absorptions was only possible in films below 0.06 mm thick. However, little additional information could be gained by such resolution, so that spectra from thick films with enhanced detail of the weaker vibrations were considered valid for the elucidation of possible changes on processing with reactive agents. FT-IR spectra of unprocessed Huntsman 311 PS, as a thick pressed film and a thin cast film from dichloromethane are shown in Figure 4.9. Absorption bands for the thick film sample and most probable functional group assignments are given in Table 4.12. As expected from the chemical structure both aliphatic and aromatic hydrocarbon characteristics were clearly exemplified.

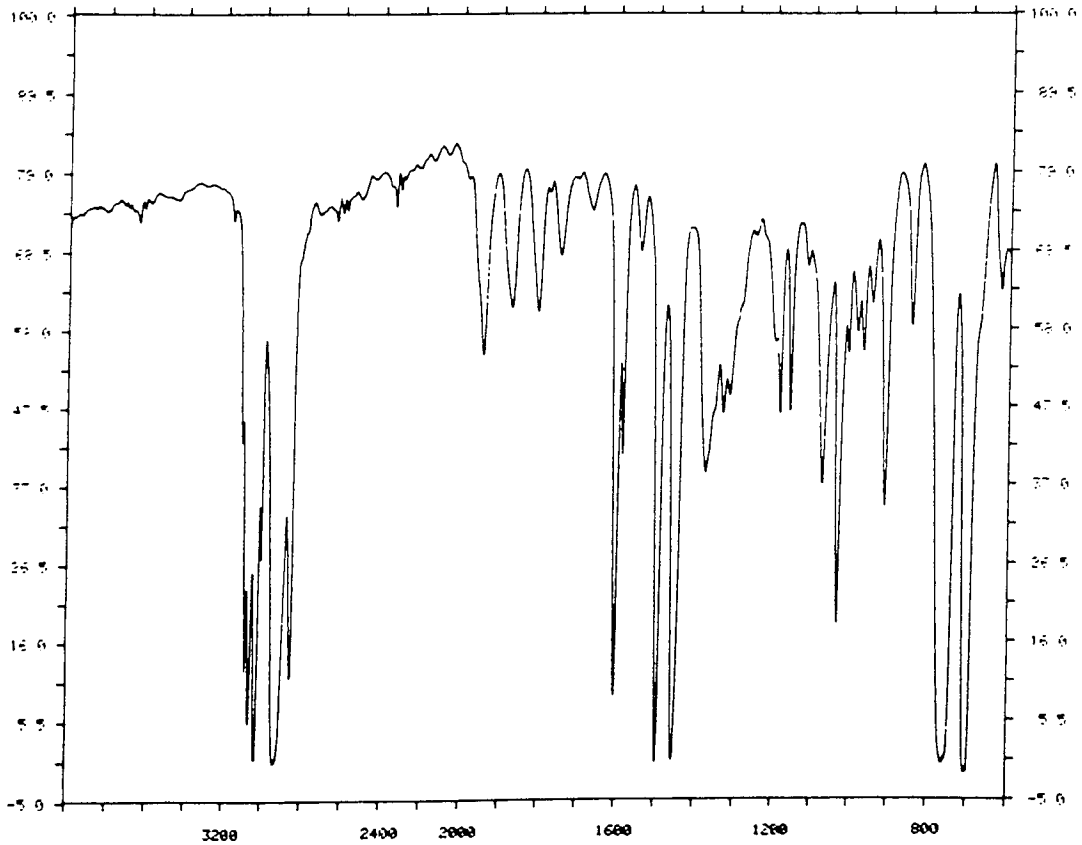
The only additional information from the fully resolved thin film spectrum (Figure 4.9b) was the splitting of asymmetrical and symmetrical vibrations in the aliphatic C-H stretching region (2927 and 2850cm^{-1}). Aromatic C-H stretching bands above 3000cm^{-1} were also resolved, but of little value. In thin films cast from dichloromethane there was no evidence of solvent, however thick films (PS precipitate fractions - typically 0.15 mm thick) were later found to show an extra peak at 1266cm^{-1} corresponding exactly to a sharp and strong absorption due to a CH_2-Cl wagging vibration from residual dichloromethane . The only other strong absorption from the solvent could be a C-Cl stretch at 740cm^{-1} which would have overlaped with the very strong aromatic C-H out-of-plane bending of the polystyrene.

Figure 4.9 **FT-IR spectra of unprocessed polystyrene (Huntsman 311).**

a) **Pressed film, 0.2mm thick.**



b) **Cast film from dichloromethane, 0.05mm thick.**



No differences were seen in the FT-IR of pressed films from virgin PS (H311), the opened-chamber control (4KA5) nor from the opened-chamber control with initiator pre-addition (7KA6). Similarly for films cast from the soluble fractions directly after dichloromethane extraction and the precipitated PS fractions, all FT-IR spectra were all equivalent and no different to the corresponding parent film samples prior to extraction.

Table 4.12 Major absorption bands and probable functional assignments in the infra-red spectrum of polystyrene (pressed film of unprocessed Huntsman 311, 0.2mm thick - Figure 4.9a).

	Peak (cm^{-1})	Intensity	Assignment
A	3080	very strong	aromatic C-H stretching (unresolved)
B	2940	very strong	aliphatic C-H stretching (unresolved)
C	1944, 1871 1803 1747, 1668	medium medium weak	combination and overtone bands for mono-substituted benzene ring
D	1602, 1584 1542 1495	strong weak strong	(doublet) C=C stretching within aromatic ring (unresolved)
E	1455	strong	methylene scissoring (in-plane C-H bending)
F	1373, 1330	strong & broad	methylene twisting and wagging (out-of-plane C-H bending)
G	1182, 1155	strong & sharp	aromatic C-H in-plane bending
H	1070, 1029 965, 908, 842	medium to strong	skeletal aliphatic C-C stretching
I	757	very strong	aromatic C-H out-of-plane bending
J	697	very strong	aromatic ring out-of-plane bending (coupled with 757 band = mono-substitution)

4.2.7 FT-IR Analysis of TRIS, PS/TRIS Compositions and Extracted Fractions.

The FT-IR spectrum of TRIS (trimethylolpropane triacrylate) was obtained from a neat smear of the liquid between KBr discs (Figure 4.10). Attachment of the three alpha,beta unsaturated acrylate ester groups to the aliphatic trimethylpropane backbone intensified absorptions from the key ester and vinyl vibrations, as shown in the list of major peaks and assignments in Table 4.13.

Table 4.13 Major absorption bands and probable functional assignments in the infra-red spectrum of TRIS (liquid film between Kbr discs - Figure 4.10).

	Peak (cm^{-1})	Intensity	Assignment
A	3100, 3040	weak	vinyl C-H stretching
B	2970 2800	medium weak	aliphatic methyl and methylene C-H stretching
C	1729	very strong	carbonyl C=O stretching (frequency lower than saturated ester due to vinyl conjugation)
D	1636, 1620	medium	vinyl C=C stretching (frequency lowered and intensity enhanced due to conjugation with carbonyl)
E	1467	medium	aliphatic & alcoholic methylene scissoring (in-plane C-H bending)
F	1409	strong & sharp	vinyl terminal methylene scissoring (in-plane C-H bending)
G	1296 1271 1187	strong strong very strong	multiple bands from ester C-O stretching (correct for alpha,beta unsaturated ester)
H	1063	strong	skeletal aliphatic C-C stretching
I	986	strong	olefinic vinyl C-H out-of-plane bendng
J	810	strong & sharp	skeletal aliphatic C-C stretching for iso-propyl centre

Figure 4.10 **FT-IR spectrum of TRIS (trimethylolpropane triacrylate) - liquid film between KBr discs.**

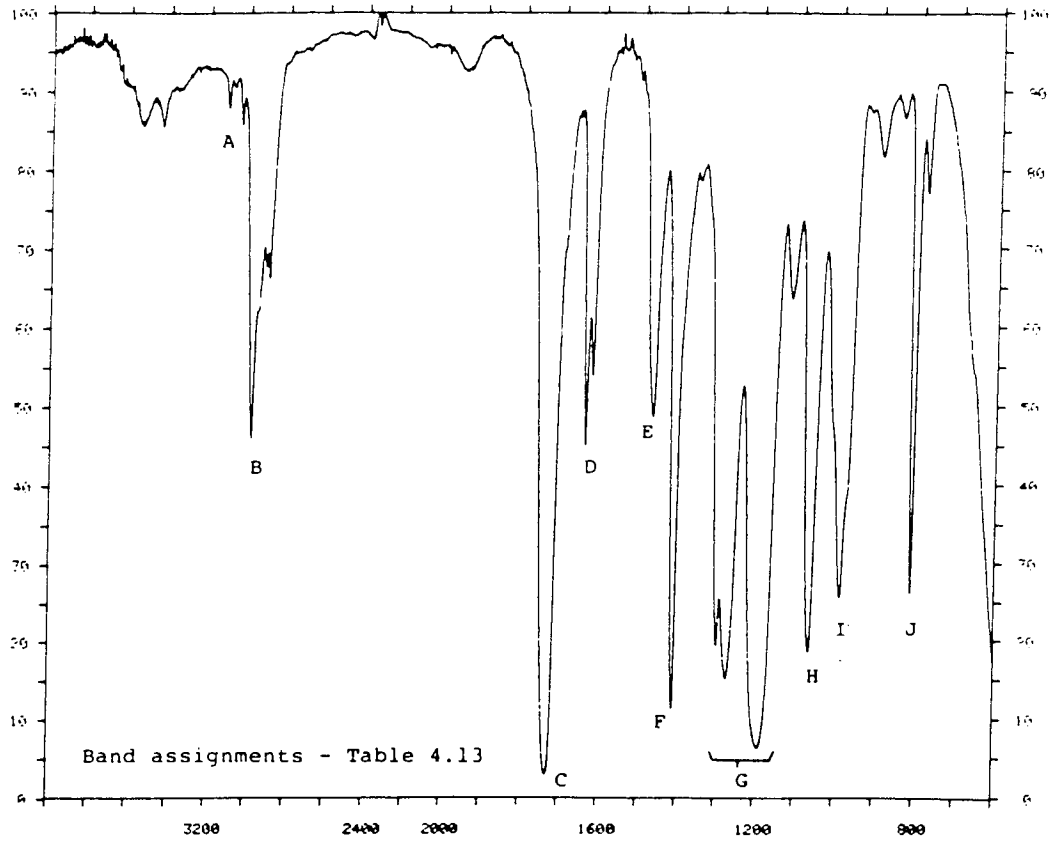
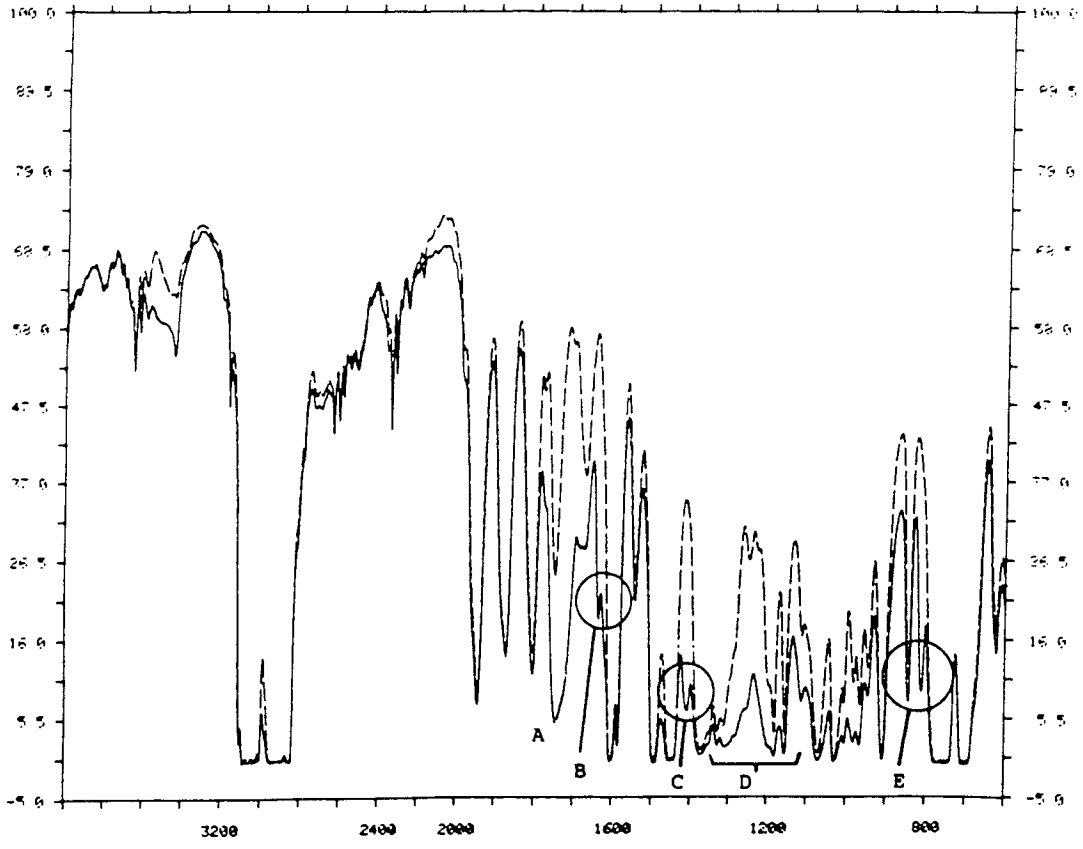


Figure 4.11 **Comparison of FT-IR spectra of polystyrene and a physical mixture with TRIS. (- - - - - - : PS film 0.23mm thick, ——— : same PS film with a smear of liquid TRIS)**



To determine which absorptions would be useful in the analysis of TRIS-modified PS compositions, the spectrum of a physical mixture (from a thin liquid film of TRIS on a piece of PS film) was compared to that of the same film alone (Figure 4.11). Resolvable differences between the two spectra, as indicated on the Figure, were obtained ;

A - most obvious was a strong, broad peak around 1730cm^{-1} due to the TRIS carbonyl C=O stretching. However a substantial contribution to this peak was from the underlying 1747cm^{-1} combination/overtone band of the thick PS film.

B - a sharp, medium intensity peak at 1636cm^{-1} due to the TRIS vinyl C=C vibration was distinct on the shoulder of the first strong band from PS aromatic C-C stretching at 1602cm^{-1}.

C - at 1408cm^{-1} further vinyl character of the TRIS (from terminal methylene scissoring) was apparant in a region of minimum absorbance from the PS spectrum.

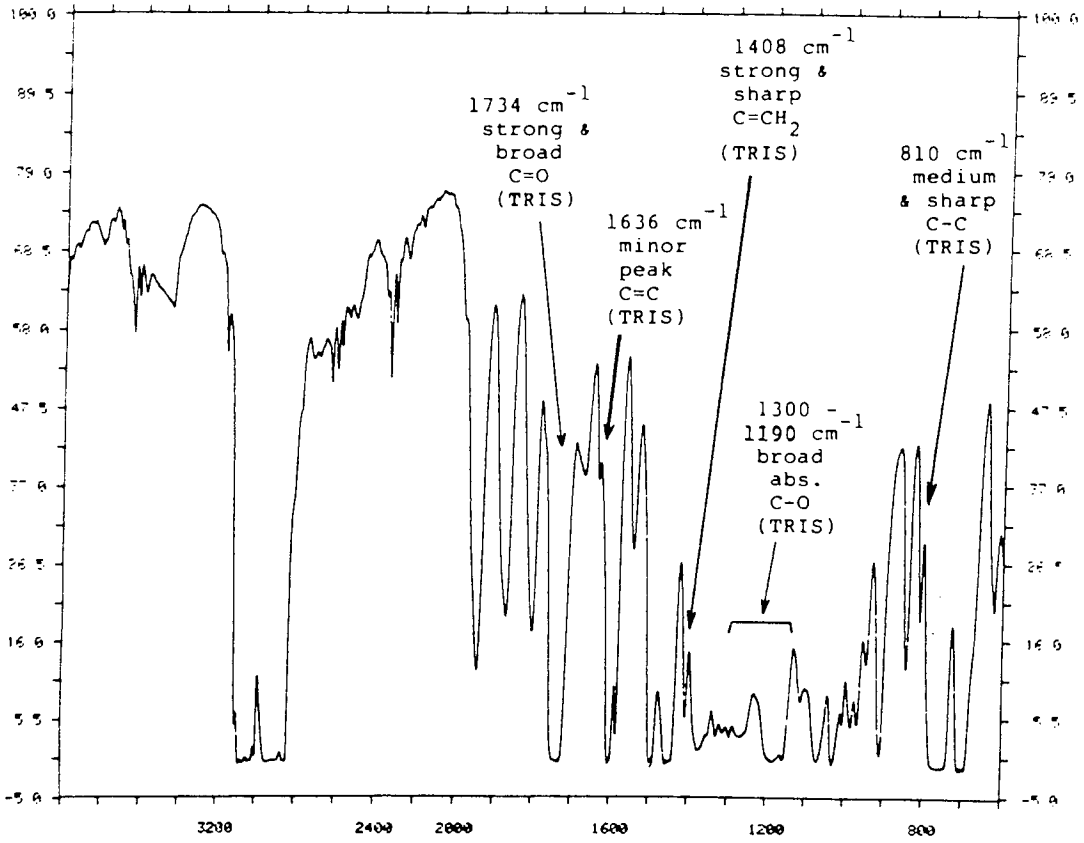
D - between 1300 and 1190cm^{-1} there was higher absorption from the overlap of PS methylene & aromatic C-H bending modes and multiple bands from the TRIS ester vibrations.

E - the sharp absorption of skeletal C-C stretching at the iso-propyl centre in TRIS was prominent at its 810cm^{-1} position on the edge of the very strong PS aromatic C-H out-of-phase bending band.

Distinct differences were found in the infra-red spectra of PS/TRIS key cells and corresponding extracted fractions (Figure 4.12 and 4.13). There was some variation in the initial TRIS content before extraction for different cells according to the carbonyl band intensity (at 1730cm^{-1}). Carbonyl intensity was also found to differ between spectra from the initial film and the corresponding recovered precipitate for most samples after normalising for film thickness. The contribution of PS homopolymer to all spectra was

Figure 4.12 **FT-IR spectra of PS reactively processed with a 5% TRIS addition without any initiator (4KA6).**

a) **initial film, 0.21mm thick, before extraction ("I" Scheme 4.1).**



b) **precipitate recovered from soluble fraction after extraction, film cast from dichloromethane, 0.21mm thick ("P" Scheme 4.1).**

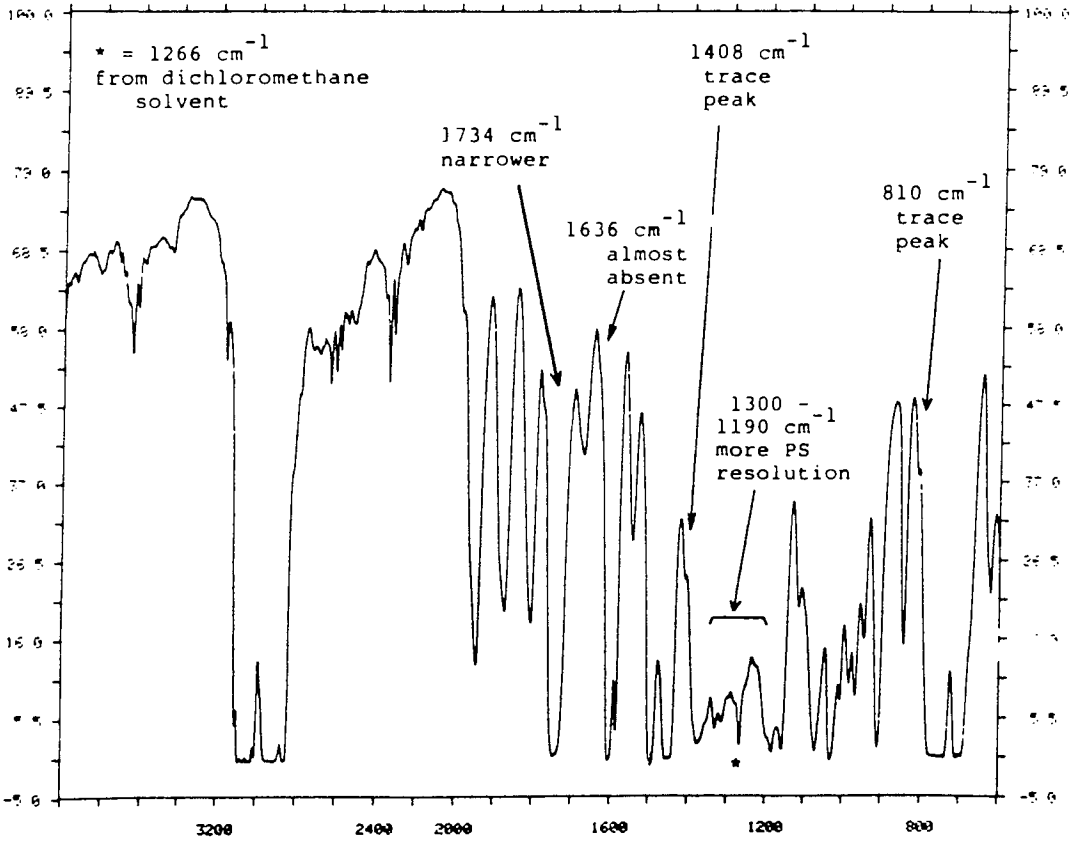
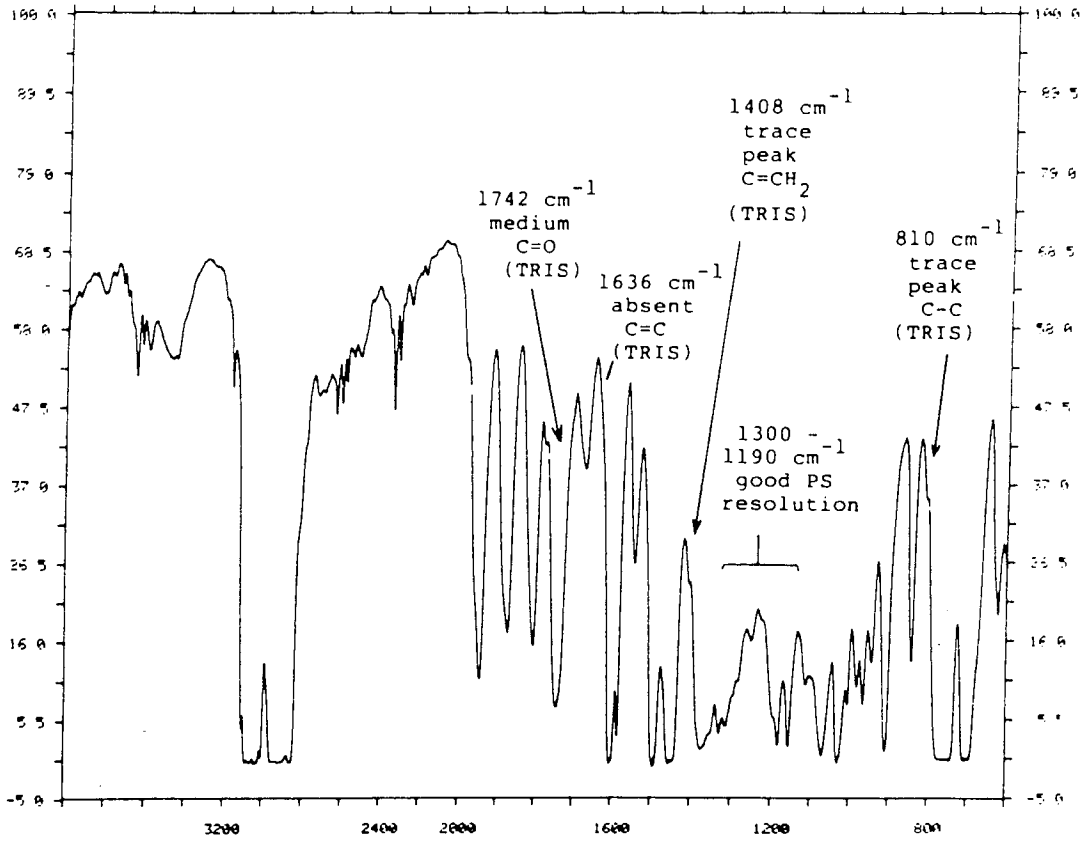
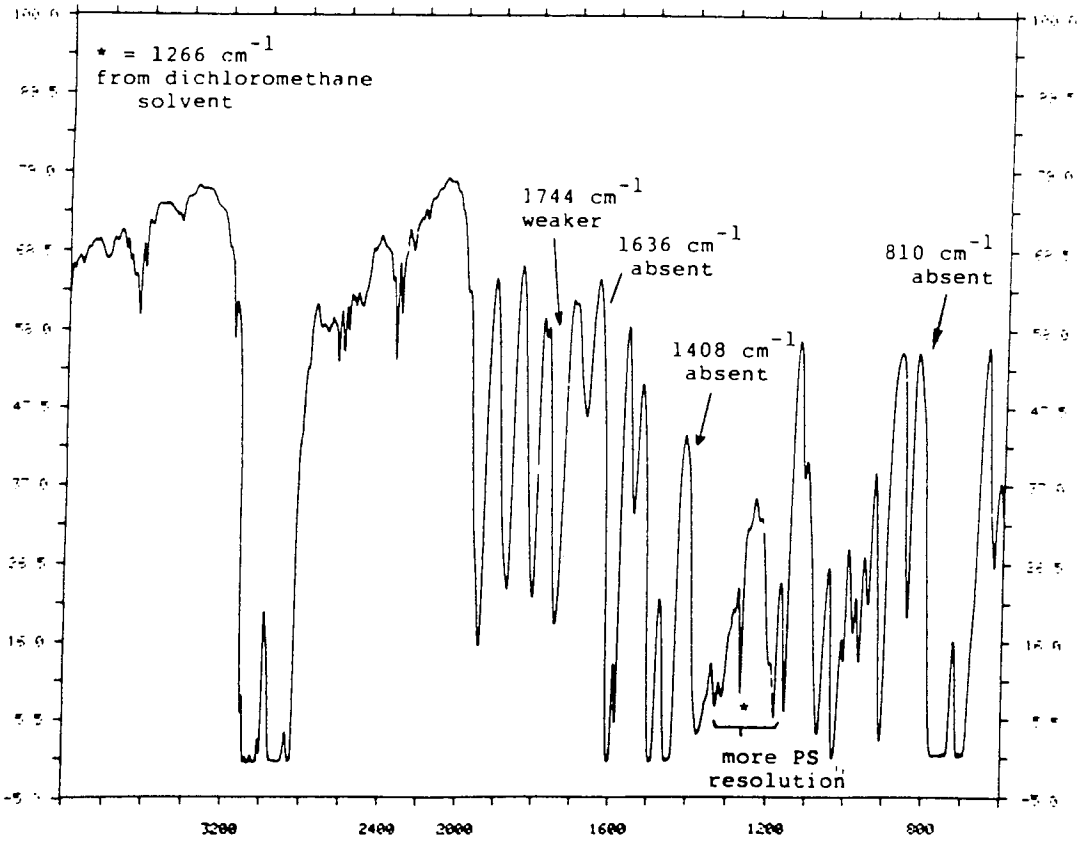


Figure 4.13 **FT-IR spectra of PS reactively processed with a 5% TRIS addition at 0.01 molar ratio FRI:RA (3KA5).**

a) **initial film, 0.21mm thick, before extraction ("I" Scheme 4.1).**



b) **precipitate recovered from soluble fraction after extraction, film cast from dichloromethane, 0.17mm thick ("P" Scheme 4.1).**



constant, albeit thickness dependant, no structural changes could be resolved. Spectra of films cast from soluble fractions after extraction were generally similar to those from initial films and are not considered any further. Other qualitative changes between different initial samples or recovered precipitates were also noted :

i. - bands from TRIS vinyl unsaturation (1636 and 1408 cm^{-1}) were much less significant or even absent in the compositions with FRI than in the physical mixture,

ii. - greater resolution of PS bands between 1300 and 1190cm^{-1} was found in low TRIS content samples due to the loss of multiple ester vibrations,

iii. - changes in the contribution of TRIS iso-propyl stretching absorption (810cm^{-1}) were also seen to vary with TRIS concentration.

These features are exemplified in Figures 4.12a and 4.12b of the initial spectrum of 4KA6 (5% TRIS, nil FRI) and from the precipitate of the dichloromethane soluble fraction from 4KA6 after mixing with methanol. Bands for TRIS were weaker in the precipitate fraction, especially from the vinyl unsaturation ; at 1408cm^{-1} methylene scissoring was only just perceptible and the vinyl C=C strectching at 1636cm^{-1} was practically absent. This was a common feature to all PS/TRIS compositions. Figures 4.13a & 4.13b are of the initial film of 3KA5 (5% TRIS, 0.01 FRI:RA) and precipitate fraction. TRIS concentration, given primarily by the carbonyl absorption, was lower in this initial sample than for the previous example (4KA6). This was reinforced by the reduced influence of TRIS ester C-O vibrations between 1300 and 1190cm^{-1} and the considerably lower intensity of iso-propyl stretching at 810cm^{-1}. Vinyl unsaturation was only just suggested by a trace peak at 1408cm^{-1}. In the precipitate fraction this characteristic was totally absent and the indicated TRIS content was further reduced. A qualitative assessment of bands in these diagnostic areas was made for all the PS cells tested (Table 4.14).

Table 4.14 **Qualitative assessment of bands in diagnostic regions of FT-IR spectra from key PS/TRIS cells ; initial samples before extraction (I) and precipitate fractions post-extraction (P).**

Sample	1734 cm^{-1} PS Ar-H & TRIS C=O	1636 cm^{-1} TRIS C=C	1408 cm^{-1} TRIS $CH=CH_2$	1300-1190 cm^{-1} TRIS C-O & PS C-C	810 cm^{-1} TRIS C-C
4KA6 I	strong & broad	minor peak	strong & sharp	broad absorbance	medium & sharp
4KA6 P	strong, narrower	almost absent	trace peak	some PS resolution	trace peak
2KA5 I	strong & broad	minor peak	strong & sharp	broad absorbance	medium & sharp
2KA5 P	strong, narrower	almost absent	trace peak	some PS resolution	trace peak
3KA5 I	medium	absent	trace peak	good PS resolution	trace peak
3KA5 P	weaker	absent	absent	more PS resolution	almost absent
3KA6 I	strong & broad	almost absent	trace peak	broad absorbance	trace peak
3KA6 P	strong & broad	absent	almost absent	broad absorbance	trace peak
5KA6 I	strong & broad	almost absent	trace peak	broad absorbance	trace peak
5KA6 P	strong & broad	absent	almost absent	some PS resolution	almost absent

For the most significant diagnostic peaks, peak area measurements (minus baselines) were made using the software of the FT-IR from TRIS key cell initial samples and precipitate fractions (Table 4.15). Relevant peaks were also quantified from the control spectra of TRIS, the PS/TRIS physical mixture and unprocessed PS (H311). An internal reference peak from the PS component ($1803cm^{-1}$) was included in all samples to allow nomalisation for variable film thickness. Peak areas from the TRIS CH_2=CH bending band ($1409cm^{-1}$) were only just determinable in the controls and 5% TRIS with no or 0.001 molar ratio FRI:RA initial samples (4KA6 & 2KA5), confirming the insignificance of unsaturation in other reactive test cells and all precipitate fractions.

The ratio of each TRIS carbonyl peak area to the internal reference peak area was taken to give a quantitative indication of TRIS content normalised for film thickness by the use of the PS reference peak (Table 4.15). This ratio was further used to determine the binding level of TRIS to the PS, ie. the relative amount of TRIS inseparable from the PS, after the loss on extraction of free TRIS, compared to the initial TRIS content. The contribution of the underlying PS Ar-H band was accounted for in the calculation of binding level since if a sample was to show zero binding, with all of the initial TRIS content removed on extraction, the remaining peak area would be entirely from the PS Ar-H band. Binding levels were calculated according to equation 4.1 for all PS/TRIS samples (Table 4.16).

$$\textbf{TRIS binding level (\%)} = \frac{R_P - R_R \times 100}{R_I} \quad \text{(equation 4.1)}$$

where

R_P is the $1734cm^{-1}/1803cm^{-1}$ peak area ratio from the PS preciptate film (FT-IR "P" - Scheme 4.1)

R_I is the $1734cm^{-1}/1803cm^{-1}$ peak area ratio from the initial PS film (FT-IR "I" - Scheme 4.1)

R_R is the $1734cm^{-1}/1803cm^{-1}$ peak area ratio of the PS reference (= 0.29)

Table 4.15 **Diagnostic peak area measurements (minus baselines) from FT-IR spectra of TRIS, PS & PS+TRIS controls and PS/TRIS key cells - initial films before extraction ("I") and dichloromethane-cast films of recovered precipitate from soluble fraction on extraction ("P" {refer to Scheme 4.1}).**

Sample	Film Thickness (mm)	$1803cm^{-1}$ PS Ar-H (1842-1775)	$1734cm^{-1}$ TRIS C=O (1842-1775)	$1408cm^{-1}$ TRIS CH_2=CH (1842-1775)
TRIS	-	nil	46.17	10.27
PS	0.23	14.24	4.14	nil
PS + TRIS	0.23	13.98	37.32	7.39
4KA6 I	0.21	10.89	90.94	1.16
4KA6 P	0.21	11.28	60.09	< 0.1
2KA5 I	0.21	10.68	90.93	0.36
2KA5 P	0.14	8.12	47.08	< 0.1
3KA5 I	0.21	11.70	23.75	< 0.1
3KA5 P	0.17	10.78	12.47	< 0.1
3KA6 I	0.20	10.45	85.75	< 0.1
3KA6 P	0.17	9.82	67.56	< 0.1
5KA6 I	0.22	11.69	79.24	< 0.1
5KA6 P	0.21	10.06	55.64	< 0.1

Table 4.16 **Relative TRIS concentrations according to $1734cm^{-1}/1803cm^{-1}$ peak area ratio and binding level of TRIS to PS (using equation 4.1) for PS control and PS/TRIS key cells.**

Sample	[TRIS] $1734cm^{-1}/1803cm^{-1}$ peak area ratio	% Binding of TRIS to PS
PS	(0.29)	-
4KA6 I	8.35	51.7
4KA6 P	5.32	
2KA5 I	8.51	64.6
2KA5 P	5.79	
3KA5 I	2.03	42.9
3KA5 P	1.16	
3KA6 I	8.21	80.3
3KA6 P	6.88	
5KA6 I	6.78	77.3
5KA6 P	5.53	

Initial TRIS concentration, as given by the peak area ratio, was similar in several of the samples. For the 5% TRIS addition at 0.01 molar ratio FRI:RA (3KA5) however, the TRIS content was reduced to about a quarter of the level of other compositions. There was substantial binding of TRIS to PS, shown by the high relative amounts of unextractable TRIS carried through to the recovered precipitate fractions ; even for a 5% addition of TRIS without any initiator to PS on procesing (4KA6) around 50% of the interlinking agent became bound to the PS. Addition with 0.001 molar ratio FRI:RA (2KA5) increased the binding level further to almost 65%. Higher initiator concentration reduced TRIS binding to below 43%, and at the lowest absolute content of TRIS (3KA5). The greatest binding levels, to 80%, were given by pre-addition of initiator to PS before processing, independent of the FRI content at addition of TRIS (3KA6 and 5KA6), although without initiator in the mixture (3KA6) a higher absolute TRIS concentration was incorporated in the precipitate fraction after extraction.

4.2.8 FT-IR Analysis of DVB, PS/DVB Compositions and Extracted Fractions.

The FT-IR spectrum of DVB (divinylbenzene) was obtained from a film of the neat liquid between KBr discs (Figure 4.14). It was recognised that the DVB used was a technical grade composed of a mixture of 55% divinylbenzene and the remainder ethylvinylbenzene, both present in meta-and para-isomers. The resulting FT-IR spectrum was consistent with this composition ; strong vinyl and aromatic characteristics were seen, meta- and para-substitution were both accounted for and the presence of aliphatic methyl and methlylene groups were also resolved (Table 4.17).

Table 4.17 **Major absorption bands and probable functional assignments in the infra-red spectrum of DVB (liquid film between Kbr discs - Figure 4.14).**

	Peak (cm^{-1})	Intensity	Assignment
A	3088	strong	aromatic C-H stretching
B	3050, 3007	medium	vinyl C-H stretching
C			aliphatic C-H stretching :
	2966	strong	methyl CH_3- antisymetrical
	2931	medium	methylene CH_2- antisymetrical
	2873	medium	methyl and methylene symetrical
D	1950 - 1870 1727	weak	overtone and combination bands from substituted benzene ring
E	1820	medium	overtone from vinyl C-H bending
F	1631	medium, sharp	vinyl C=C stretching (enhanced intensity due to conjugation with aromatic ring)
G	1596, 1578 1511 1401	medium	(doublet) skeletal aromatic ring C=C stretching
H	1485	medium	methylene symmetrical C-H bending
I	1453	medium	methylene antisymmetrical C-H bending
J	1282	weak	aromatic C-H in-plane bending
K	1167, 1119 1093, 1028	weak	aromatic C-H bending and/or skeletal C-C stretching
L	990, 907	very strong	vinyl C-H out-of-plane bending
M	907, 802 709	very strong strong	aromatic C-H out-of-plane bending aromatic ring out-of-plane bending [characteristic of meta (1,3) substitution]
P	846	strong	aromatic C-H out-of-plane bending [characteristic of para (1,4) substitution]

Figure 4.14 **FT-IR spectrum of DVB (divinyl benzene) - liquid film between KBr discs.**

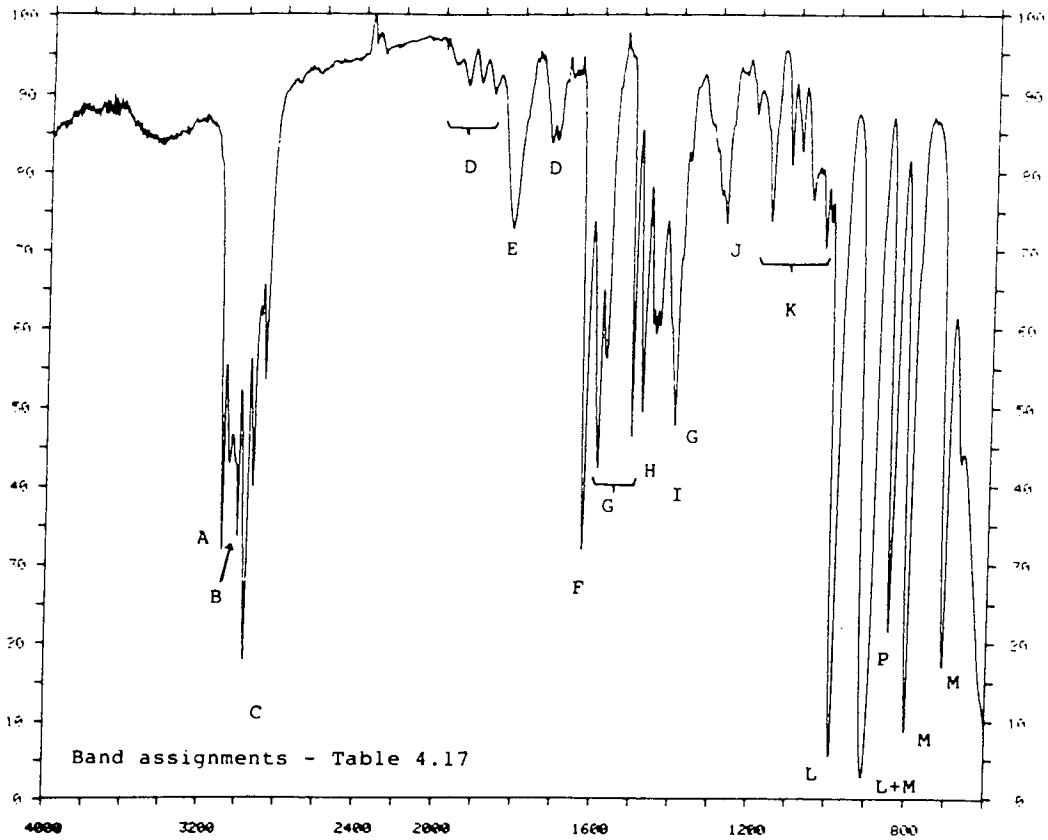
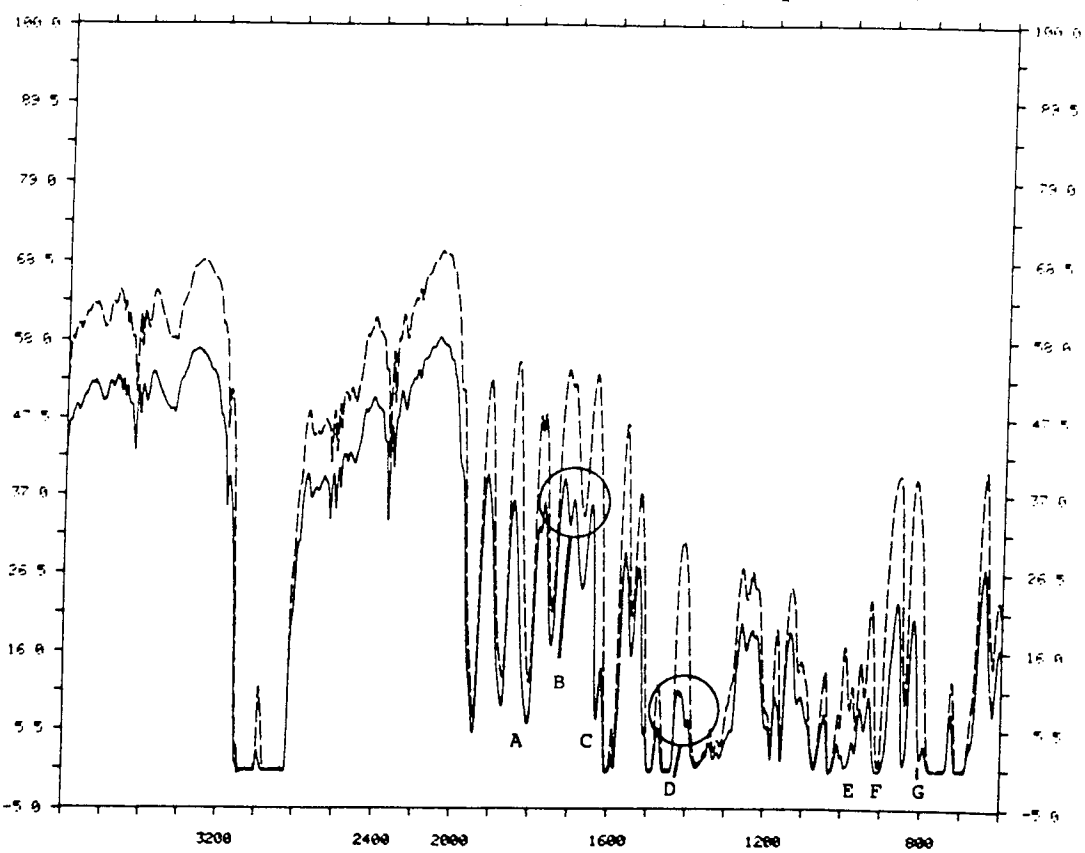


Figure 4.15 **Comparison of FT-IR spectra of polystyrene and a physical mixture with DVB. (- - - - - : PS film 0.23mm thick, ——— : same PS film with a smear of liquid DVB)**



The spectrum of a physical mixture of PS and DVB was compared to that of the same film alone (Figure 4.15). Differences between the two were very slight and on the whole due to unsaturation in the DVB ;

A - in the aromatic overtone region, the PS 1805cm^{-1} band was broadened by overlap of the more intense vinyl overtone from DVB.

B - an additional weak peak at 1727cm^{-1} in the mixture was from a minor overtone of the different aromatic substitution in DVB.

C - at 1631cm^{-1} a sharp, medium intensity absorption due to the vinyl C=C stretch in DVB was identified on the shoulder of the stronger aromatic C-C stretching band (1603) from both PS and DVB. This was a key peak for the presence of vinyl unsaturation in reactive mixtures.

D - a band from aromatic C-C stretching in DVB at 1400cm^{-1} was on the edge of a stronger PS absorption at 1373cm^{-1} due to C-H rocking and wagging.

E - within a noisy PS region, due to aliphatic C-C stretching, absorbance at 990cm^{-1} was heightened by the very strong DVB vinyl C-H bending vibration. This was difficult to quantify due to adjacency of minor peaks, but supplemented data from the key 1631cm^{-1} absorption.

F - considerable broadening of the 908cm^{-1} band was found due to overlap of PS skeletal C-C stretching and the very strong combined DVB vibration from vinyl and aromatic C-H out-of-plane bending.

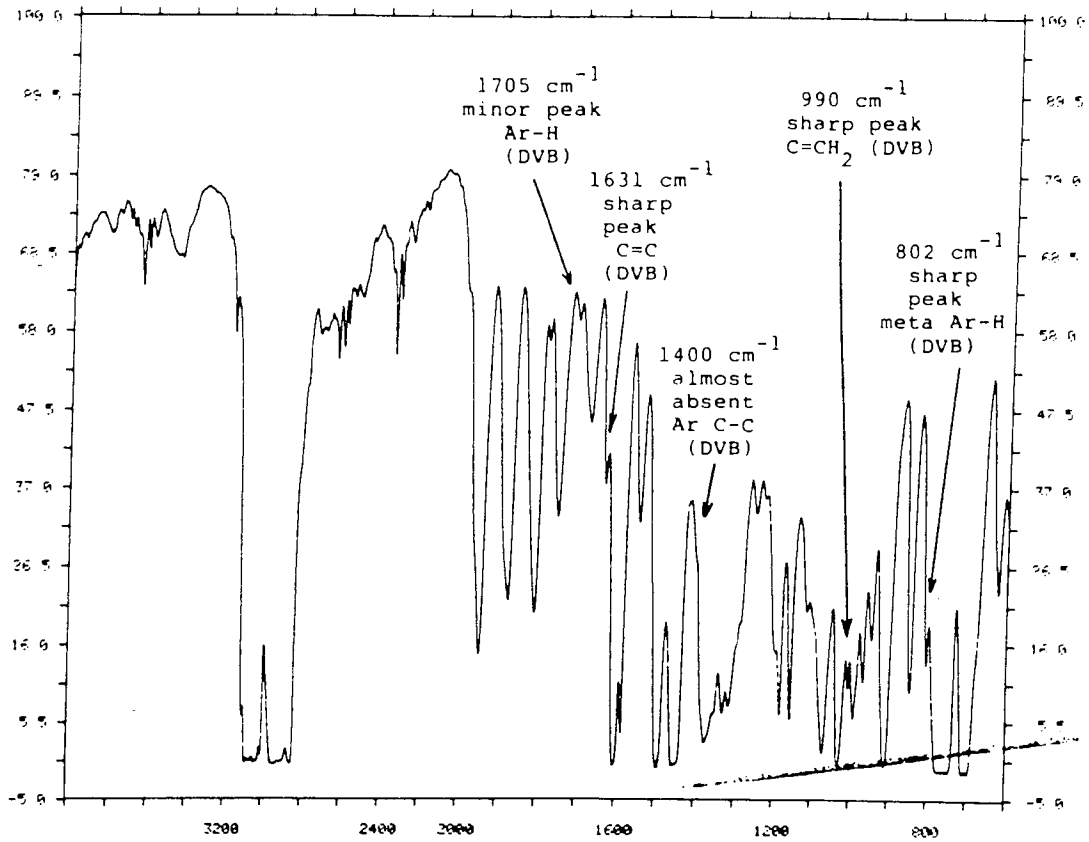
G - a significant peak at 802cm^{-1} could be resolved. This was the central band of the meta-substituted vinylbenzene components and was sufficiently clear of the broad PS Ar-H (mono-substituted) band to give a give a useful measure of DVB content in mixtures.

The infra-red activity of DVB in the test cells and extracted fractions examined was found to be exceedingly low. Thus the majority of information obtained was negative by the absence of key absorptions. All initial spectra had similar minor peaks at 1727cm^{-1} showing the presence of DVB (by a characteristic Ar-H overtone), though the intensity was too low for accurate peak area measurement. Other regions of absorbance from the DVB aromatic centre (1400, 908 and 802cm^{-1}) were even less useful - only 3KA8 (5% DVB, no FRI) gave a distinct peak from meta Ar-H bending at 802cm^{-1} (Figure 4.16a). The other PS/DVB samples (1KA8 and 8KA8) gave no noticeable increases above the PS spectra in these DVB aromatic regions. 3KA8 was also the only cell to detail any unsaturation ; sharp, but low intentsity peaks at 1631 and 990cm^{-1} (from C=C stretching and vinyl C-H bending) were present.

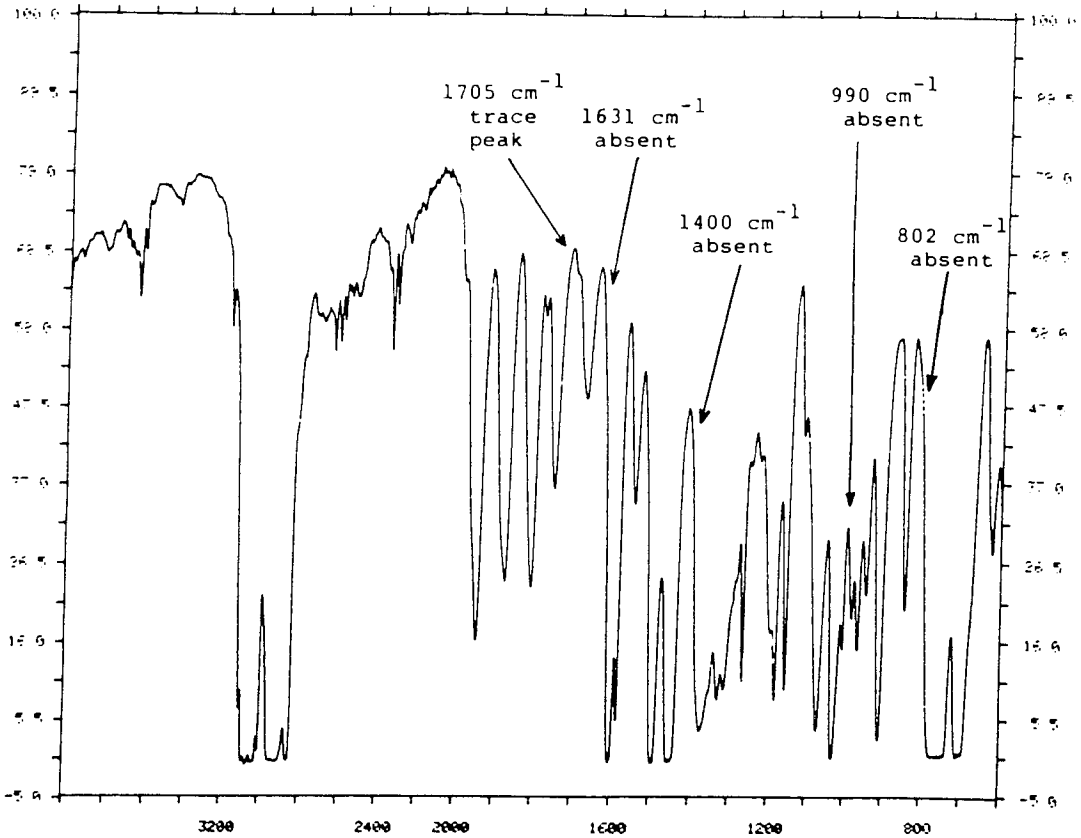
Cast films of the soluble fractions direct from the extracted liquor were very thin and all absorptions correspondingly weak such that DVB influence was not discernable. All recovered precipitate fractions gave similar spectra (eg 3KA8P - Figure 4.16b) ; the only DVB characteristic was very slight absorption at 1727cm^{-1}, lower than in the initial films. Peaks associated with unsaturation were absent and other DVB regions totally clear. Precipitate films, cast from dichloromethane, gave an additional sharp band at 1266cm^{-1} from residual solvent. Polystyrene contribution was identical in all test cells and fractions (correcting for film thickness), no changes could be resolved.

Figure 4.16 **FT-IR spectra of PS reactively processed with a 5% DVB addition without any initiator (3KA8).**

a) **initial film, 0.21mm thick, before extraction ("I" Scheme 4.1).**



b) **precipitate recovered from soluble fraction after extraction, film cast from dichloromethane, 0.21mm thick ("P" Scheme 4.1).**



4.2.9 NMR Spectroscopy of Reactively Processed Polystyrene Compositions (Extracted Fractions).

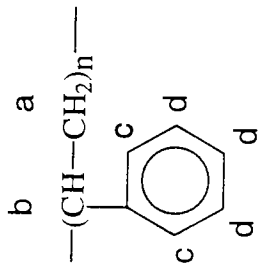
Both proton and ^{13}C NMR spectroscopy were carried out on precipitated fractions ("P" Scheme 4.1) from the dichloromethane solvent extraction (Scheme 2.5) of key PS controls and reactively processed cells with TRIS and DVB (Table 4.10) using solutions of the readily soluble cotton-wool-like precipitate fractions in deuterated chloroform. Spectra gave a considerable amount of information, with some interferences and signal noise (particularly from the ^{13}C technique), as expected for a polymeric material having a distribution of similar nuclei in slightly differing chemical or structural environments. It was thus difficult to fully resolve spectra, but effort was made to focus on specific resonances of fairly certain origin and to quantify any differences between samples.

In the proton NMR spectra of all cells particularly broad peaks were attributable to PS structural units, whereas in some samples other very sharp resonances were believed to arise from interferences (7.24ppm from $CHCl_3$ contamination of $CDCl_3$ solvent, 2.16ppm from H_2O and 1.5ppm from an unassigned source). The spectrum and major peak assignments for a control PS (unprocessed Huntsman 311 in $CDCl_3$) are given in Figure 4.17 and those of TRIS and DVB reactive agents (also in $CDCl_3$) in Figures 4.18 and 4.19. The only positive indication of the presence of reactive agent in any of the reactively processed PS cells was for 2KA5 (5% TRIS, 0.001 FRI:RA) in which a minor resonance from the TRIS methylene -O-CH_2- unit was apparent at 4.05ppm (Figure 4.20). Peak intensities and integrals of significant peaks for all samples were measured (Table 4.18) and analysed to determine if any differences in the relative concentrations of functional centres were discernible. The only instance in which the relative intensity of both methylene and aromatic protons to methine protons in PS (ratio of peak integrals for 1.43: 1.85 ppm and 7.04 : 1.85 ppm) were significantly different to the unprocessed control

(H311) was that of 5KA6 (5% TRIS, 0.001 FRI:RA + FRI pre-addition : Figure 4.21), in which depletion of methine protons was indicated, suggesting a higher level of TRIS grafting along the PS backbone at the tertiary carbon centre. For DVB additions (3KA8, 1KA8, 8KA8), it was not possible to quantify with confidence any relative gain in the contribution of aromatic protons, which may have confirmed effective modification by DVB, as the only cell in which this was suggested (8KA8 - 5% DVB at 0.01 FRI:RA with FRI pre-addition : Figure 4.22) gave much lower total integral values (due to a more dilute analyte solution ?).

Table 4.18 **Proton NMR of reactively processed PS and control precipitate fractions ("P" Scheme 4.1) from extraction scheme in deuterated chloroform solvent.**

Peaks (ppm)	Peak intensities and integrals								
	H311	**4KA6**	**2KA5**	**3KA5**	**3KA6**	**5KA6**	**3KA8**	**1KA8**	**8KA8**
RA		TRIS	TRIS	TRIS	TRIS	TRIS	DVB	DVB	DVB
FRI:RA		nil FRI	0.001	0.01	nil FRI +FRI	0.001 + FRI	nil FRI	0.01	0.01 + FRI
a:									
1.43	12.6	11.8	12.6	12.4	12.4	12.5	9.78	12.5	7.6
integral	57261	41624	52065	43650	55689	51585	43242	64338	22876
b:									
1.85	5.2	4.9	5.1	5.1	5.2	5.2	3.9	5.2	3.2
2.06	1.1	1.0	1.1	1.1	1.2	1.0	0.7	1.2	0.4
integral	28725	21471	25182	22057	28673	24769	22417	32534	8342
c:									
6.49	8.1	7.6	8.1	8.1	8.0	8.0	6.4	8.1	5.3
6.58	11.1	10.6	11.1	11.2	11.0	11.1	8.8	11.1	7.1
integral	53376	40706	44328	44085	51734	46256	44586	59047	21348
d:									
7.04	23.0	21.4	23.0	23.0	22.9	23.0	18.2	23.0	14.3
7.08	22.5	22.0	22.5	22.6	21.8	22.5	17.5	22.7	13.8
integral	79579	60432	68100	65500	77875	73172	56866	92363	32332
other peaks (ppm)			2.28 4.05 (minor)						



peak	ppm
a	1.45
b	1.9
c	6.5
d	7.0

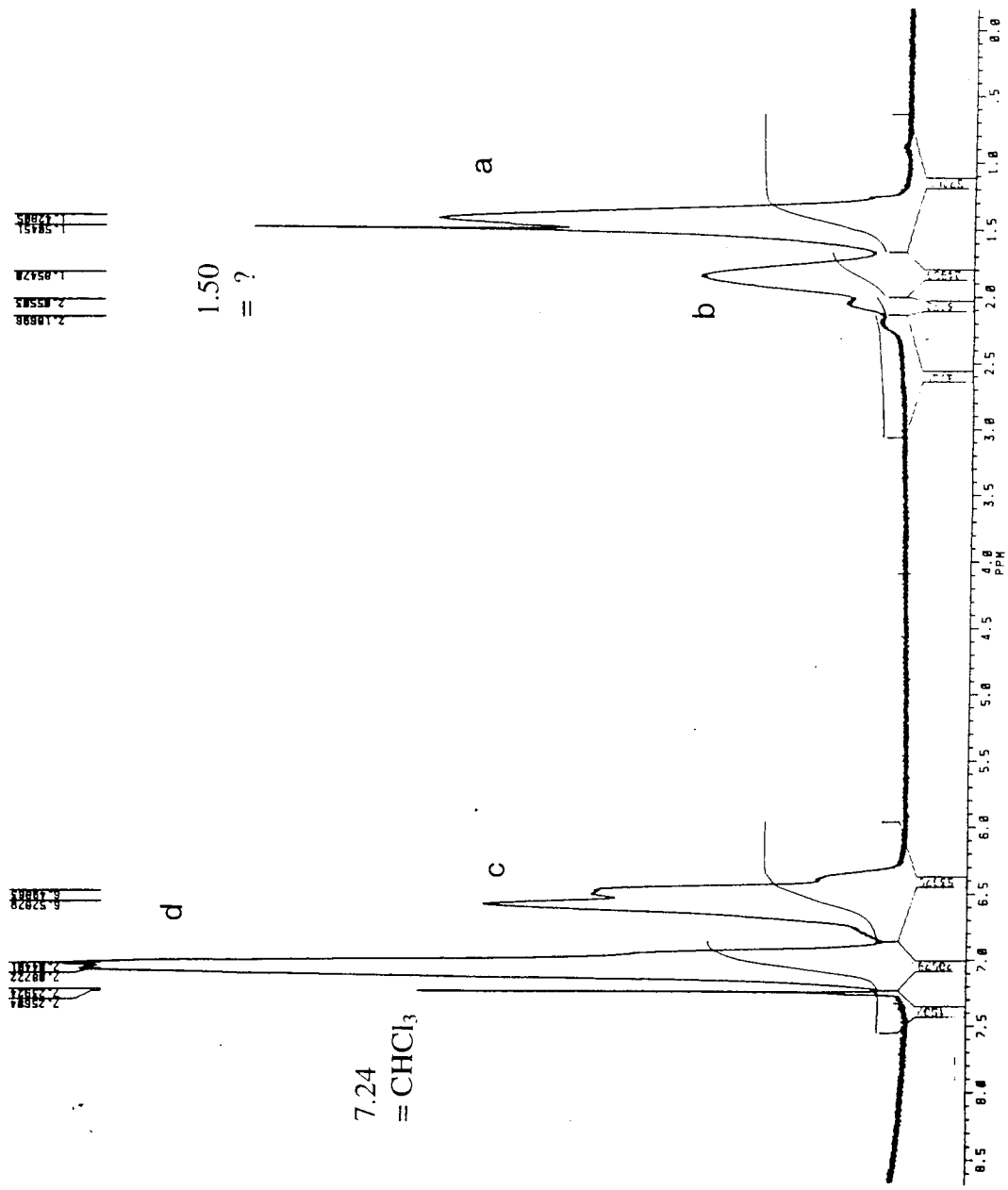
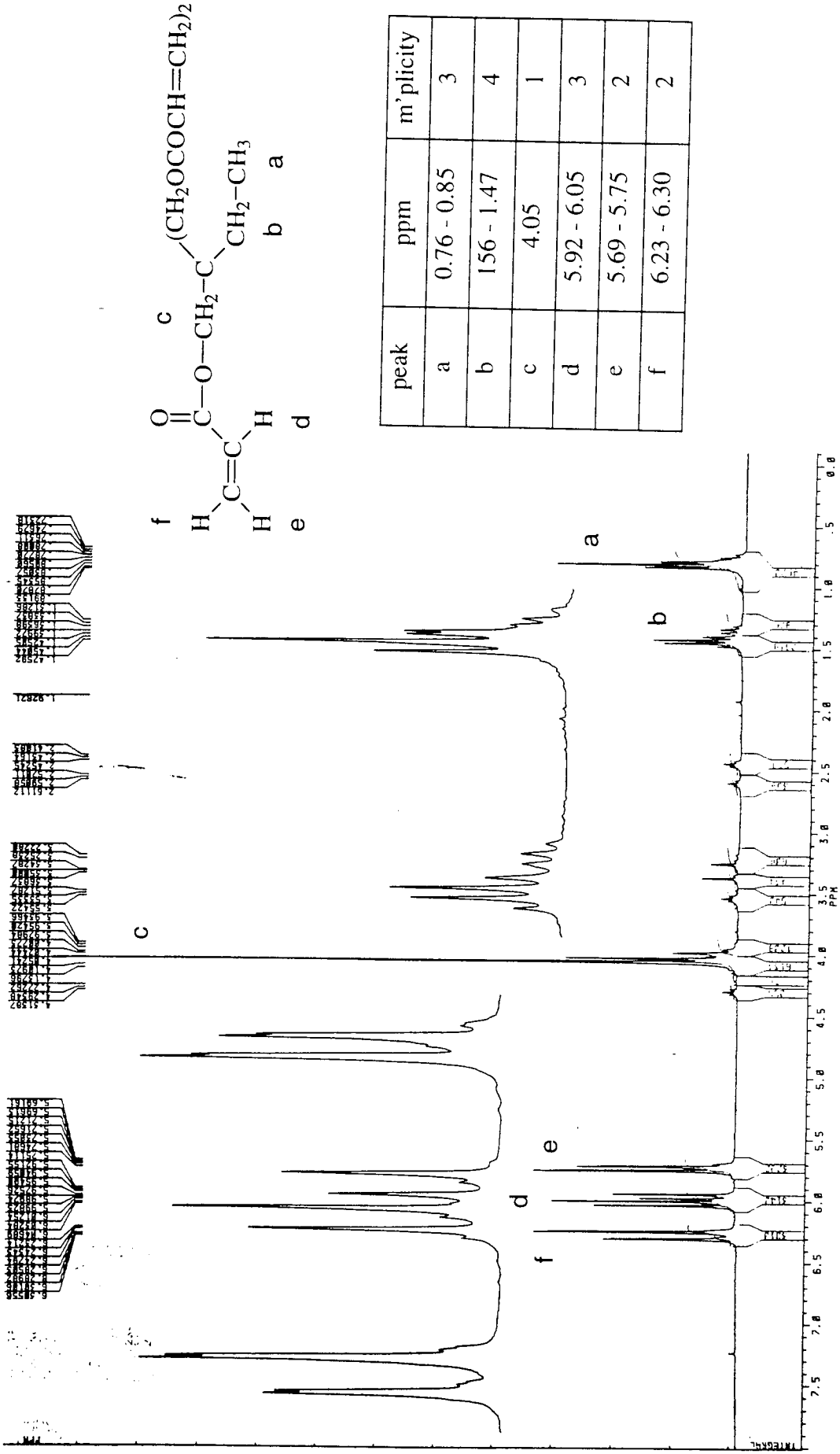
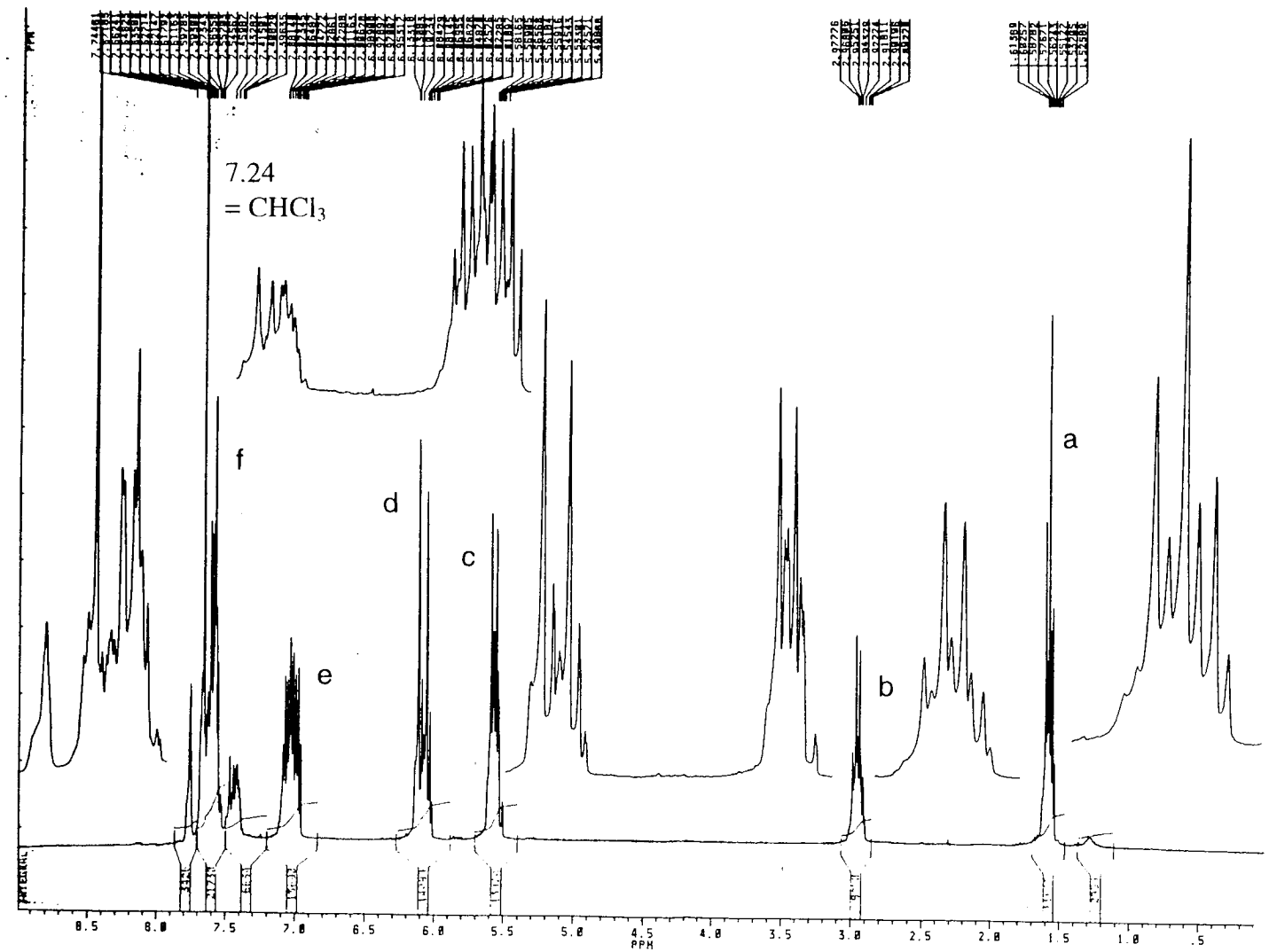


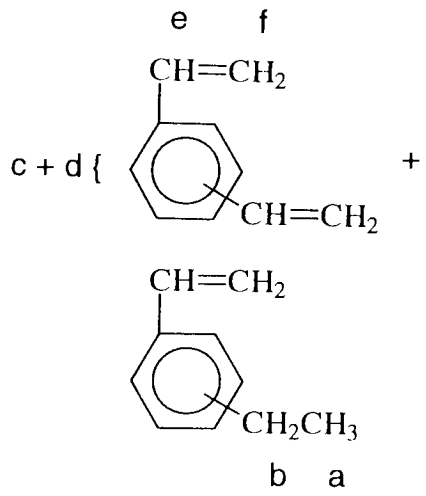
Figure 4.17 Proton NMR spectrum of unprocessed H311 PS precipitate fraction ("P" Scheme 4.1) in $CDCl_3$.



peak	ppm	m'plicity
a	0.76 - 0.85	3
b	156 - 1.47	4
c	4.05	1
d	5.92 - 6.05	3
e	5.69 - 5.75	2
f	6.23 - 6.30	2

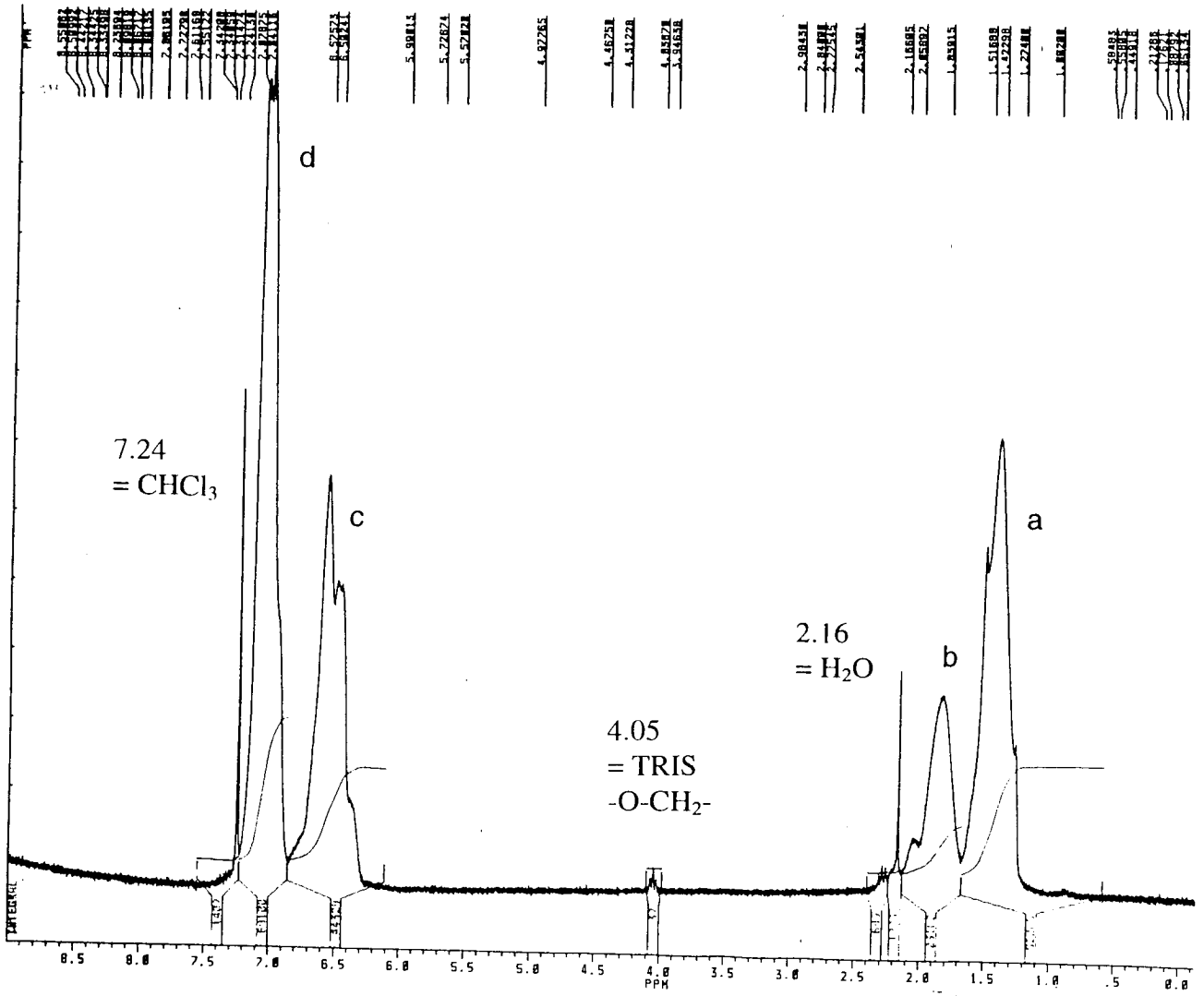
Figure 4.18 Proton NMR spectrum of TRIS in $CDCl_3$.

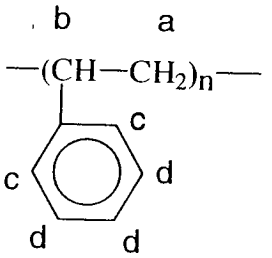




peak	ppm	m'plicity
a	1.52 -1.61	3
b	2.89 - 2.97	4
c	5.49 - 5.58	2
d	6.01 - 6.13	2
e	6.95 - 7.08	6
f	7.54 - 7.67	2

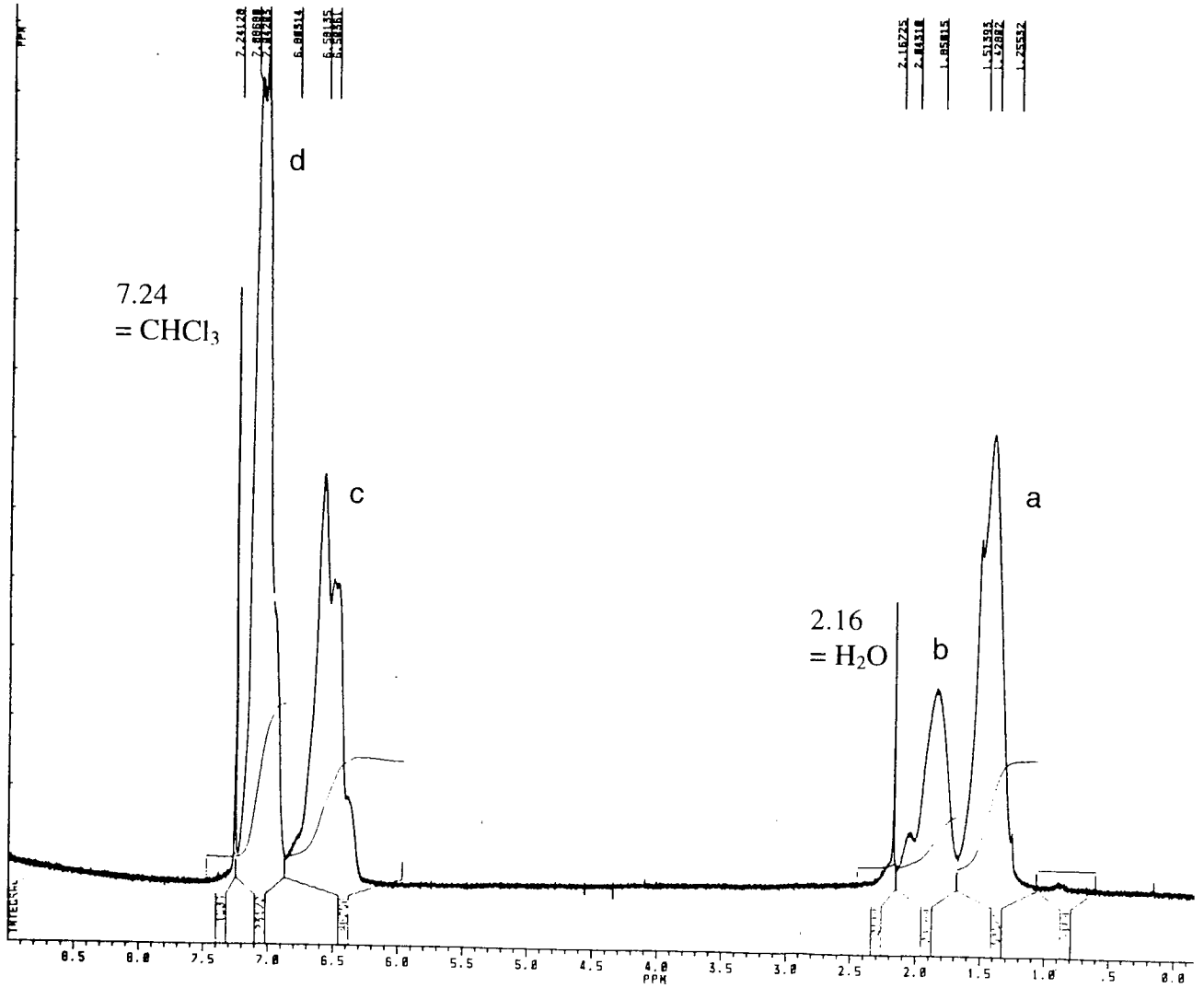
Figure 4.19 **Proton NMR spectrum of DVB in $CDCl_3$.**

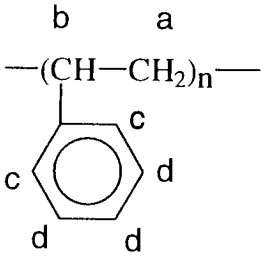




peak	ppm
a	1.45
b	1.9
c	6.5
d	7.0

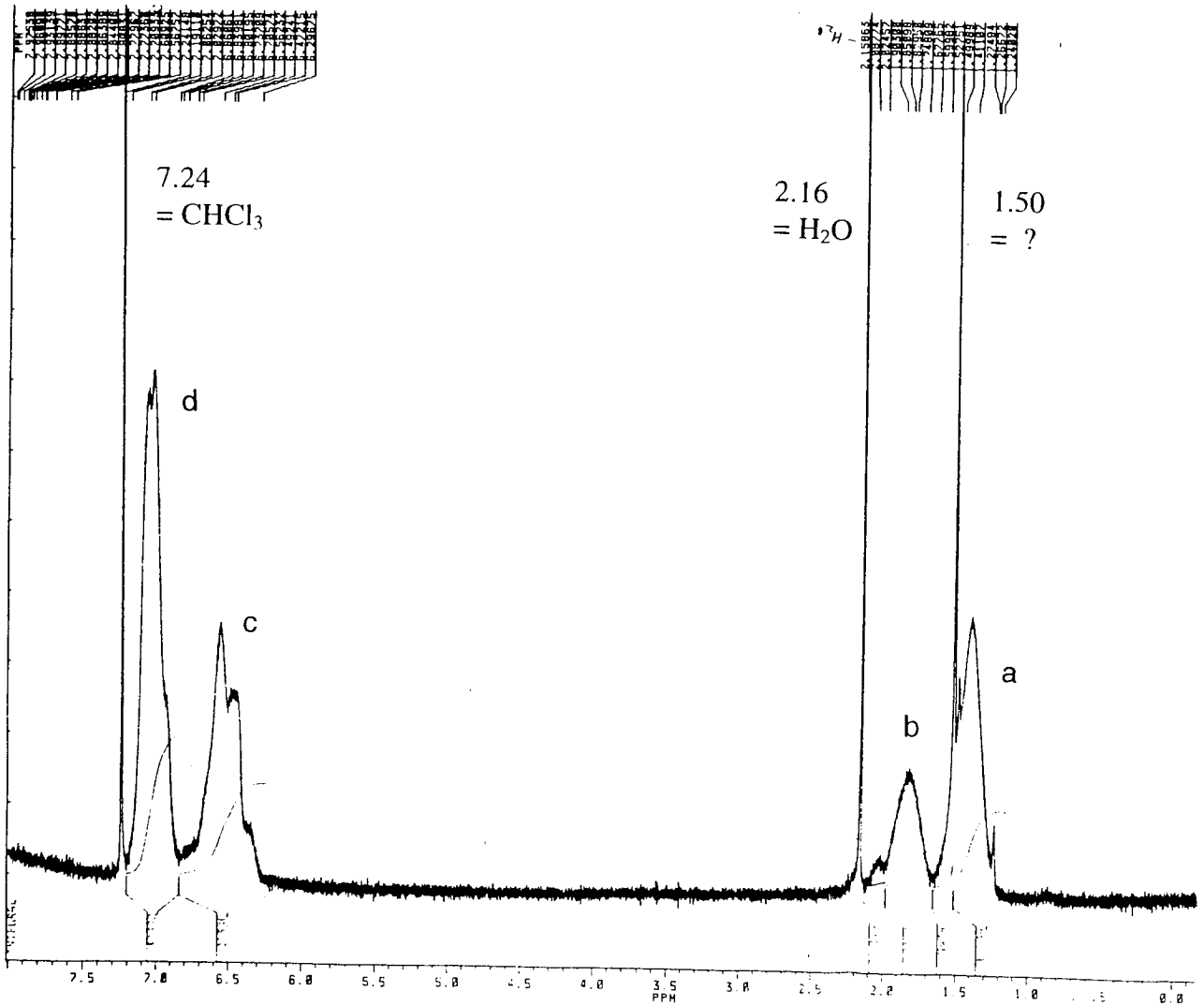
Figure 4.20 **Proton NMR spectrum of reactively processed PS 2KA5 (5% TRIS, 0.001 FRI:RA) precipitate fraction ("P" Scheme 4.1) in $CDCl_3$.**

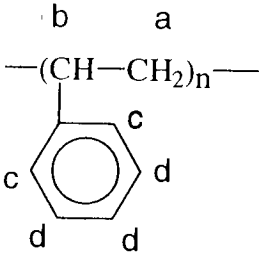




peak	ppm
a	1.45
b	1.9
c	6.5
d	7.0

Figure 4.21 **Proton NMR spectrum of reactively processed PS 5KA6 (5% TRIS, 0.001 FRI:RA, +FRI pre-addition) precipitate fraction ("P" Scheme 4.1) in $CDCl_3$.**





peak	ppm
a	1.45
b	1.9
c	6.5
d	7.0

Figure 4.22 **Proton NMR spectrum of reactively processed PS 8KA8 (5% DVB, 0.01 FRI:RA, + FRI pre-addition) precipitate fraction ("P" Scheme 4.1) in $CDCl_3$.**

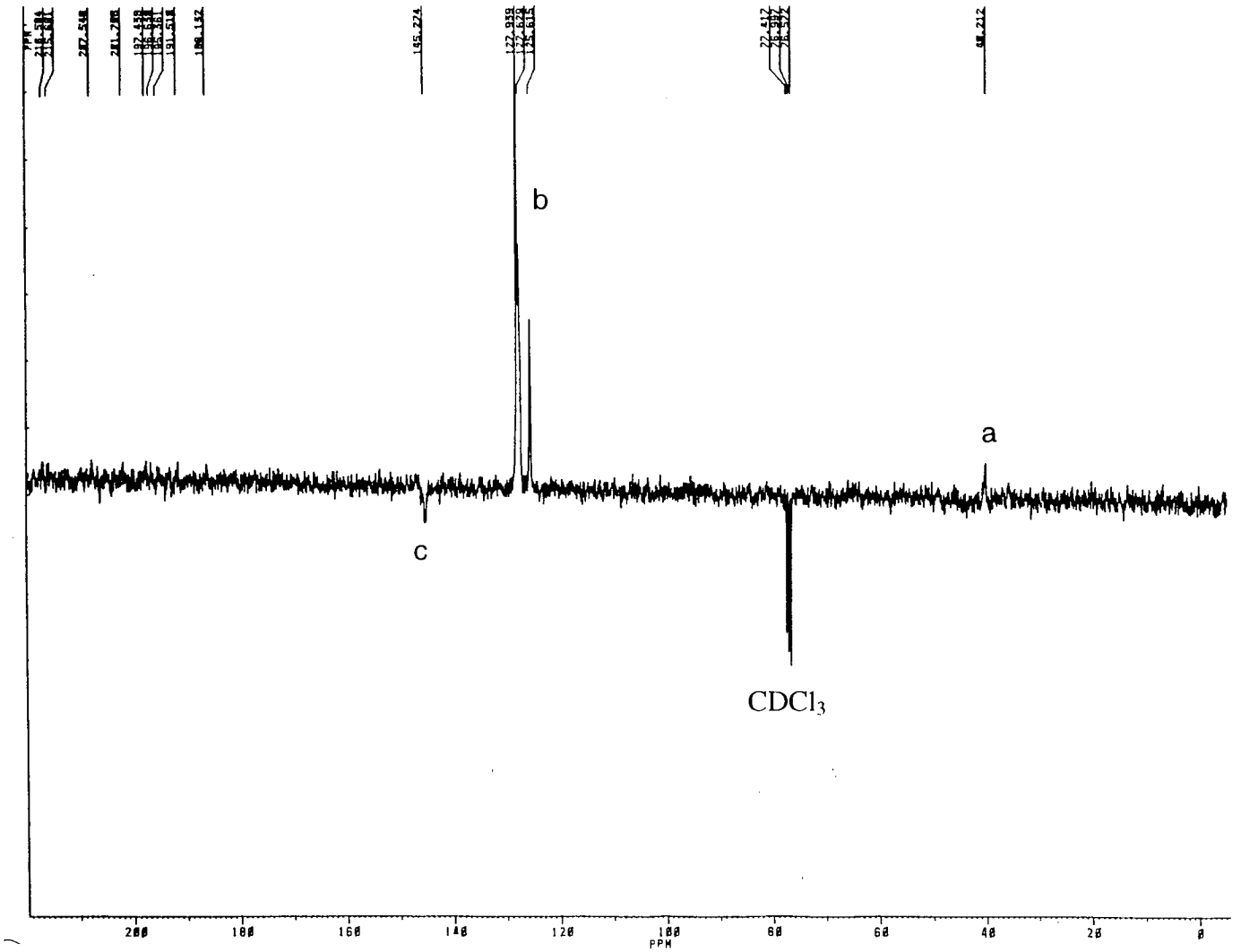
^{13}C NMR of reactively processed and control PS precipitated fractions ("P" Scheme 4.1) gave low quality spectra in which a dynamic range effect was believed to arise from the resonance intensity of dominant PS functionalities causing lower concentration functions to be almost entirely masked by system noise. The main peak assignments that could be resolved are given in Figure 4.23, 4.24 and 4.25 for Huntsman 311 unprocessed PS, TRIS and DVB. There was no positive confirmation of the presence of functional centres from TRIS or DVB in the precipitate fractions of any samples, the main effect was an increased multiplicity of bands for the intense aromatic ^{13}C PS resonances in some of the reactively processed cells (4KA6, 3KA5, 3KA6, 3KA8 : Figures 4.26-4.29 & Table 4.19). One possible reason for this was that grafting of modifier may have occurred at the tertiary carbon site in the PS backbone which would then have produced slight adjustments in the chemical shift of the aromatic carbons through β and γ effects from the position of substitution. This could also tie in with the occurrence of an additional peak from a fully substituted carbon centre (-ve at 44ppm) in some of these cells (Table 4.19). This suggests that in these instances the ^{13}C NMR method used, although unable to provide data on the absolute level of reactive agent grafting (perhaps not unexpected at yields below 80% for 5% additions of modifier {from extraction/FT-IR analysis - Section 4.2.7} and with the natural abundance of ^{13}C being inherently low), may indicate reactive agent grafting frequency along the PS backbone. The specific cases in which grafting frequency was thus sufficiently high enough to produce significant changes in ^{13}C NMR spectra (at 44ppm and additional aromatic peaks at 125 & 127ppm) were ;

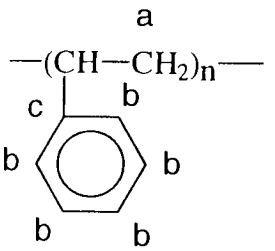
4KA6 (5% TRIS, no FRI)	- Figure 4.26
3KA6 (5% TRIS with no FRI, FRI pre-addition to PS)	- Figure 4.27
3KA8 (5% DVB, no FRI)	- Figure 4.29

At this first level of NMR analysis direct information on the chemical modification of PS by TRIS and DVB reactive modifiers was thus not readily apparent, however the perceived power of this technique[152,153] is such that perhaps with the assistance of an experienced polymer NMR spectroscopist, the selection of alternative methods (possibly two-dimensional NMR) and the use of NMR modelling/computational methods could develop further some of the indications suggested in the present study.

Table 4.19 Significant ^{13}C NMR peaks of precipitate fractions ("P" Scheme 4.1) from solvent extraction for reactively processed PS and controls (Table 4.10) in $CDCl_3$ using ^{13}C Pendant NMR technique.

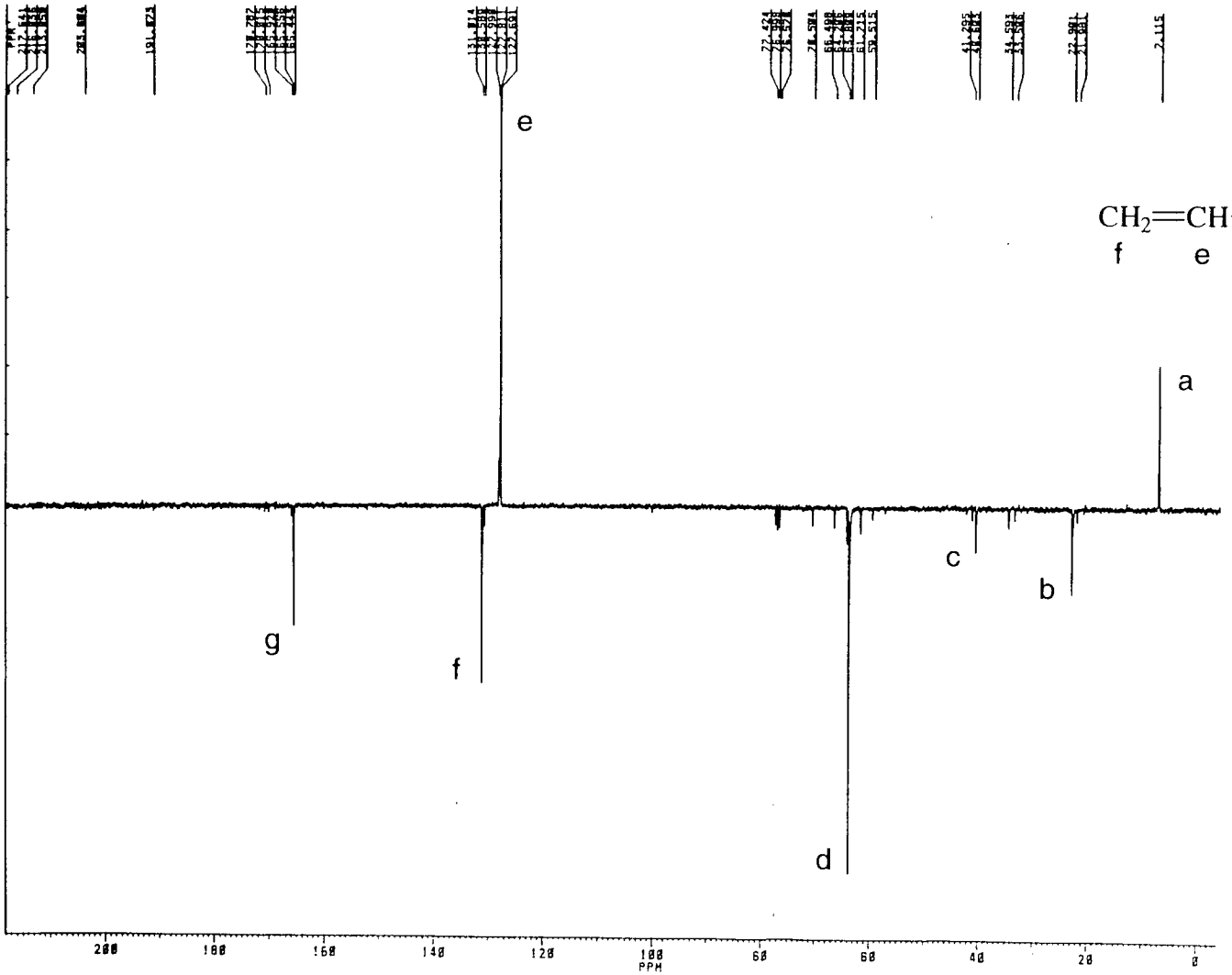
Cell RA FRI:RA	PS ^{13}C NMR Measured Absorptions (ppm), sign and intensity					
	methylene	tertiary C (?)	(?)	aromatic C	aromatic C	substituted aromatic C
H311 -	40.2 + 0.91			125.6 + 5.2	127.6 + 7.5 127.9 + 12.0	145.3 - 0.86
4KA6 TRIS nil FRI	40.3 + 1.1	44.2 - 0.55	100.1 - 0.99 100.4 - 0.6	125.5 + 2.5 125.6 + 4.5	127.2 + 2.3 127.4 + 3.7 127.6 + 6.9 127.9 + 12.1	143.5 - 0.61 145.1 - 1.2
2KA5 TRIS 0.001	40.4 + 2.4			125.6 + 5.9	127.6 + 4.4 127.9 + 12.0	144.2 - 1.6
3KA5 TRIS 0.01	40.3 + 2.1			125.5 + 3.3 125.6 + 5.1	127.4 + 3.9 127.6 + 6.9 127.9 + 12.0	147.2 - 1.1
3KA6 TRIS nil FRI + FRI	40.3 + 1.1	44.2 - 0.5	100.0 - 1.0	125.5 + 2.8 125.6 + 4.7	127.4 + 3.9 127.6 + 6.9 127.9 + 12.0	145.2 - 1.0
5KA6 TRIS 0.001 + FRI	40.6 + 0.84	44.0 - 0.56	101.3 - 1.1	125.6 + 5.0	127.6 + 7.4 127.9 + 12.0	145.2 - 0.94
3KA8 DVB nil FRI	43. 8 + 1.4			125.5 + 2.1 125.6 + 4.1	127.2 + 1.7 127.4 + 3.3 127.6 + 6.6 127.9 + 12.1	145.2 - 2.0
1KA8 DVB 0.01	44.1 + 1.0			125.6 + 4.8	127.6 + 7.2 127.9 + 12.0	145.2 - 1.7
8KA8 DVB 0.01 + FRI	40.3 + 1.5			125.6 + 4.9	127.6 + 7.2 127.9 + 12.0	149.2 - 0.8

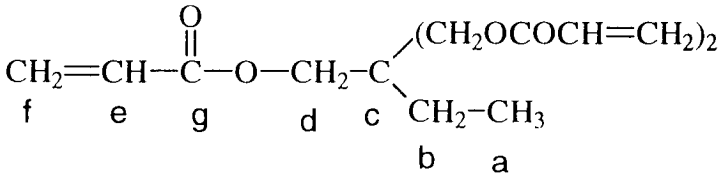




peak	ppm	sign
a	40.2	+
b	125.6 127.6 127.9	+ + +
c	145.3	–

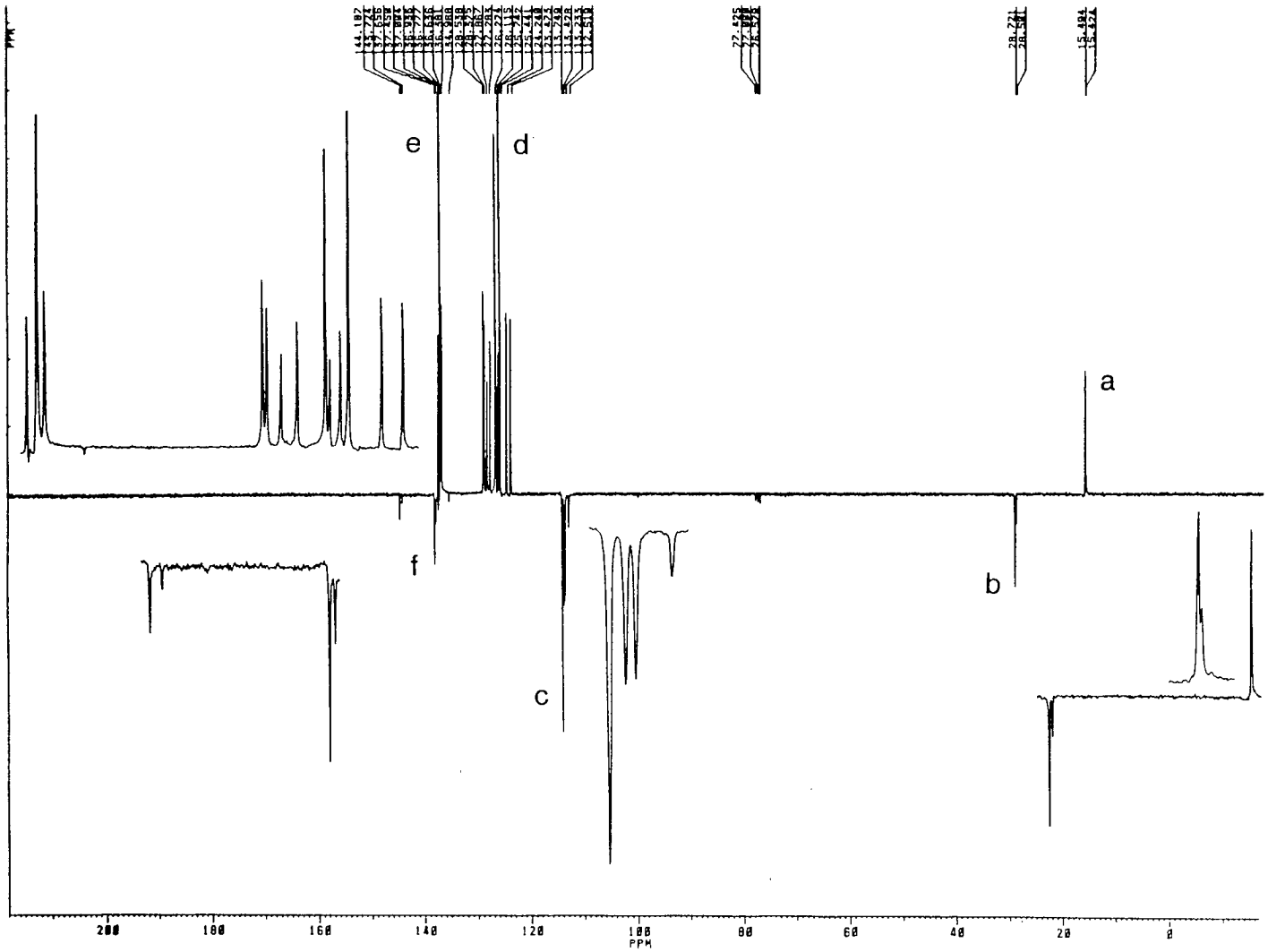
Figure 4.23 Carbon-13 NMR spectrum of unprocessed H311 PS precipitate fraction ("P" Scheme 4.1) in $CDCl_3$.

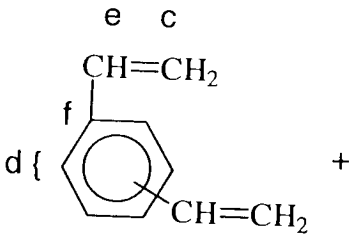


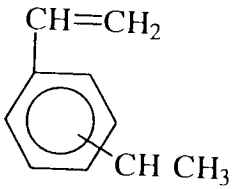


peak	ppm	sign
a	7.1	+
b	22.9	–
c	40.6	–
d	63.8	-
e	127.7	+
f	131.0	-
g	165.4	-

Figure 4.24 Carbon-13 NMR spectrum of TRIS in $CDCl_3$.

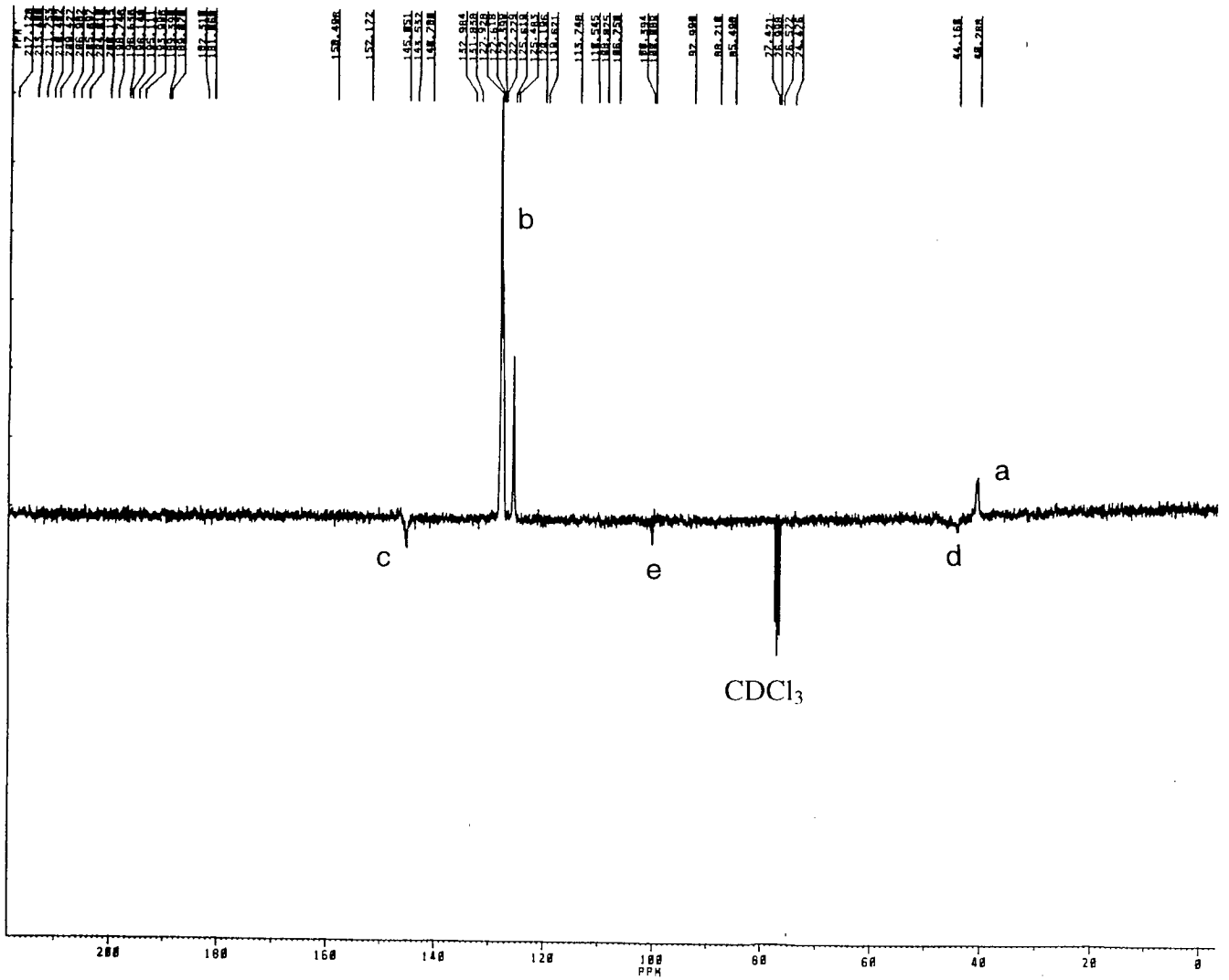






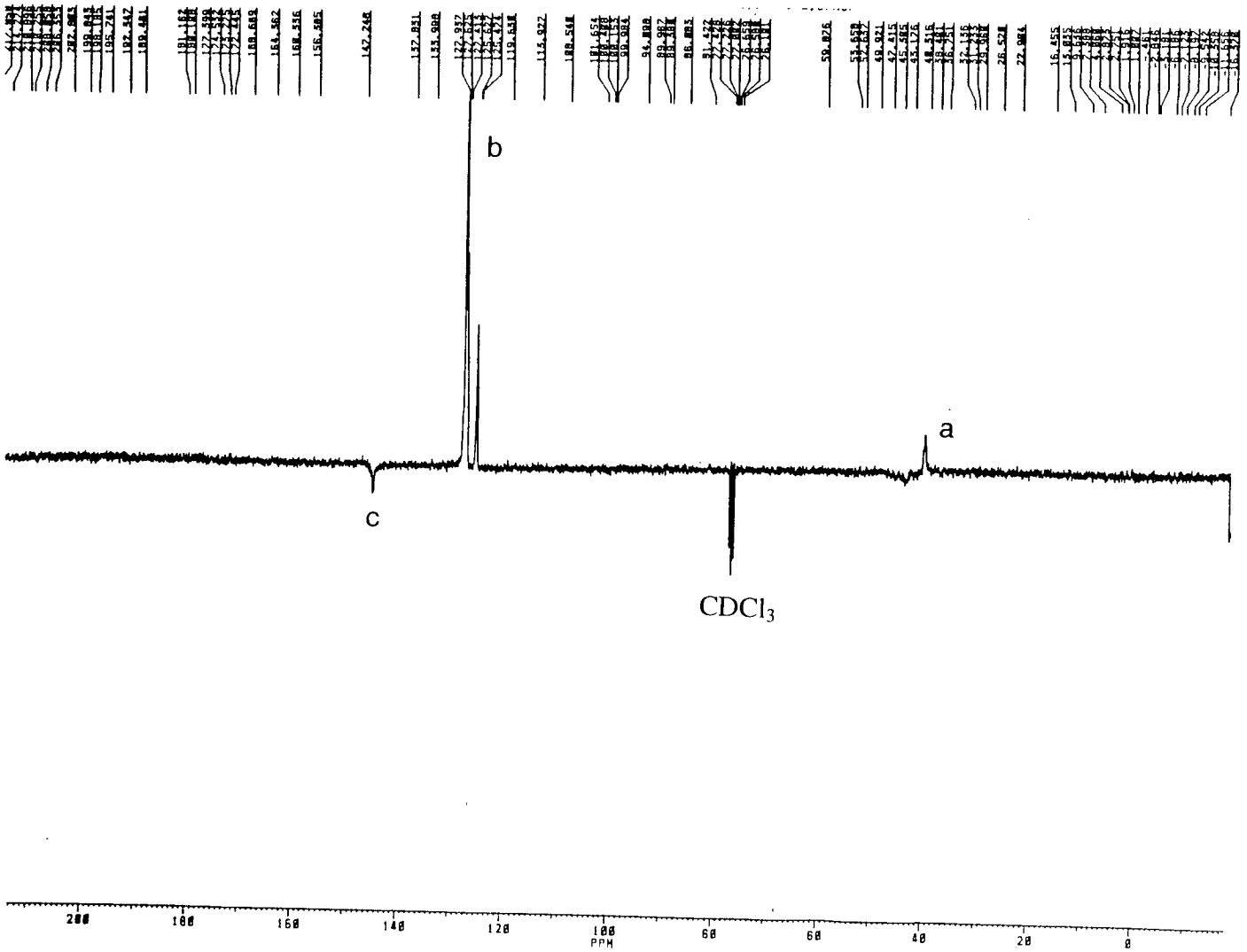
peak	ppm	sign
a	15.5	+
b	28.7	–
c	113.7	–
d	125.4	+
e	126.3	+
f	137.7	-

Figure 4.25 Carbon-13 NMR spectrum of DVB in $CDCl_3$.



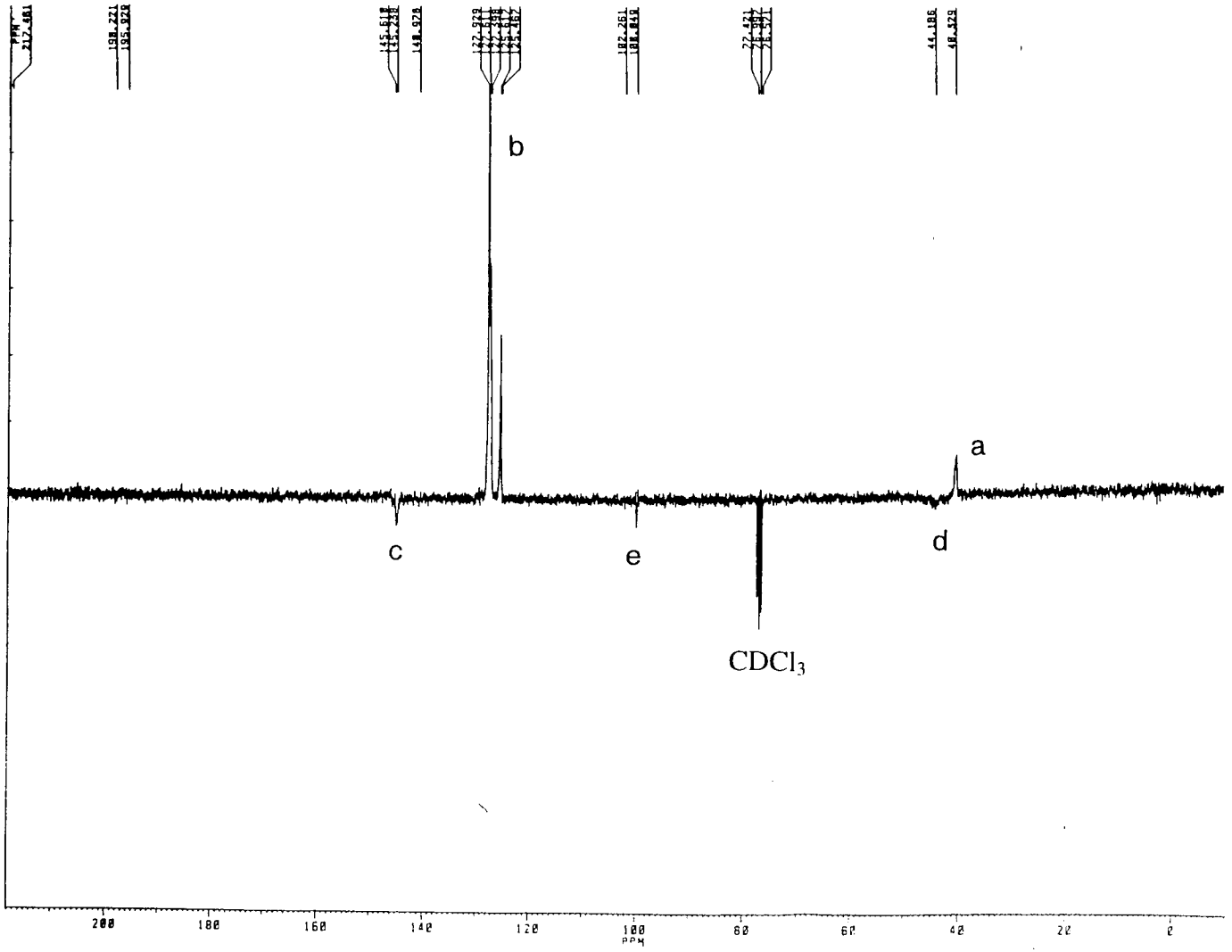
peak	ppm	sign
a	40.3	+
b	125.5	+
	125.6	+
	127.2	+
	127.4	+
	127.6	+
	127.9	+
c	143.5	-
	145.1	-
d	44.2	-
e	100.1	-
	100.4	-

Figure 4.26 **Carbon-13 NMR spectrum of reactively processed PS 4KA6 (5% TRIS, no FRI) precipitate fraction ("P" Scheme 4.1) in $CDCl_3$.**



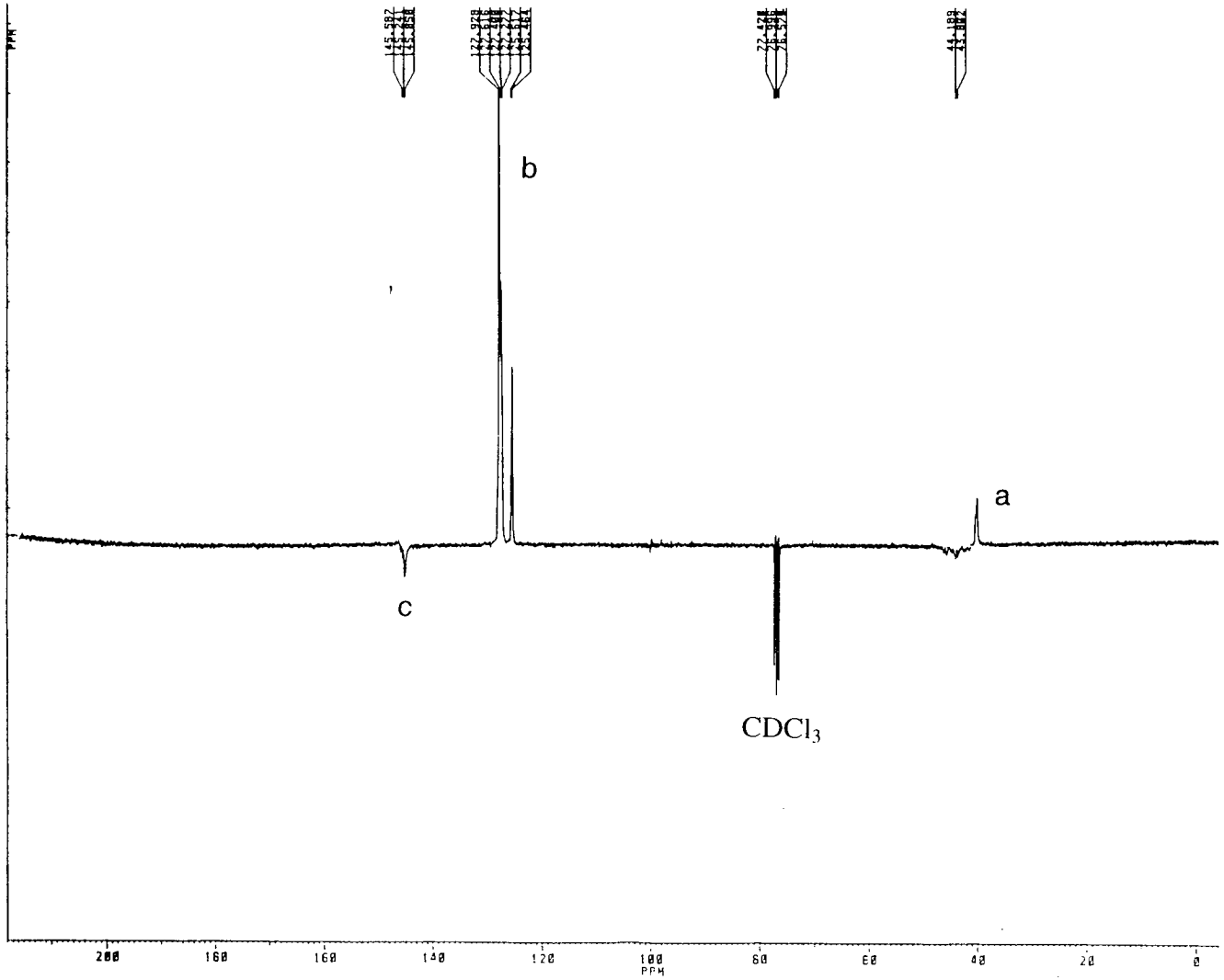
peak	ppm	sign
a	40.3	+
b	125.5	+
	125.6	+
	127.4	+
	127.6	+
	127.9	+
c	147.2	-

Figure 4.27 Carbon-13 NMR spectrum of reactively processed PS 3KA5 (5% TRIS, 0.01 FRI:RA) precipitate fraction ("P" Scheme 4.1) in $CDCl_3$.



peak	ppm	sign
a	40.3	+
b	125.5	+
	125.6	+
	127.4	+
	127.6	+
	127.9	+
c	145.2	-
d	44.2	-
e	100.0	-

Figure 4.28 **Carbon-13 NMR spectrum of reactively processed PS 3KA6 (5% TRIS, nil FRI, + FRI pre-addition) precipitate fraction ("P" Scheme 4.1) in $CDCl_3$.**



peak	ppm	sign
a	43.8	+
b	125.5	+
	125.6	+
	127.2	+
	127.4	+
	127.6	+
	127.9	+
c	145.2	-

Figure 4.29 **Carbon-13 NMR spectrum of reactively processed PS 3KA8 (5% DVB, nil FRI) precipitate fraction ("P" Scheme 4.1) in $CDCl_3$.**

4.2.10 DSC Analysis of Reactively Processed Polystyrene Compositions.

DSC heating scans were made as detailed in Section 2.10 on pressed film samples of all key reactively processed PS cells and controls (Table 4.10), and dichloromethane cast films of precipitated fractions from extraction analysis ("P" Scheme 4.1). A PS glass transition was discernible for all samples and the glass transition temperature (Tg) measured in every case (Table 4.20). Replicate testing on samples of unprocessed PS showed the main source of error in the Tg measurement (assessed to be ± 0.5°C) to be the selection of construction lines for the difference in heat capacity before and after a glass transition due to an overshoot in the heat flow curve (Figure 4.30). This a characteristic feature in the DSC analysis of highly amorphous polymers such as PS and is believed to arise from the enthalpy change for the glass transition being determined by some relationship between the heating rate of analysis and sample thermal history.[154] This was supported by initial scans at 20°C per minute in which the overshoot was more pronounced ; reduction to 10°C per minute lessened this feature, but also decreased the pre- and post-Tg heat flow curve difference indicating that even lower scan rates would not be advantageous. For dichloromethane cast films ("P" Scheme 4.1) the shape of heat flow curves was even further strained by the presence of a drop in heat capacity before passing through the glass transition, coupled with the post-Tg overshoot (Figure 4.31). This is again a feature of a balance between heating rate and sample molecular history, with free volume and entropic factors also being involved in this case. In the present study these effects were thus not quantified and the recommendation that curve shape be ignored for Tg measurement by determination of the intersection point[154] was accepted.

By reference to measured Tg values for the series of PS cells analysed (Table 4.20) several distinct effects were realised. A large drop in Tg (5°C) was found for the processed control (4KA5 - no RA addition but chamber opened for 20s at 3 minutes)

Figure 4.30 **DSC trace of unprocessed H311 PS (pressed film, 8.12mg ; 30-150°C at 10°C per minute) in glass transition region.**

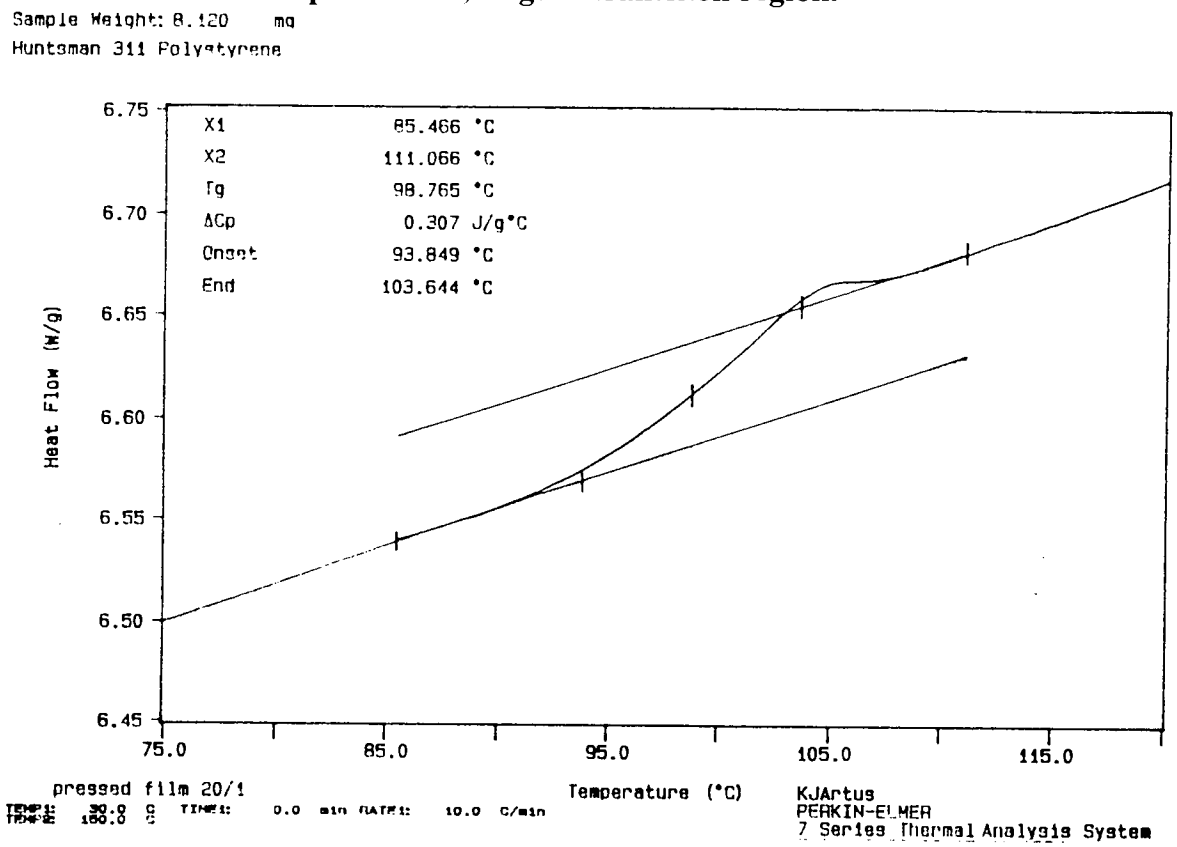


Figure 4.31 **DSC trace of unprocessed H311 PS precipitate fraction ("P" Scheme 4.1 - dichloromethane cast film, 8.48mg ; 30-150°C at 10°C per minute) in glass transition region.**

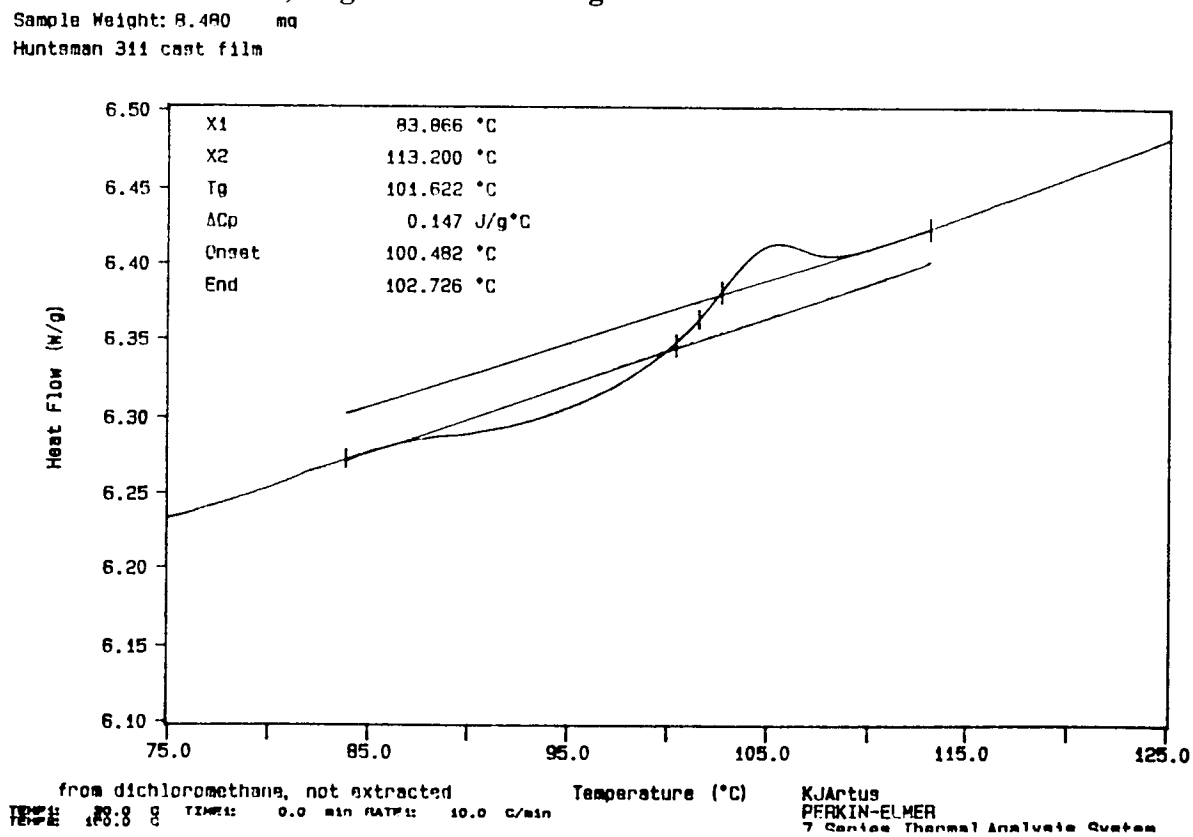


Table 4.20 **Measurements of PS glass transitions of key PS cells (Table 4.10) from DSC analysis (7-10mg samples, 30-150°C scan at 10° per minute).**

			Measured PS glass transition (°C)					
			Pressed film		Dichloromethane cast film			
Cell	RA	FRI:RA	before extraction	Tg shift vs 4KA5	without extraction	soluble "S" fraction	precipitated "P" fraction	Tg shift vs 4KA5
H311	unprocessed		99.9	/	101.9	98.6	104.7	/
4KA5	nil (opened)		94.9	/			105.4	/
7KA6	nil (opened) + FRI		95.5	+ 0.6			106.1	+ 0.6
4KA6	TRIS	nil FRI	90.6	- 4.3			105.9	+ 0.5
2KA5	TRIS	0.001	94.9	+ 0.1			105.3	+ 0.1
3KA5	TRIS	0.01	95.1	+ 0.2			105.2	- 0.1
3KA6	TRIS + FRI	nil FRI	96.1	+ 1.2			105.7	+ 0.3
5KA6	TRIS + FRI	0.001	98.6	+ 3.7			104.7	- 0.7
3KA8	DVB	nil FRI	70.8	- 24.1		73.3	104.9	- 0.4
1KA8	DVB	0.01	98.1	+ 3.2			106.1	+ 0.6
8KA8	DVB + FRI	0.01	97.7	+ 2.7			104.8	- 0.6

Note : "S" and "P" fractions refer to Scheme 4.1

compared to the unprocessed Huntsman 311 PS. It was recognised that PS Tg can be related to molecular weight and molecular weight distribution,[82,155] but in the absence of cofirmatory analysis of these specific samples such a large change could not be assigned solely to reduction in MW of the processed PS. A more probable cause would be changes associated with the different thermal histories of "as supplied" and processed polymer, indeed the data presented on H311 PS film cast from dichloromethane solvent without extraction (Table 4.20) shows that a two degree change may be affected by the molecular history effect of this route alone. Comparisons between cells were thus made relative to the processed control (4KA5) rather than unprocessed H311 PS.

In all cases the Tg of dichloromethane cast films of PS precipitate fractions from extraction ("P" Scheme 4.1) were significantly higher (above 104°C) than pressed films before extraction (eg 4KA5 Table 4.20). This effect again could be assigned in part to the preparation route and major changes on a molecular level of polymer chain arrangements in the amorphous glass phase. However in this instance it was recognised that there was a significant possibility of upward shifts in PS molecular weight distribution by loss of low molecular weight fractions on extraction, which would produce increases in the resulting glass transition temperature. This was further supported considering the Tg measurement of the soluble "S" extraction fraction for unprocessed H311 (98.6°C) which was not at the same high level as the precipitate "P" fraction (104.7°C) after possible separation of soluble, low molecular weight components. However without confirmation by PS MWD measurements of precipitate fractions, comparisons of Tg changes would be limited to within this series, rather than by reference to whole fractions.

The largest differences in Tg's for reactively processed PS cells were found with TRIS and DVB additions without initiator (4KA6 and 3KA8 respectively). TRIS alone gave a small reduction in Tg (4.3°), whereas DVB produced a staggering 24° drop to a measured Tg of 70.8°C. Plasticisation was believed to have been evident in both cases, but not surprisingly with the molecularly similar DVB producing the greater effect. A related compound reported for use as a diluent in PS, to lower Tg and hence processing temperatures, is ethylbenzene, for which only a 1% by weight addition to PS decreases the PS Tg by 6°.[82] As shown by measurements on precipitate from the extraction scheme, removal of the plasticising, free reactive agent regenerated a PS fraction with Tg not significantly different to the control (4KA5 "P" fraction), whereas the soluble "S" fraction before free DVB separation showed the effects of plasticisation (Tg = 73.3°C Table 4.20).

Significant increases in Tg above control values were limited to complete compositions before extraction ; all dichloromethane cast samples of precipitate "P" fractions from the extraction scheme were within ± 0.7°C of the 4KA5 "P" control value which could not, even at the highest difference, be taken as a significant change with the assigned error in Tg determination at ± 0.5°C. This may have shown that the chemical modifications effected in the precipitated (soluble) PS fraction (and measured by alternative methods, particularly FT-IR ; Section 4.2.7) were not so great as to dramatically alter the molecular state of this portion ; it became essentially a functionalised analogue of the host PS. Nevertheless for the entire (unextracted) products of reactive processing, significant rises in Tg above the 4KA5 control were found for ;

3KA6 (5% TRIS with no FRI, except FRI pre-addition)	+ 1.2°C
5KA6 (5% TRIS at 0.001 FRI:RA, with FRI pre-addition)	+ 3.7°C
1KA8 (5% DVB at 0.01 FRI:RA)	+ 3.2°C
8KA8 (5% DVB at 0.01 FRI:RA, with FRI pre-addition)	+ 2.7°C

These increases may well have been cumulative from different effects within the whole compositions (such as partial PS or reactive agent cross-linking) but it was hoped that some links could be found with other analyses of these products and processing behaviour to develop an overall rational for the chemical modifications of PS attempted (Section 4.3.2).

4.3 DISCUSSIONS.

In this study of polymer modification the main aim was to determine the effectiveness of different approaches for subsequent application in the reactive blending of the two polymers of interest. Torque behaviour during reactive processing was monitored as an "on-line" indication of the effects of TRIS and DVB addition to PS and EPDM. An underlying premise was that torque increases were the result of interlinking agent reaction, with the reservation that this might not be completely due to the targeted reaction with polymer (Section 3.3.2). Validation of this principle was of prime importance to elucidate the effects of different approaches and confirm the optimum conditions. To this end, possible reaction mechanisms for PS, PS/TRIS & PS/DVB were considered. Using the models developed from this, combined with the relationships between process and analytical data, a critical assessment of modification effectiveness was achieved.

4.3.1 Possible Reaction Mechanisms of PS, TRIS and DVB During Modification of Polystyrene With Interlinking Agents.

Understanding was sought for the possible reaction mechanisms of the polystyrene, TRIS and DVB components involved in the reactive modification of PS ; for each individually (degradation of PS or polymerisation of RA) and the most probable outcomes of simultaneous reaction during processing. There were three areas considered :

i. - thermo-oxidative degradation of polystyrene during processing (Section 4.3.1.1) ;

ii. - polymerisation of the triacrylate interlinking agent (TRIS) and possible reaction with PS (Section 4.3.1.2) ;

iii. - polymerisation of divinyl benzene interlinking agent (DVB) and possible reaction with PS (Section 4.3.1.3).

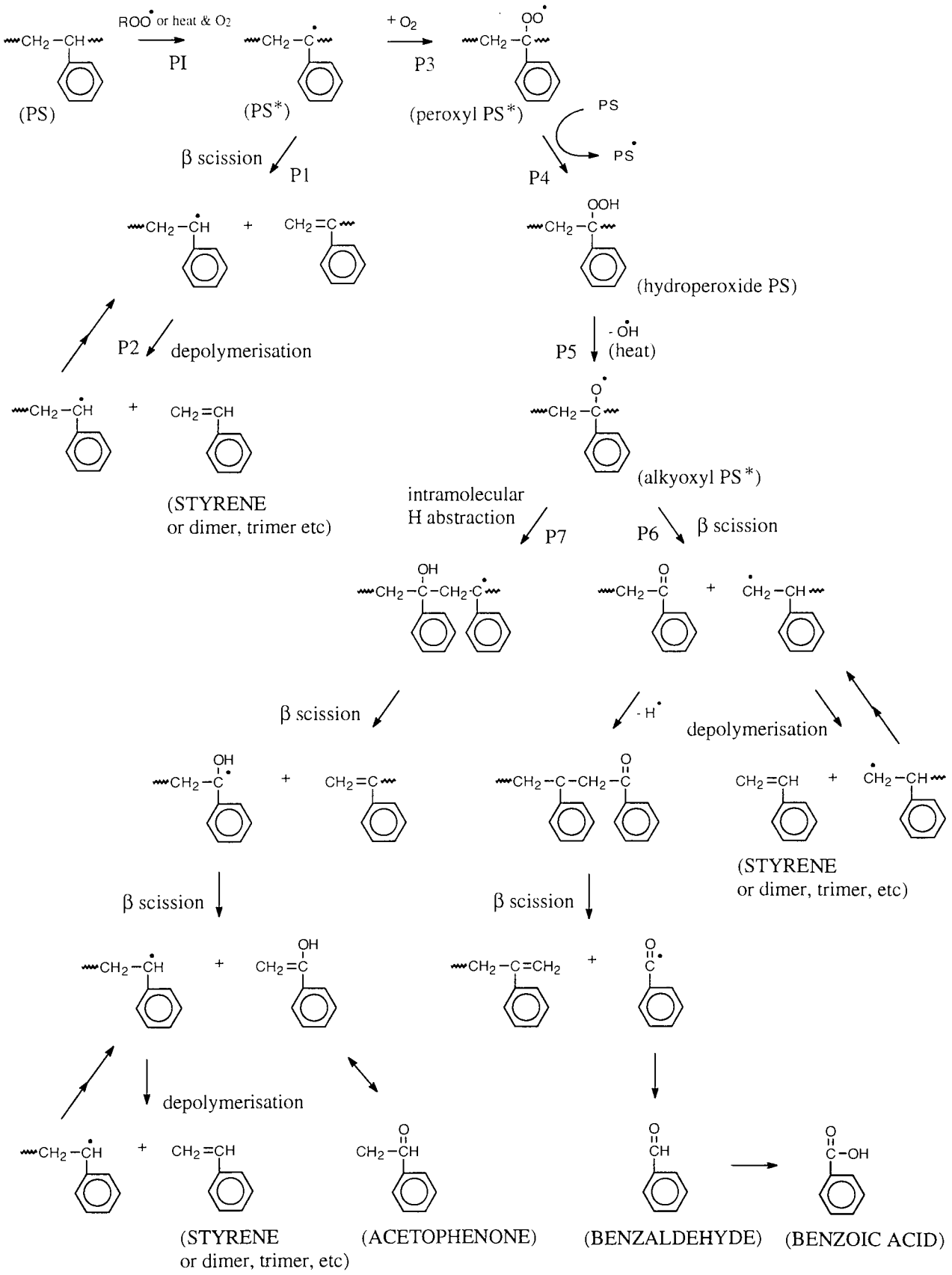
4.3.1.1 Thermo-oxidative Degradation of Polystyrene.

Polystyrene is considered to be inherently stable during processing and in general service under normal conditions, nevertheless there are some useful reports detailing the extent and routes of degradation over a wide range of conditions.[142-148] When polystyrene degrades it does so by a classical free radical chain reaction mechanism ; Scheme 4.2 shows routes most appropriate to the "standard processing conditions" (<220°C and presence of limited amount of oxygen). Thermal degradation of PS in the absence of oxygen, is initiated by random chain scission and proceeds rapidly above 300°C, producing significant weight loss and sharp decrease in average molecular weight. At lower temperatures there is some decrease in molecular weight without any weight loss, controversially ascribed to initiation by the thermal scission of weak links in the polymer backbone.

However, the presence of oxygen greatly reduces the activation energy for thermal degradation, allowing initiation by the thermal scission of tertiary C-H bonds (PI - Scheme 4.2) to produce polystyryl macro-radicals (PS^*). Peroxide radical initiators are also effective PS^* producers by tertiary hydrogen abstraction,[142] whereas secondary hydrogens can only be attacked by much stronger radicals, such as chlorine (Cl^*).[143]

Propagation may proceed by β-scission of the PS^* (P1 - Scheme 4.2) or by reaction with oxygen (P3). Polystyryl radical reaction with oxygen is $x10^6$ faster than with another PS molecule and is thus the favoured route until all the oxygen is depleted.[142] Combination of PS^* radicals and crosslinking does not occur at processing temperatures, chain scission predominates (P1) leading to styrene evolution by depolymerisation (P2) and formation of a lower molecular weight vinyl-ended polystyrene chain.

Scheme 4.2 **Thermo-oxidative degradation of polystyrene (under processing conditions - maximum 200°C & limited oxygen).** [142-148]



Returning to the polystyryl radical - oxygen reaction, the peroxyl radical formed (P3) readily yields hydroperoxide by hydrogen abstraction (P4: from other PS chains[143] continuing the generation of PS^* and internally by intramolecular attack[144]). The hydroperoxide is thermally unstable (P5) and the alkoxyl radical generated (PSO^*) is a highly reactive transition state, undergoing rapid β-scission (P6) or intramolecular hydrogen abstraction (P7). There are then many possible reactions to a variety of oxgenated products and styrenic monomer, dimer, trimer and substituted compounds ; the relative yields depending upon the processing conditions experienced.[145-148] Termination is predominantly by the elimination of volatile products from unstable radicals, macro-radical recombination is not favoured until oxygen is depleted, when disproportionation reaction may occur yielding saturated and unsaturated chain ends. Reaction paths shown in Scheme 4.2 are suggested routes to the major products determined by thermo-oxidative degradation of PS at 224°C by Vu Duc et al[148] ; in decreasing order - styrene > styrene dimer > benzaldehyde > benzoic acid > acetophenone.

In summary, key points of polystyrene thermo-oxidative degradation to note in the context of the present work are :

☺ PS thermo-oxidative degradation will not be extensive by processing in a closed mixer at a temperature of 180°C ;

☹ oxygen or peroxide initiators will encourage PS degradation ;

☺ polystyryl radicals are the primary species available for reaction with other functional groups ;

😐 oxygen plays a dominant role in propagation ;

😐 several pathways produce unsaturated chain ends to polystyrene ;

☹ chain scission will lead to decreased molecular weight.

4.3.1.2 Polymerisation of the Triacrylate Interlinking Agent (TRIS) and Possible Reactions With Polystyrene.

The triacrylate interlinking agent, TRIS, may be viewed simply as an unsymmetrically substituted vinyl monomer, with an acrylic acid ester as the substituent. In this trifunctional reagent the three reactive centres will all be equivalent so that initially the reactivity of a single vinyl end group in an acrylate environment may be examined.

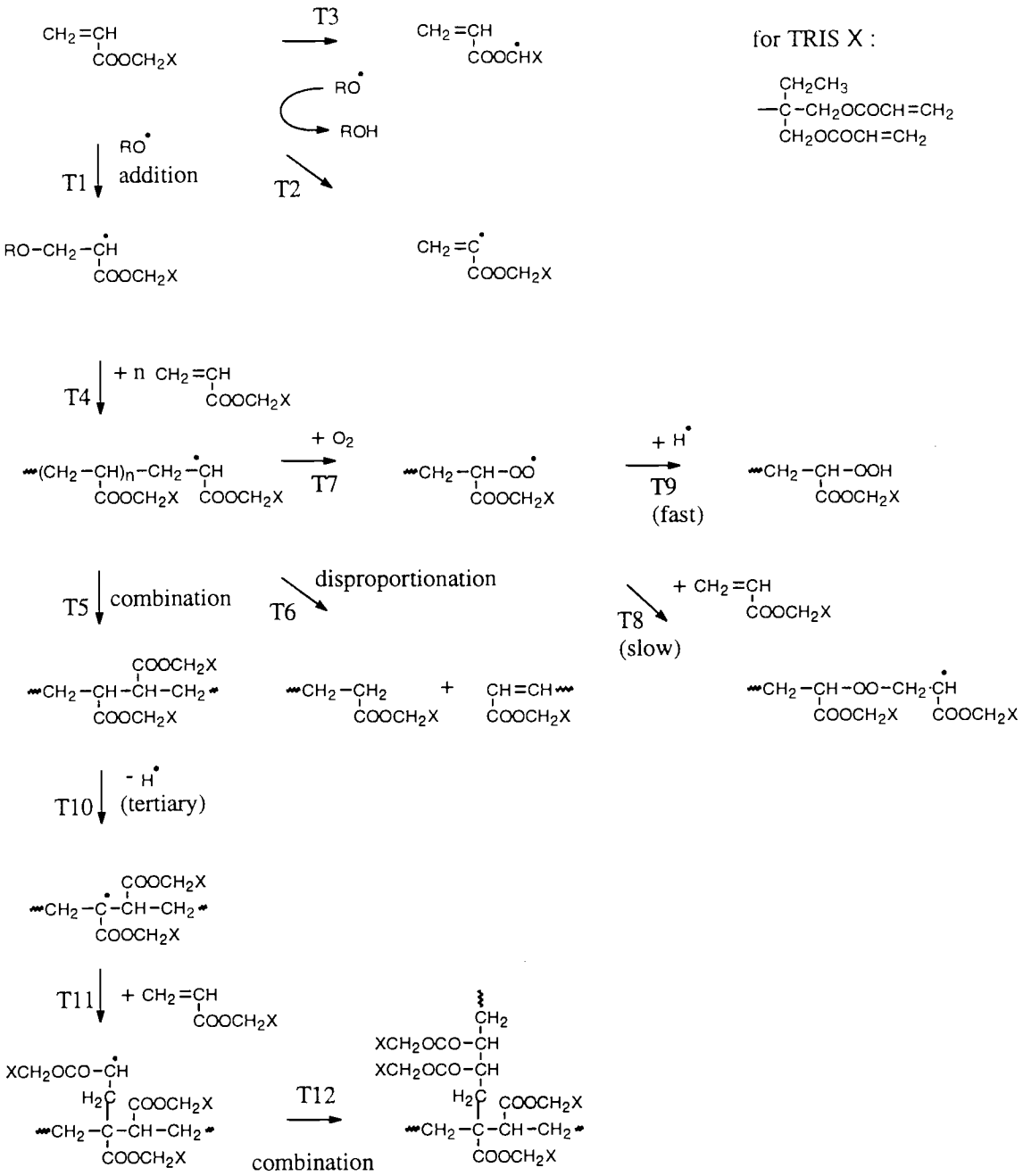
Acrylates readily polymerise or copolymerise through classical free radical chain reaction mechanisms[149] (Scheme 4.3). Initiation is easily achieved by oxygen radical initiators, both by double bond addition (T1 : Scheme 4.3) and hydrogen abstraction from other centres in the molecule (T2 & T3) ; the relative proportions depending on the acrylate structure, though addition may predominate as with methyl methacrylate.[149]

Propagation follows by head-to-tail growth of the polymeric radical by attack on monomer unsaturation (T4). Termination is by combination of polymeric radicals (T5) or disproportionation (T6).

An important aspect of acrylate polymerisation is marked inhibition in the presence of oxygen, due to competitive addition between monomer and oxygen. Reaction of a polyacrylate radical with oxygen is extremely rapid (T7), but the terminal peroxyl radical produced reacts slowly with monomer (T8) and is more prone to termination (T9). The overall effect of oxygen is to slow the rate of reaction and reduce polymer chain length.

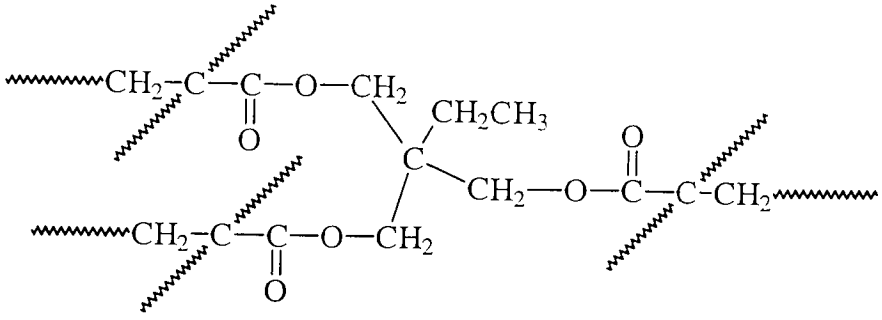
An additional factor during polymerisation of even mono-functional acrylates is the ease of cross-linked network formation. This is due to labile hydrogen abstraction (T10) preceeding branch growth at alpha-carbon sites (T11), and termination by combination with other TRIS macro-radicals (T12).[150]

Scheme 4.3 **Polymerisation of triacrylate monomer.**



For the trifunctional acrylate used in the present study (TRIS), network formation would be expected to be even more extensive, with every pendant acrylate group capable of initiation and reaction, providing the possibility of cross-links between many other polyTRIS chains (**XVIII**).

XVIII

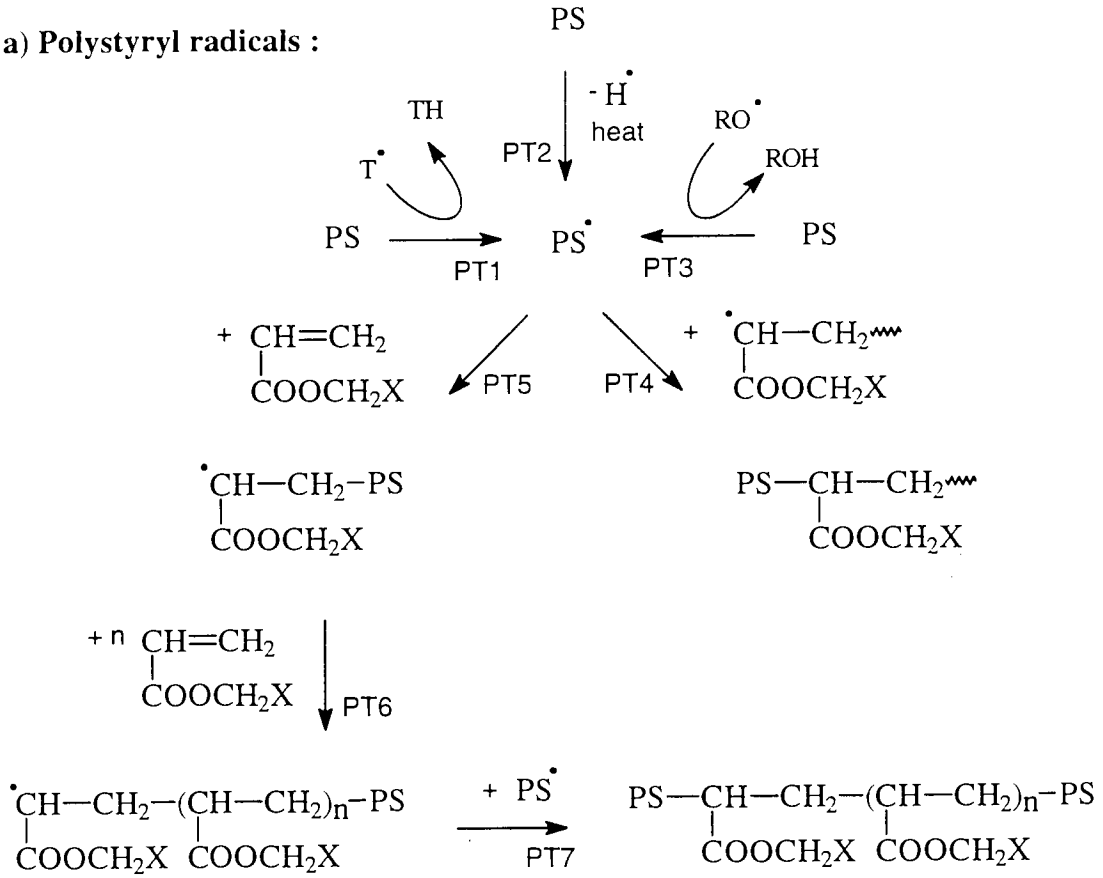


Reaction of TRIS interlinking agent with PS may at first seem to be a non-starter because of the lack of any reactive centre in the PS, however once polystyryl radicals (PS^*) are initiated greater opportunities arise. This may be by tertiary hydrogen abstraction from a polystyrene chain to a terminating polyacrylate radical (PT1 - Scheme 4.4), by oxygen-catalysed thermal scission (PT2) or, with greater effectiveness, if peroxide radical initiators are present (PT3). The reactive PS^* may then combine with a polyacrylate radical, producing grafting of the acrylate chain or network to the host polymer (PT4). PS^* may also attack unsaturation in acrylate monomer or residual unsaturation in polymerised acrylate (pendant to the main chain or network) may be attacked by PS^*, resulting in the addition of TRIS to polystyrene (PT5) and providing a radical centre on the grafted branch for further propagation of acrylate reaction (PT6) or even coupling with another polystyryl radical to produce cross-linked PS (PT7).

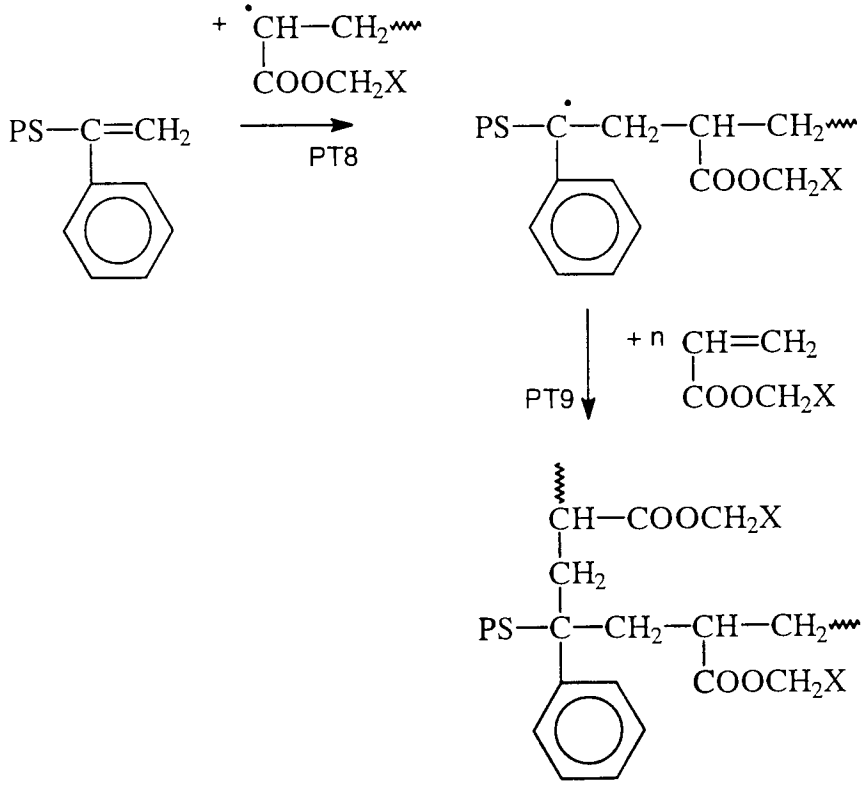
If conditions favour PS degradation, then further opportunity for polyacrylate radical addition to PS (PT8) would be created via unsaturated chain ends produced by beta-scission of PS^* and other routes (Scheme 4.2). The influence of oxygen would also be

Scheme 4.4 **Reaction of polystyrene and triacrylate monomer during reactive processing.**

a) Polystyryl radicals :



b) PS unsaturated end groups :



important since this could inhibit TRIS polymerisation and enhance PS degradation such that more frequent grafting of shorter chains or only partially polymerised networks of the interlinking agent might be encouraged.

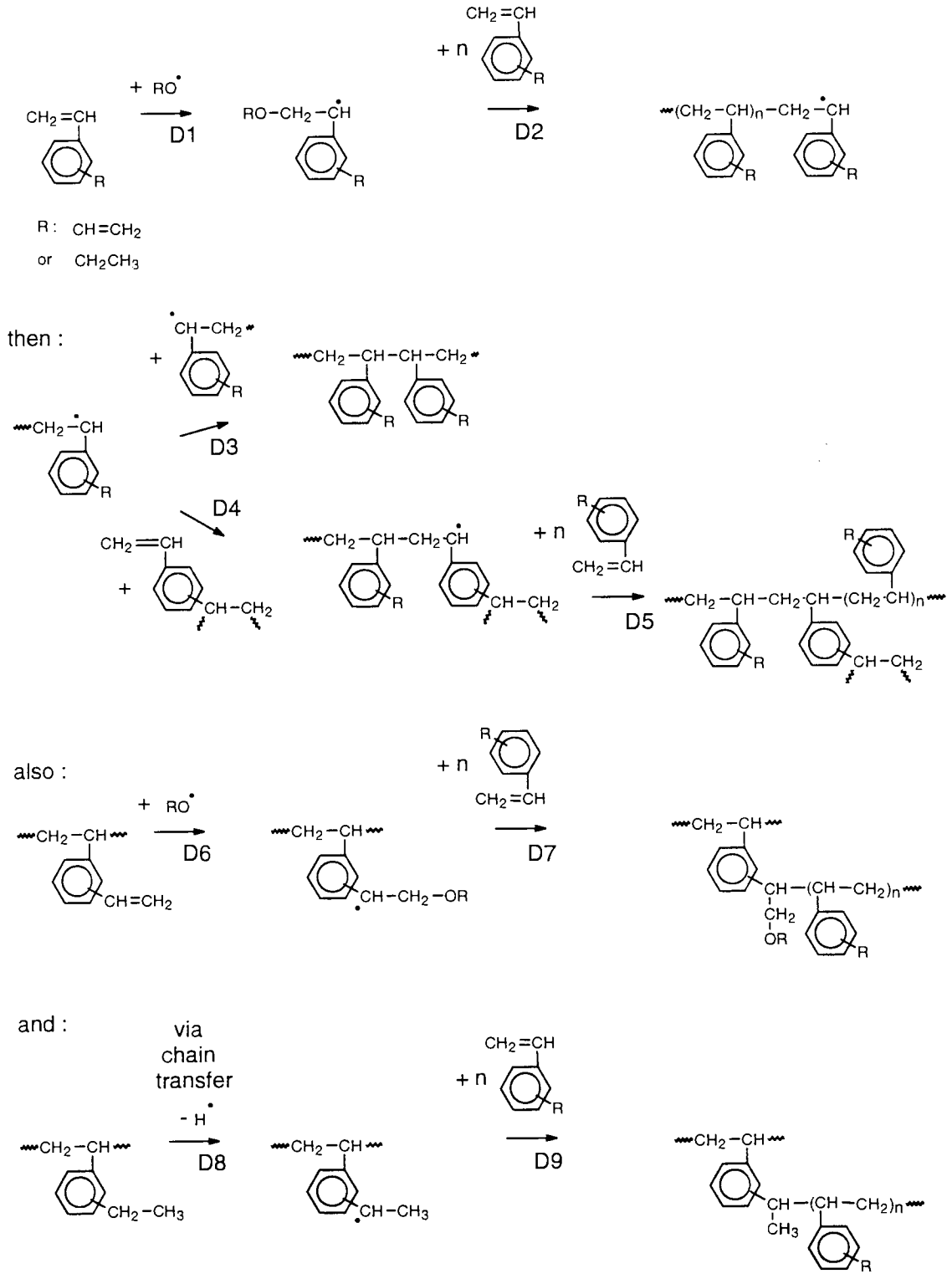
There is thus a strong potential for the modification of PS by TRIS through several reaction pathways to several possible products. Due to the high reactivity of the three functionalities within TRIS, grafting of linear or lightly branched chains to the PS host, although a desirable modification, may not be preferred ; TRIS cross-linking may predominate. Polystyrene reaction is certainly reliant upon the generation of reactive radical sites and thus may be the limiting factor. Therefore perhaps the final outcome arises from the relative degree of initiation within each component, which may be influenced by the choice of processing strategy. It was hoped that examination of torque behaviour and product analysis would confirm this thesis (Section 4.3.2).

4.3.1.3 Polymerisation of Divinylbenzene Interlinking Agent (DVB) and Possible Reactions With Polystyrene.

Divinylbenzene homopolymerises and copolymerises by the free radical chain reaction mechanism common to other substituted vinyl monomers (Scheme 4.5). The principle reaction pathways would be expected to be similar to those for styrene monomer, though because of the two vinyl groups in DVB, resulting polymer is cross-linked.[82] Furthermore, some account must also be made of the major amount of ethylvinylbenzene (45%) present in the technical grade of DVB used.

Styrene monomer is capable of thermal self-initiation, generating sufficient radicals for the propagation of an accelerating chain reaction to high molecular weight polymer.[82] Organic peroxides are particularly effective radical initiators, by addition to the vinyl group (D1 : Scheme 4.5), generating stable benzylic radicals. These allow predominantly

Scheme 4.5 **Polymerisation of divinylbenzene monomer.**



head-to-tail addition of monomer to the radical as linear polymer readily propagates (D2). The principal mode of termination has been shown to be by combination (D3) rather than disproportionation ; there being scant evidence for the latter even at temperatures above 80°C.[82]

With the introduction of a second vinyl group off the phenyl ring (R : $CH{=}CH_2$), cross-linking may follow by addition to a pendant vinyl from another chain (D4). Continued growth by addition of monomer (D5), produces extended branch or highly networked structures. Long chain branching may also be produced by initiation of pendant vinyl groups (D6) and propagation by subsequent monomer addition (D7). Although not effective in styrene polymerisation, chain transfer can be quite significant for substituted styrenics.[82] For the ethyl substituents (R : CH_2CH_3) in the ethylvinyl benzene fraction of the "technical" DVB used, abstraction of methylene hydrogen may thus occur by reaction with a radical centre on another molecule (D8). Further addition of monomer (D9), pendant vinyl groups or combination with other polymeric radicals may follow, generating branched and cross-linked networks.

Possible PS/DVB reactions (Scheme 4.6) would be very similar to those for PS/TRIS (Scheme 4.4) and again hinge on the in-situ generation of reactive centres in the polystyrene, namely polystyryl radicals and unsaturated chain ends via PS degradation (Scheme 4.2). PS/DVB reaction could then follow by :

☺ PS^* combination with DVB^* (PD1 - Scheme 4.6) ;

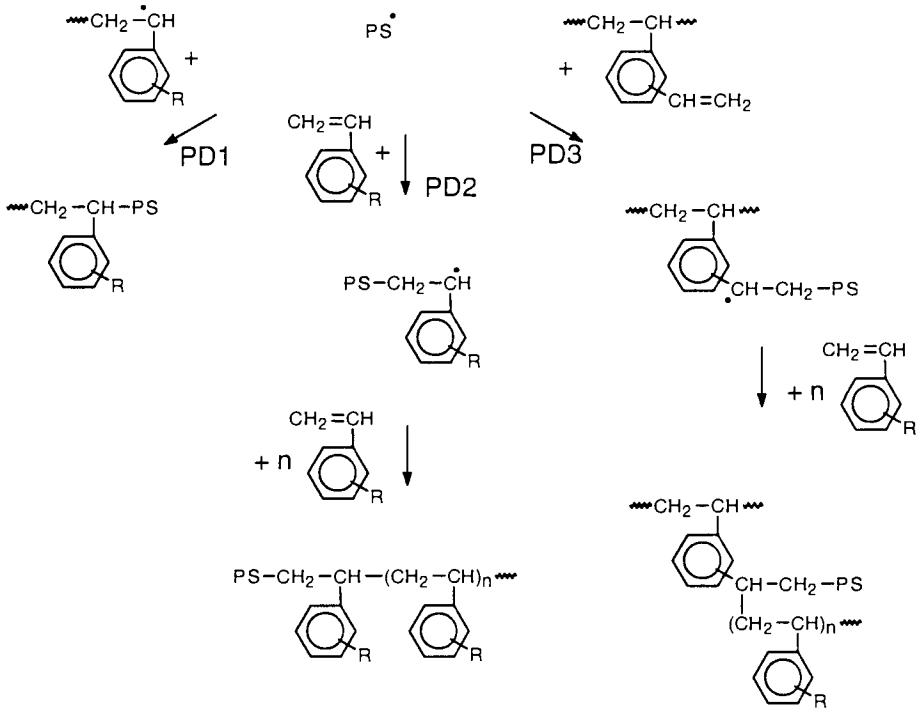
☺ addition of PS^* to vinyl centres in DVB monomer (PD2) or pendant vinyl groups in partially polymerised DVB (PD3) ;

☺ addition of DVB^* to PS unsaturated chain ends (PD4).

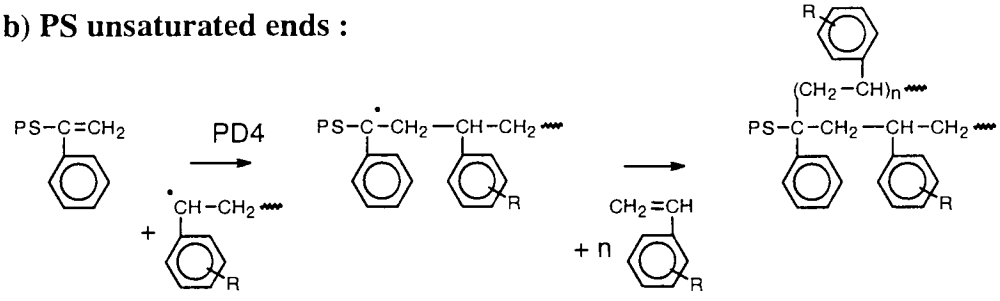
DVB becomes highly branched and cross-linked on polymerisation, thus PS modified by grafted DVB networks may be the most likely outcome, with some long range PS cross-linking via different segments of the DVB network also possible.

Scheme 4.6 Reaction of polystyrene and DVB during reactive processing.

a) Polystyryl radicals :



b) PS unsaturated ends :



4.3.2 Influence of Key Process Parameters on the Outcome of Polystyrene Reactive Processing With TRIS and DVB.

It was recognised that torque changes experienced during the reactive processing of PS with TRIS or DVB interlinking agents gave some insight to the ongoing chemical changes in the mixtures. Reaction between the PS and either reactive agent was believed possible, but competitive with TRIS or DVB polymerisation, especially in the presence of initiator, resulting in extensive cross-linking of the multi-functional monomers. The influence of controlling process parameters on the balance between the desired PS modification and competitive interlinking agent self polymerisation was thus critical. This was indicated by direct comparison of the torque and product characteristics of key compositions and confirmed by the analysis of highlighted process cells.

From the process data two functions were derived to quantify the torque behaviour of all samples. Peak and final torques were normalised for differences in the absolute position of torque curves arising during the initial mixing period by subtraction of the internal reference torque (T_3 - the 3 minute value : Figure 3.9) for each cell ;

$$\mathbf{dT_p = T_p - T_3} \quad \text{and} \quad \mathbf{dT_{10} = T_{10} - T_3} \quad \text{(Nm)}$$

where dT_p - peak torque (T_p) less the T_3 reference,

dT_{10} - final torque (T_{10}) less the T_3 reference,

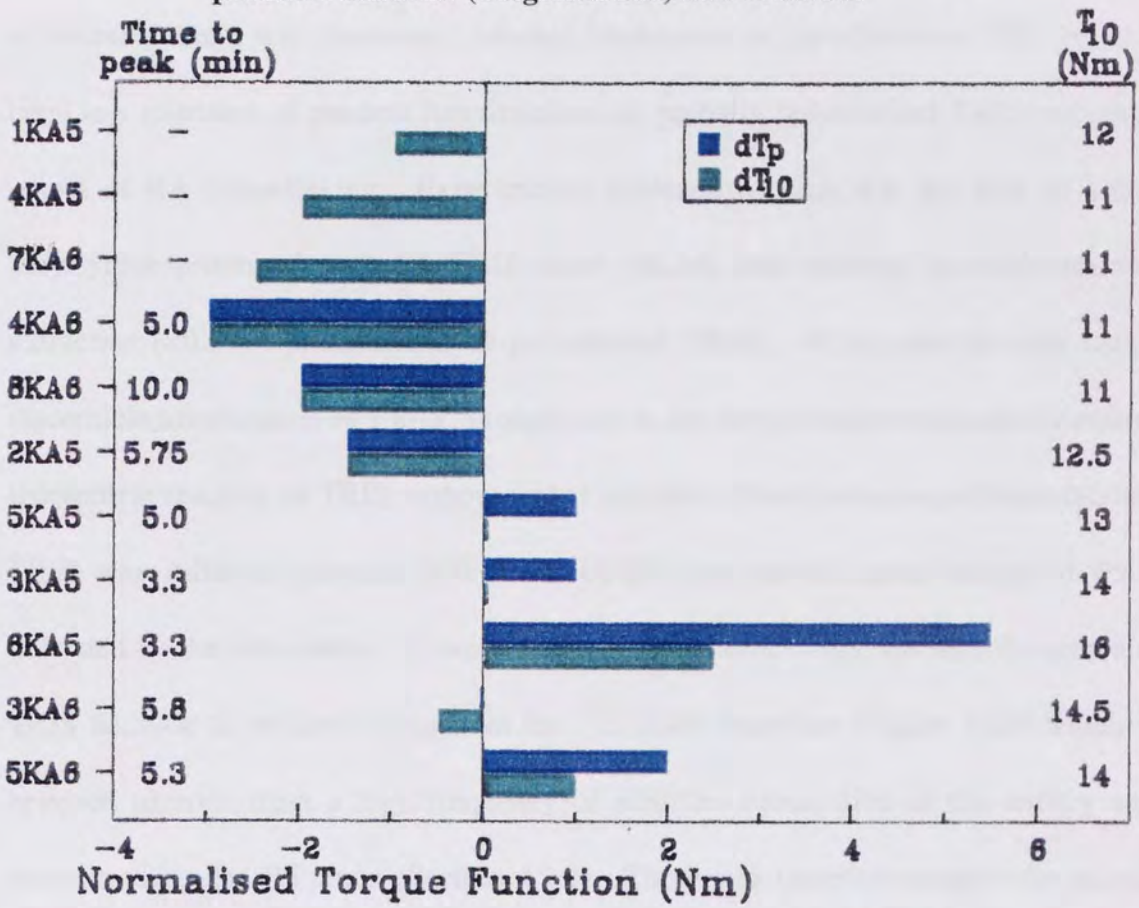
By comparison of these functions, the significance of different approaches and control parameters became apparent (Figures 4.32 and 4.33). It was found that all reactive agent additions gave an immediate, large torque drop followed by a variable increase ; rate of rise, extent and final outcome all depended on the choice of RA, addition level and initiator concentration (Section 4.2.1 and 4.2.2). Initiator pre-addition also had an important influence on the TRIS modification of PS.

4.3.2.1 Triacrylate Interlinking Agent (TRIS).

Although increasing TRIS addition gave higher torque rises, as shown by the dT_p and dT_{10} functions (Figure 4.32 - 5 & 10% additions at zero, 0.001 and 0.01 FRI:RA molar ratios), increased modification effectiveness was not suggested. Torque gains above reference points and clearly above control curves were only achieved from the higher TRIS additions (10% with FRI present) coupled with an adverse effect on product quality ; becoming opaque, rather than transparent, and loaded with solid particles. Solids were consistent with the formation of polymerised TRIS, separating from the PS phase due to inherent incompatibility and extensive cross-linking. The presence of these particles may indeed have been a contributory factor in the torque increases realised in these cells, having a similar effect to the action of fillers where just minor concentrations (<2%) can cause upwards of 10% increase in melt viscosity.[135,137] There was thus no benefit in raising the addition level of interlinking agent since this appeared to shift the balance between polymer modification and reactive agent polymerisation towards an undesirable outcome.

The behaviour of high and low TRIS without FRI was important ; there was some rise from minimum torque after addition, which for 5% TRIS ended below the reference points and controls (4KA6 - Figure 4.2a and by dT_p & dT_{10} - Figure 4.32). This could be explained by limited reaction of TRIS only partially negating the lubricating action of fluid reagent (Section 3.3.2). This was evident as a minor plasticisation effect of free TRIS, shown by a reduced PS Tg in the as-processed portion only. At 10% TRIS without FRI, torque rise was slower, but did continue until the end of mixing, still finishing lower than control and reference levels (8KA6 - Figure 4.2b). Both cells suggested that reaction of TRIS occurred during processing with PS in the absence of FRI, presumably due to

Figure 4.32 **Normalised torque functions and analysis for PS (H311) with TRIS additions at various FRI:RA ratios, incorporating pre-addition of peroxide initiator (Trigonox 101) and controls.**



Sample Cell	Addition package			Analysis			
	TRIS %	FRI:RA	+ FRI %	initial solids	swelling (extraction)	insoluble gel %	bound TRIS %
1KA5	nil	nil	nil	no	-	-	-
4KA5	nil	(opened)	nil	no	no	nil	-
7KA6	nil	(opened)	0.05	no	no	nil	-
4KA6	5	nil	nil	no	yes	< 0.5	52
8KA6	10	nil	nil	no	-	-	-
2KA5	5	0.001	nil	minor	yes	0.5	65
5KA5	10	0.001	nil	yes	-	-	-
3KA5	5	0.01	nil	yes	no	3.6	43
6KA5	10	0.01	nil	many	-	-	-
3KA6	5	nil	0.03	no	yes	nil	80
5KA6	5	0.001	0.05	minor	yes	< 0.5	77

thermal initiation and chain transfer propagation mechanisms (Section 4.3.1.2), at a lower rate than when catalysed by added initiator, reaction continuing slowly until all interlinking agent was consumed. Another implication of the absence of FRI would have been less initiation of pendant functionalities in partially polymerised TRIS, reducing the extent of RA cross-linking. Experimental evidence for this was the lack of solids in polystyrene processed with 5% TRIS alone (4KA6) and minimal insoluble residue on extraction (<0.5% ; presumed to be polymerised TRIS). 4KA6 was the only cell with discernible unsaturation by FT-IR, though only in the sample before extraction, confirming incomplete reaction of TRIS without added initiator. Nevertheless significant binding of TRIS was achieved (around 50% from FT-IR) and partial cross-linking of PS was indicated by the observation of swelling during extraction. This was also the only simple TRIS addition to produce changes in the ^{13}C NMR spectrum (Figure 4.26) which were believed to arise from a high frequency of modifier substitution at the tertiary carbon position along the PS chain (Section 4.2.9). There was therefore support for polystyryl radical generation by thermally produced $TRIS^{*}$, some further grafting of TRIS as fully reacted networks and cross-linking with other PS chains ; confirming reactions proposed earlier in Scheme 4.4 (Section 4.3.1.2). Furthermore, the lack of active unsaturation in PS-bound TRIS (from all cells) suggested that this modification route would not necessarily provide a reactive product suitable for a two-stage reactive blending process.

Initiator concentration had much greater influence on the outcome of interlinking agent reaction than addition level alone. At higher FRI:RA ratio the rate of torque rise was increased, peak torques were reached earlier and higher final torques were attained (as for 3KA5 in Figure 4.32). Torque rise was equated with consumption of reactive agent which firstly required sufficient initiation before self-propagating reaction commenced and was

therefore accelerated by increasing the concentration of organic initiator. For all cells with the higher FRI:RA ratio peak torque was above the reference point (dT_p positive) and final torque was equal to or higher than control and reference levels. With TRIS at this high FRI:RA ratio, products were adversely affected by heavy solids contamination, as shown by a residue on extraction of over 60% of the TRIS content for a 5% addition at 0.01 molar ratio FRI:RA (3KA5) ; indicating an extreme degree of interlinking agent polymerisation under these conditions. Binding to PS was also reduced in this case to below that without FRI (3KA5 < 4KA6) and, with the absence of swelling during extraction, there was no evidence for any PS cross-linking. Proton and ^{13}C NMR also gave no indication of any significant chemical changes in the PS. Thus the balance between desirable modification of polymer and competitive reactions was unfavourable with high initiator concentration when intimately mixed with interlinking agent. This was especially so from the most extreme TRIS addition, 10% TRIS at 0.01 FRI:RA molar ratio (6KA5) which produced the sharpest torque peak (Figure 4.2b), highest T_{10} level and dT_p & dT_{10} functions of all PS cells (Figure 4.32), but also having the most adverse appearance and coarsest solids loading. Since both cells at high FRI:RA (3KA5 & 6KA5) gave large torque increases, and TRIS polymerisation was apparently favoured, this supported the belief that the solids content contributed more to increased ultimate torque than any molecular changes arising from TRIS modification of the PS.

By consideration of the combined data in Figure 4.32, the relative proportions of PS-grafted TRIS, self-polymerised TRIS and residual "free" TRIS (soluble portion) within each key cell were estimated (Table 4.21). Appraisal of the modification of PS, for TRIS and FRI added as an intimate mixture, showed low initiator concentration (0.001 molar ratio : 2KA5) to be most effective ; grafting was increased above the value without FRI at

the expense of "free" TRIS, whilst limiting solids content and torque during processing to acceptable levels. Indeed 2KA5 was the only case in which the characteristics of TRIS could be positively identified in a proton NMR spectrum (Figure 4.20). With a tenfold rise in FRI:RA ratio (3KA5) modification effectiveness was reduced due to predominance of TRIS polymerisation, yielding phase-separated, solid particles, presumably fully cross-linked TRIS (see **XVIII** - page 194). Considering 25% of the TRIS in 2KA5 to be unreacted, it was thought that perhaps a slightly higher initiator concentration (x 2-3) may have given a little more TRIS binding, without too adverse an effect on self-polymerisation, though this would have been "fine-tuning" rather than the broader approach adopted in this work. Thus, in conclusion, 5% TRIS at 0.001 FRI:RA molar ratio was considered to be the best effort combined addition for PS modification.

Table 4.21 **The influence of initiator concentration and pre-addition on the outcome of polystyrene reactive processing with 5% TRIS interlinking agent (from the data in Figure 4.25).**

				+ FRI pre-addition	
Outcome	nil FRI with TRIS (4KA6)	low FRI:RA with TRIS (2KA5)	high FRI:RA with TRIS (3KA5)	nil FRI with TRIS (3KA6)	low FRI:RA with TRIS (5KA6)
TRIS grafting to PS	50 %	65 %	40 %	80 %	75 %
TRIS self-polymerisation	< 10 %	10 %	> 60 %	NIL	< 10%
"free" TRIS	> 40 %	25 %	NIL	20 %	15 %
PS cross-linking	yes	yes	NO	yes	yes

The effect of initiator pre-addition on the modification of PS was clearly beneficial (Table 4.21). Grafting was significantly raised to 80% for direct addition of TRIS alone (3KA6), without any self-polymerisation. Additional bands were found in the ^{13}C NMR spectrum (Figure 4.28 & Table 4.19), suggesting a high frequency of graft sites along the PS backbone. Torque for 3KA6 increased over PS controls and TRIS alone without any FRI (4KA6, Figure 4.3b), but did not rise above the T_3 internal reference, as shown by dT_p & dT_{10} torque functions (Figure 4.32). However, TRIS with an optimum FRI:RA ratio added to FRI-pre-treated PS (5KA6) did give peak and final torques above reference and controls, though with some solids present. In this formulation, total TRIS grafting was improved over the same addition without pre-treatment (2KA5), but competitive interlinking agent polymerisation, although reduced, was still appreciable. Furthermore in 5KA6, ^{13}C NMR was not indicative of a multiplicity of graft sites (no additional aromatic C bands - Section 4.2.9), supporting chain gowth of TRIS from occasional PS graft sites. Partial cross-linking was shown in this case from swelling during extraction analysis and possibly from a near four degree rise in PS Tg (the highest found - Section 4.2.10). Therefore initiator pre-addition was believed to target the generation of PS macro-radicals directly for addition to reactive unsaturation in TRIS, followed by side chain growth from monomer addition. This was preferable to generation of TRIS* when intimate with initiator, which was believed to cause substantial polymerisation of the TRIS (Scheme 4.3). Even for pre-initiated PS with combined TRIS & FRI addition (5KA6), this latter process was still effective. Thus, the best overall outcome of all cells was achieved from FRI pre-addition to PS and 5% TRIS addition without any further initiator (3KA6).

The benefit of this novel concept of targeting PS radical formation for reactive modification and overcoming interlinking agent polymerisation was graphically realised by considering possible molecular structures of the products and apportioning relative

yields according to key PS/TRIS process formulations (Scheme 4.7). It was thought that the frequency of TRIS grafting to the PS, the degree of TRIS polymerisation and level of PS cross-linking were all influenced by the process conditions, according to the amount and predominant target of initiation ;

i. - at minor TRIS initiation (4KA6 - no FRI), self-polymerisation was very limited, suggesting that grafted side-chains would be short (n1 low - Route A : Scheme 4.7), but could cause partial PS cross-linking (y1). Frequent graft sites (m1 high) were indicated by ^{13}C NMR (Figure 4.26), even with PS initiation reliant on low TRIS* concentration.

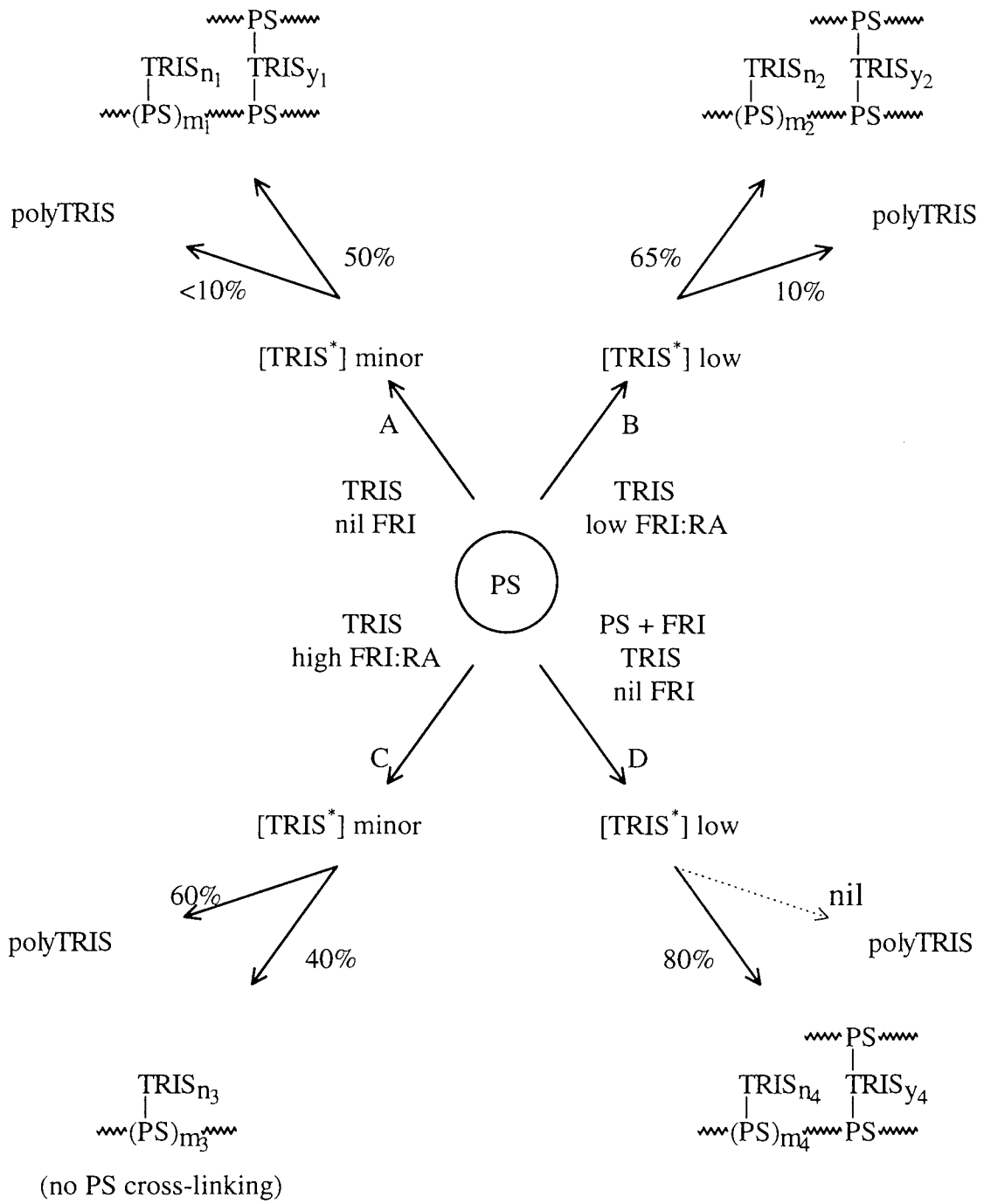
ii. - at intermediate TRIS initiation (2KA5 - low FRI:RA), polyTRIS formation was not high, but graft size must have been raised (n2>n1 - Route B : Scheme 4.7) since a higher total binding level (65% by FT-IR) was found at a lower PS graft frequency (m2<m1), according to an unmodified ^{13}C NMR spectrum.

iii. - TRIS polymerisation was excessive at high initiator levels (3KA5), such that total binding was reduced (50%), of infrequently grafted (m3 low), extensive and fully saturated TRIS networks (n3 high - Route C: Scheme 4.7), which prevented PS cross-linking.

iv. - by targetting PS* directly (3KA6 - TRIS with no FRI, +FRI to PS), TRIS binding exceeded all other cells (80%) and was achieved with zero TRIS polymerisation in the absence of initimate FRI. The product of this winning formulation was believed to have a high graft frequency (from ^{13}C NMR, Figure 4.28) of possibly short TRIS side chains (m4 high, n4 low - Route D : Scheme 4.7), which again did not preclude PS cross-linking.

More complete analysis of these modified products to better quantify graft frequency and modifier chain length (m and n) would be a further step forward to improve understanding of the proposed mechanisms ongoing during reactive processing and thus aid further enhancement of modification effectiveness.

Scheme 4.7 **Relative proportions and possible molecular structures of products from PS/TRIS reactive processing under different conditions.**



$m4 > m1 > m2 > m3$?

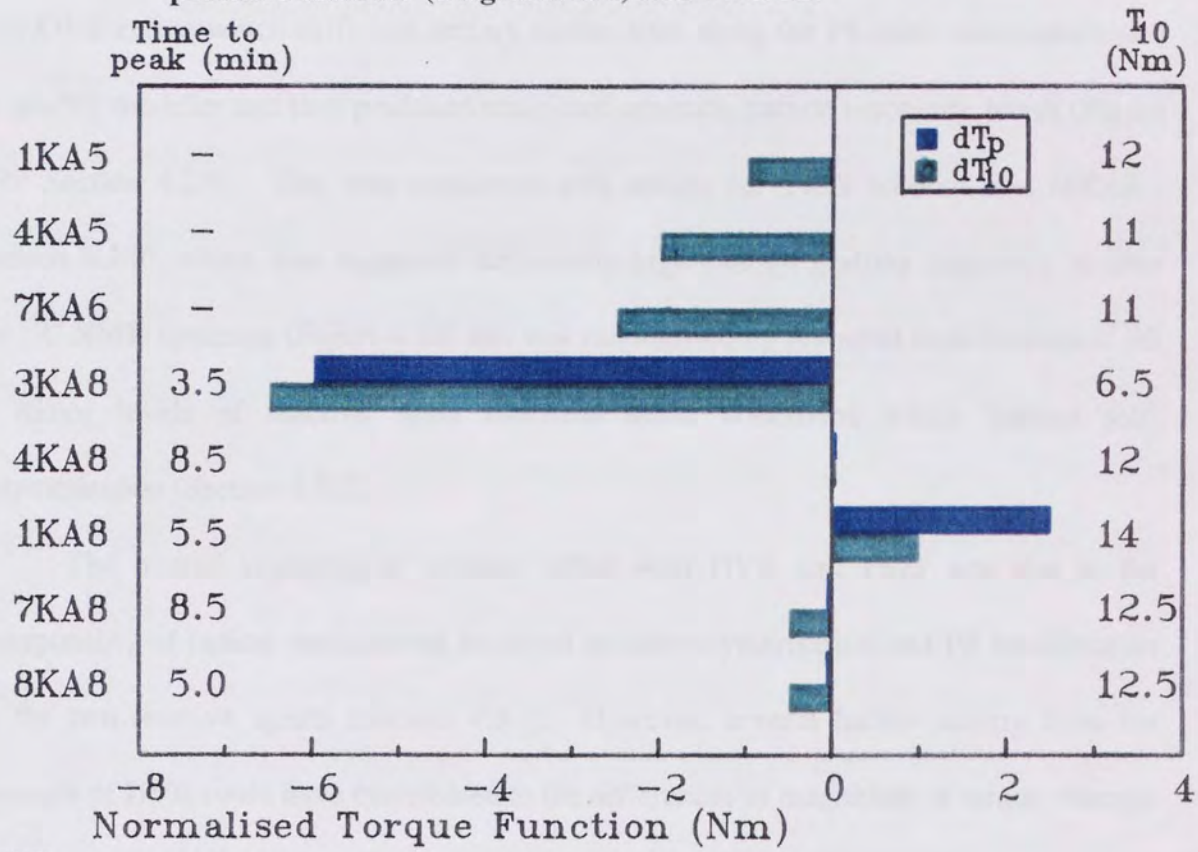
$n3 >> n2 > n1 \approx n4$?

4.3.2.2 Divinylbenzene Interlinking Agent (DVB).

The behaviour of DVB in reactive processing with PS was on the whole similar to TRIS though there were contrasting differences in the magnitude of some effects and particular reaction outcomes. Increasing initiator concentration produced the same trend as with TRIS (Section 4.3.2.1) ; rate of torque rise, torque maximum and final torque were all raised, as shown by dT_p & dT_{10} in Figure 4.33. At the highest FRI:RA ratio (1KA8) torque increased significantly above controls (Figure 4.4 & 4.33) and was the only case to do so without any obvious solids formation or adverse effect on appearance. Extraction analysis indicated that this high torque was achieved without substantial cross-linking of the PS (no swelling observed), though a significant rise in PS Tg was found for this cell (Section 4.2.10). A minor residue on extraction (0.5%), presumably of fully networked DVB, may have contributed to both increases in torque and Tg of the as-processed composition. This insoluble fraction was equivalent to only 10% of the DVB addition and was considerably lower than for TRIS at the same initiator concentration (3KA5 : Table 4.11 - 3.6% residue = 60% of added TRIS).

Torque rise was much slower at the lower initiator concentration, but did ultimately reach control and reference levels (4KA8, Figure 4.4). However, unlike TRIS (4KA6, Figure 4.2a), DVB without FRI (3KA8) gave only slight torque rise before remaining at a stable level well below reference point and controls (Figure 4.4 & 4.33) ; final torque was approximately 50% of control PS. Thus without initiator, DVB modification of PS did not appear favourable ; a major portion of the fluid reactive agent was unreacted and remained as an exceptionally effective plasticiser to the PS (Section 3.3.2), as confirmed by the 20°C drop in whole fraction Tg which was not evident post-extraction (Section 4.2.10). This was further substantiated by FT-IR analysis, 3KA8 being

Figure 4.33 **Normalised torque functions and analysis for PS (H311) with DVB additions at various FRI:RA ratios, incorporating pre-addition of peroxide initiator (Trigonox 101) and controls.**



KEY

Sample Cell	Addition package			Analysis		
	DVB %	FRI:RA	+ FRI %	initial solids	swelling (extraction)	insoluble gel %
1KA5	nil	nil	nil	no	-	-
4KA5	nil	(opened)	nil	no	no	nil
7KA6	nil	(opened)	0.05	no	no	nil
3KA8	5	nil	nil	no	no	nil
4KA8	5	0.001	nil	no	-	-
1KA8	5	0.01	nil	no	no	0.5
7KA8	5	nil	0.07	no	-	-
8KA8	5	0.01	0.05	no	no	0.5

the only cell to show unsaturation before extraction and only minimal bound DVB after extraction (Figure 4.29 & Table 4.19). However ^{13}C NMR indicated that 3KA8 was the only DVB cell in which sufficient tertiary carbon sites along the PS chain were substituted by grafted modifier and thus produced additional aromatic carbon resonance bands (Figure 4.29 Section 4.2.9). This was consistent with results for TRIS without FRI (4KA6 : Section 4.2.9), which also suggested sufficiently high enough grafting frequency to alter the ^{13}C NMR spectrum (Figure 4.26) and was rationalised by favoured modification of PS at minor levels of reactive agent initiation under conditions which limited self-polymerisation (Section 4.3.2).

The overall similarity of initiator effect with DVB and TRIS was due to the commonality of radical mechanisms involved in self-polymerisation and PS modification by the two reactive agents (Section 4.3.1). However, several factors arising from the structure of DVB could have contributed to the differences in magnitude of torque changes and reaction outcome for PS/DVB.

The reactivity of DVB^* was thought to be lower than that of $TRIS^*$ possibly because of stabilisation by transfer of the radical centre around the associated benzene ring. Coupled with certain DVB miscibility in PS from their inherent chemical similarity, there was perhaps increased probability of PS^* initiation by the more stable DVB radical for which the timescale and chemical environment for molecular diffusion were more favourable. Subsequent reaction of PS^* with DVB (Scheme 4.6) may have thus been encouraged, by improving the balance between modifier-polymer reaction and modifier self-reaction.

The cross-link density of DVB was reduced compared to the trifunctional TRIS, especially considering the only partial difunctionality of the DVB/EVB mixture used (even allowing for possible reaction of ethyl substituents - D8, Scheme 4.5). This would result

in polymerised DVB being less extensively networked and remaining at least partially miscible with the PS phase. Hence the limited solids content of PS/DVB cells. This was unlike the considerable second phase arising from extensive networking on full polymerisation of the triacrylate reactive agent. As polymerising DVB was likely to have remained within the major polymer phase, molecular entanglement or reaction with other PS chains was probable ; both effects capable of yielding the torque rises and increased PS Tg above control levels experienced for DVB at high initiator concentration (1KA8 - Figure 4.33 and Section 4.2.10).

The use of initiator pre-addition was apparantly not as advantageous for DVB as had been found for TRIS (Section 4.3.2.1). The total recovery of torque to control levels for an addition of DVB alone to FRI-treated PS, compared to the low non-recovered torque without initiator (7KA8 vs 3KA8 - Figure 4.5 & 4.33), was an indication of much enhanced DVB reaction presumably via peroxide-initiated PS^{*}. However with FRI included at the DVB addition, initiator pre-treatment reduced the most considerable torque gains of this otherwise top performing formulation to the control level (8KA8 vs 1KA8 - Figure 4.5 & 4.33). In both cases DSC analysis of whole compositions showed the PS Tg's to be raised above the control level and although the difference between the two cells was probably not truly significant as the PS Tg of 8KA8 was lower than that of 1KA8 (+2.7 vs +3.2 vs 4KA5 control ; Section 4.2.10), correlating with the pattern of torque changes. This torque deficiency, when modifier grafting was assumed to be at least maintained, or even increased as with FRI pre-addition for TRIS (Section 4.3.2.1), may have resulted from partial plasticisation during processing by unreacted DVB or from structural changes in the modified PS product. The latter could have arisen by reduced PS molecular weight from a higher degree of radical initiated degradative chain scission, less extensive cross-linking via limited DVB networks or a greater frequency of grafting sites

along the PS chains, having the consequence of shorter graft chains and reducing molecular entanglements, thus effecting torque viscosity. ^{13}C NMR did not in this case suggest graft frequency to be high (Section 4.2.9). The only support for any of these outcomes was the absence of cross-linking from swelling-free dissolution during extraction.

In the absence of DVB binding data from the preferred FT-IR method (Section 4.2.8) and with the only tentative indication of DVB grafting arising from a possible increased contribution from aromatic protons in the NMR spectrum of 8KA8 precipitate "P" fraction (Figure 4.22 & Table 4.18), the results of product analysis were considered insufficient to confirm with any great confidence PS reaction or quantify modification effectiveness for the DVB interlinking agent. Although plausible models for process behaviour could be proposed, it was perhaps ironic that because of the similar chemical nature of PS and DVB which was believed to enhance cross-reaction of the two, it was not possible to quantify DVB grafting by the spectroscopic techniques employed. Further investigations to identify suitable methods for the assessment of PS modification, particularly with chemically related reactive agents such as DVB, would be required for the development and optimisation of the possibilities suggested in this study.

CHAPTER 5.

OPTIMISATION OF POLYSTYRENE / EPDM REACTIVE BLENDING USING INTERLINKING AGENTS AND ANALYSIS OF MODIFICATION EFFECTS.

5.1 OBJECTIVES AND METHODOLOGY.

This phase of the research programme focused on the melt mixing of polystyrene and EPDM elastomer with the simultaneous application of the experimental reactive processing technique and the subsequent analysis of blends to optimise and determine the degree and effects of modification. It was the intention to target free-radical initiated reaction of both polymers with polymerisable interlinking agents using principles developed in the earlier work, to induce in-situ formation of interpolymer product for effective compatibilisation of otherwise immiscible blends. It was not expected, nor required, that a homogeneous alloy-like compound be produced by this route, but that the interfacial miscibility of the two dissimilar polymeric components be raised to provide advantages associated with "technologically compatibilised" multiphase blends.[32] It was hoped that improved performance could be equated with the degree of successful chemical modification in reactively processed PS/EPDM blends.

Optimisation of PS/EPDM reactive blending was based on the learnings of the initial blending investigations (Chapter 3) and especially from the extended study of PS modification (Chapter 4) since it was believed that unlocking the reaction of an essentially inert PS component was the key to effective blend modification. The dependence of reaction outcome upon initiator concentration was examined in 70/30 PS/EPDM blends at 5% TRIS additions, and also with the divinylbenzene (DVB) interlinking agent. Separation of initiator and reactive agent addition, shown to aid PS-TRIS reaction (Section 4.3.2), was also evaluated with both modifiers. Another approach attempted was the use of a mixed TRIS & DVB addition package at optimum initiator concentrations to target

favoured PS-DVB and EPDM-TRIS reactions and hence promote interpolymer formation via co-reaction of grafted modifiers. The general experimental procedure for processing and analysis were as detailed in Scheme 5.1 and all samples processed given in Table 5.1.

From processing investigations, key PS/EPDM blends and controls were selected for analysis of the physical and chemical effects of interlinking agent modification. Sheets of thin film (around 0.6mm thick) were prepared from each blend by compression moulding, after developing a method of pressing using card templates to ensure that film thickness was sufficiently even to provide samples for physical testing. A tensile test method in general agreement with ASTM D 882-83 (Tensile Properties of Thin Plastic Sheeting) was developed, using an Instron Test Station to measure tensile properties to failure of all film samples. Scanning electron microscopy of fracture surfaces from tensile testing was used for examination of blend morphology for a visual indication of the degree of compatibility between phases.

Sequential Soxhlet extraction was carried out on samples of pressed film, firstly with dichloromethane to determine the quantity of "free" PS and then toluene for "free" EPDM from the same specimen. Residual insoluble gel was assayed and from the proportions of each soluble component, gel composition was estimated to indicate the target of reactive modification and likelihood of interpolymer formation. In an attempt to confirm chemical composition FT-IR was carried out on very thin films of entire blend and extraction residue fractions, and assessment made of the differentiation of IR absorption peaks from functional centres in PS, EPDM and reactive agent components. As a further proof of reactive blend modification thermal analysis of selected blends and residue fractions was made by DSC, which was found to be a suitable technique for precise measurement of PS and EPDM component glass transitions.

Combination of the results of these simple analyses, indications from processing behaviour, and support from the knowledge of component reaction outcomes (Chapter 4), allowed important concepts in the application of interlinking agents for the reactive processing of polymer blends to be realised. Furthermore, by the correlation of compatibility levels with physical properties and reaction outcome, an understanding of the factors involved in determining the bulk performance of reactively compatibilised blends was developed.

Table 5.1 **Reference List of Samples for the Optimisation of PS/EPDM Reactive Processing Using TRIS and DVB Interlinking Agents With Organic Peroxide Free Radical Initiator (Trigonox101).**

Sample Cell	Method[1]	Rotor Speed rpm	PS[2] % w/w	EPDM[3] % w/w	RA type	RA % w/w	FRI:RA molar ratio	+ FRI % w/w
1KA7	PB	60	70	30	none	nil	nil	nil
2KA7	DA	60	70	30	TRIS	5.0	0.001	nil
3KA7	DA	60	70	30	TRIS	5.0	0.01	nil
4KA7	DA	60	70	30	TRIS	5.0	nil	nil
5KA7	C	60	70	30	none	(opened)	nil	nil
2KA8	DA	60	70	30	DVB	5.0	0.01	nil
5KA8	DA	60	70	30	DVB	5.0	0.001	nil
9KA8	DA	60	70	30	DVB	5.0	nil	nil
1KA10	C	60	70	30	none	nil	0.05	0.05
2KA10	DA	60	70	30	TRIS	5.0	0.001	0.07
3KA10	DA	60	70	30	DVB	5.0	0.01	0.07
6KA10	DA	60	70	30	TRIS + DVB	2.5 + 2.5	0.001 0.01	nil
7KA10	DA	60	70	30	TRIS + DVB	2.5 + 2.5	0.001 0.01	0.06

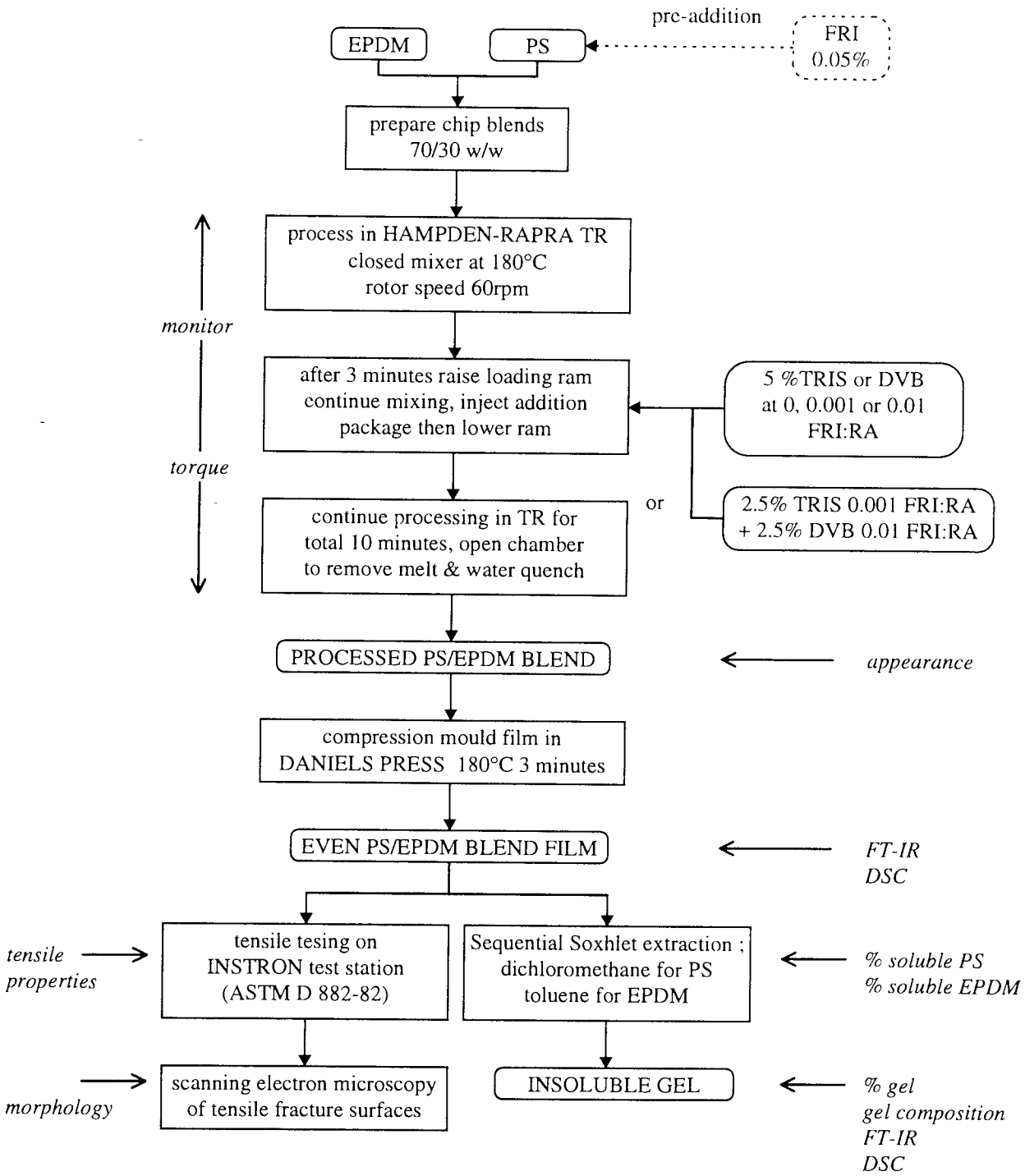
Notes :

1 : PB = physical blend (Scheme 2.1 - page 82)
DA = RA direct addition (Scheme 2.3 - page 84)
C = control

2 : PS grade ; Huntsman Crystal Polystyrene Grade 311

3 : EPDM grade ; Vistalon 2504

Scheme 5.1 **General Experimental Procedure for the Optimisation of PS/EPDM Reactive Processing with TRIS and DVB Interlinking Agents and Analysis of Key Compositions.**



5.2 RESULTS.

5.2.1 Optimisation of PS/EPDM Reactive Blending using TRIS and DVB Interlinking Agents.

In this phase of the investigation, the PS component used in all the blends was Huntsman Crystal PS (H311), rather than Dow Styron as in the initial work (Chapter 3) ; behaviour of the two grades in blends with EPDM (EXXON Vistalon 2504 - V2504) was however found to be equivalent. Nevertheless relevant control cells were processed using the second grade of PS to ensure direct comparison of test and control cells.

5.2.1.1 Effect of Initiator Concentration With TRIS Addition.

The effect of FRI:RA ratio with a 5% direct addition of TRIS was examined in a series of 70/30 PS/EPDM blends processed under standard conditions (Scheme 2.3). The pattern and outcome of torque changes was found to be greatly influenced by initiator concentration (Table 5.2 & Figure 5.1). For all TRIS additions, torque recovered after injection to levels above their three-minute reference points (T_3), and remained above the control curves (1KA7 & 5KA7) for the remainder of the mixing period. The rate of torque rise after TRIS addition was higher with increasing FRI:RA ratio. However, the highest torque peak and final torque was surprisingly from the intermediate (2KA7), rather than the highest (3KA7), FRI:RA ratio. The product at this ratio was opaque white, hard and free from any obvious inhomogeneities; unlike at the high FRI:RA ratio (3KA7) which yielded a hard off-white mass containing some quite large solid particulates.

5.2.1.2 Effect of Initiator Concentration With DVB Addition.

A series of cells for a 5% addition of DVB at different FRI:RA ratios were similarly processed to assess the effect of initiator concentration (Table 5.2). The rate of post-addition torque rise was again found to increase with FRI:RA ratio (Figure 5.2). Without any initiator (9KA8) torque after addition was not recovered, rising only slightly from the

minimum and remaining well below controls (1KA7 & 5KA7) to the end of the mixing cycle. Intermediate FRI:RA (5KA8) produced a steady torque rise to slowly reach a level equal to the T_3 torque, above control levels, and was maintained to the end of mixing. At the highest initiator concentration (2KA8) the most rapid torque rise, highest peak value and final level were all achieved ; T_{10} torque was well above the controls and other DVB additions. No adverse effects on the quality of product appearance, nor particulate contamination, were found with any DVB addition, even at the highest initiator content.

Table 5.2 **Compositions and torque behaviour of 70/30 PS (H311)/EPDM (V2504) blends reactively processed with nominally 5% TRIS or DVB additions at different FRI:RA ratios and controls processed under standard conditions.**

		Composition			Torque Behaviour			
Sample Cell	RA type	RA & FRI target (% w/w)	RA & FRI actual (% w/w)	FRI:RA molar ratio	T_3 (Nm)	Peak (Nm)	Peak (min)	T_{10} (Nm)
1KA7	none	nil		nil	13	none		12
5KA7	none	nil	(opened)	nil	12	12	3.5	11
4KA7	TRIS	5.0	4.99	nil	13	14	5.5	14
2KA7	TRIS	5.0	4.91	0.001	13.5	17	5.25	16
3KA7	TRIS	5.0	5.02	0.01	12	16	4.75	14
9KA8	DVB	5.0	5.49	nil	12	7	3.5	7
5KA8	DVB	5.0	5.49	0.001	14	14	6.25	14
2KA8	DVB	5.0	5.20	0.01	14	18	5.25	16.5

Figure 5.1 **Torque behaviour of 70/30 PS/EPDM reactively processed blends with 5% TRIS additions at different FRI:RA molar ratios and controls processed under standard conditions.**

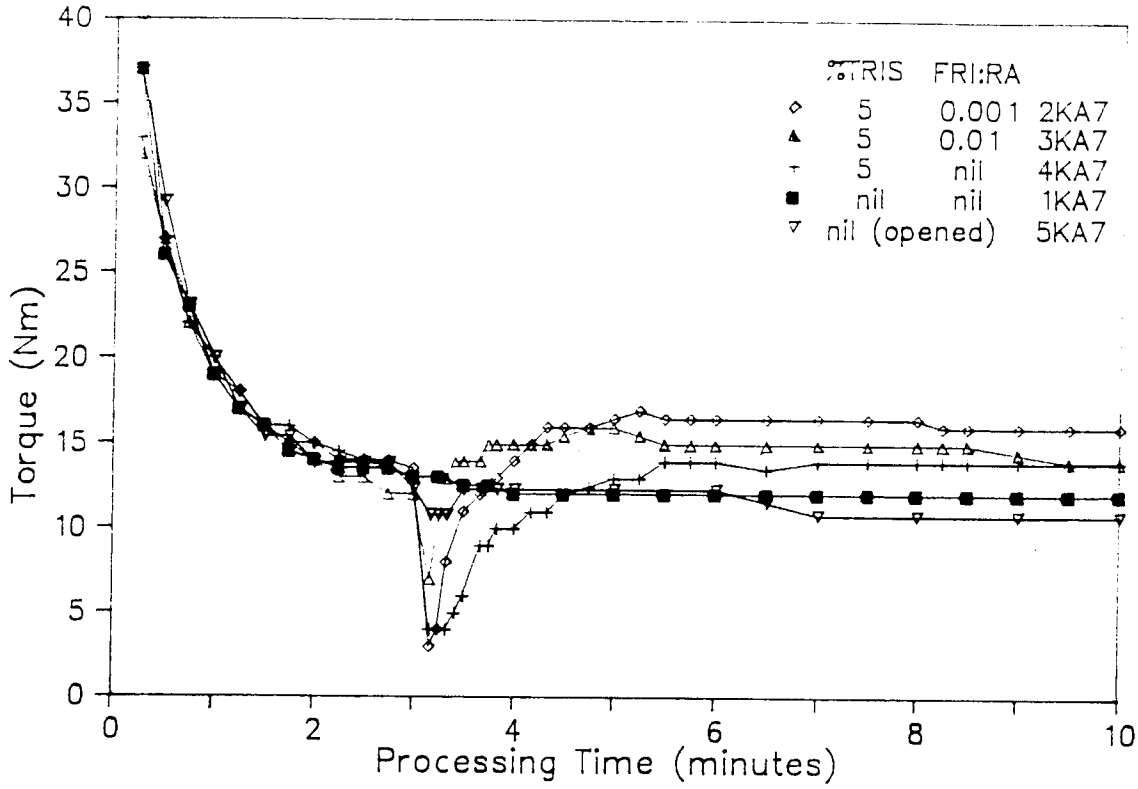
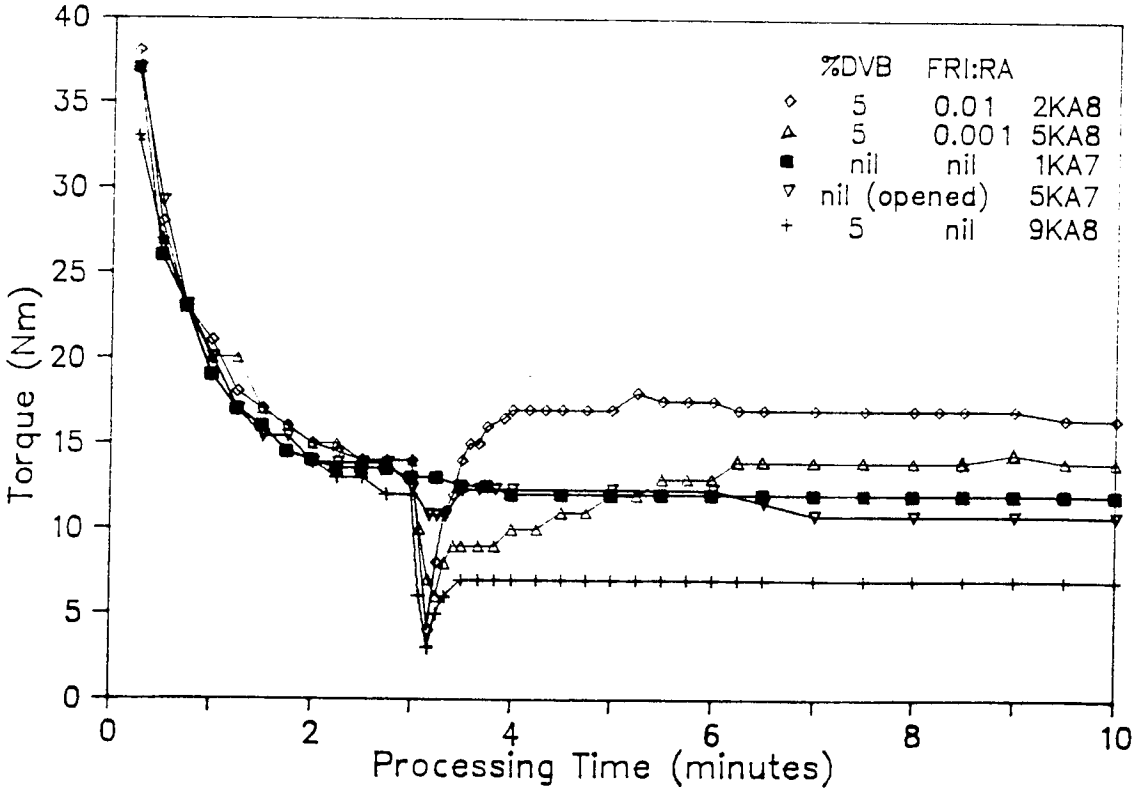


Figure 5.2 **Torque behaviour of 70/30 PS/EPDM reactively processed blends with 5% DVB additions at different FRI:RA molar ratios and controls processed under standard conditions.**



5.2.1.3 Effect of Initiator Pre-Addition (TRIS and DVB).

Torque behaviour was determined for a set of 70/30 PS/EPDM blends, with 5% TRIS or DVB additions at selected FRI:RA ratios (Table 5.3), to which peroxide initiator (Akzo Trigonox 101) was mixed with the PS prior to melt blending with EPDM. Approximately ten times the mass of initiator usually added with reactive agent was used. The control blend with FRI pre-addition (1KA10) was found to have slightly lower torque than the physical blend (1KA7) during the second half of the mixing period (Figure 5.3). Compared to TRIS at the optimum FRI:RA ratio (2KA7), no great change in torque behaviour was caused by pre-addition of initiator before processing with the same TRIS & FRI formulation (1KA10) - torque peak was slightly earlier and higher, but later torque was the same (Figure 5.3a).

The change in torque behaviour for DVB & FRI with pre-added initiator was different to the fairly neutral response with TRIS. With the optimum FRI:RA for DVB, pre-treatment with initiator (3KA10) caused supression of the expected torque rise (2KA8), reducing the rate of recovery, peak height and final torque level (Figure 5.3b).

5.2.1.4 Effect of Mixed Reactive Agents.

The behaviour of combined addition packages of both TRIS and DVB together, at optimum FRI:RA ratios for each, in a 1:1 mixture at a total 5% reactive agent addition level was compared to the ability of each alone to produce torque changes on processing (Table 5.3). Different effects were found depending on whether initiator pre-addition was employed (Figure 5.4). For TRIS & DVB addition without extra initial FRI (6KA10) the overall torque curve was lower than either TRIS or DVB alone ; rate of rise was slower, to lower maximum and final torques, but still above controls. This deficit was partly recovered by FRI pre-addition (7KA10) ; torque rise matched that of the optimum TRIS

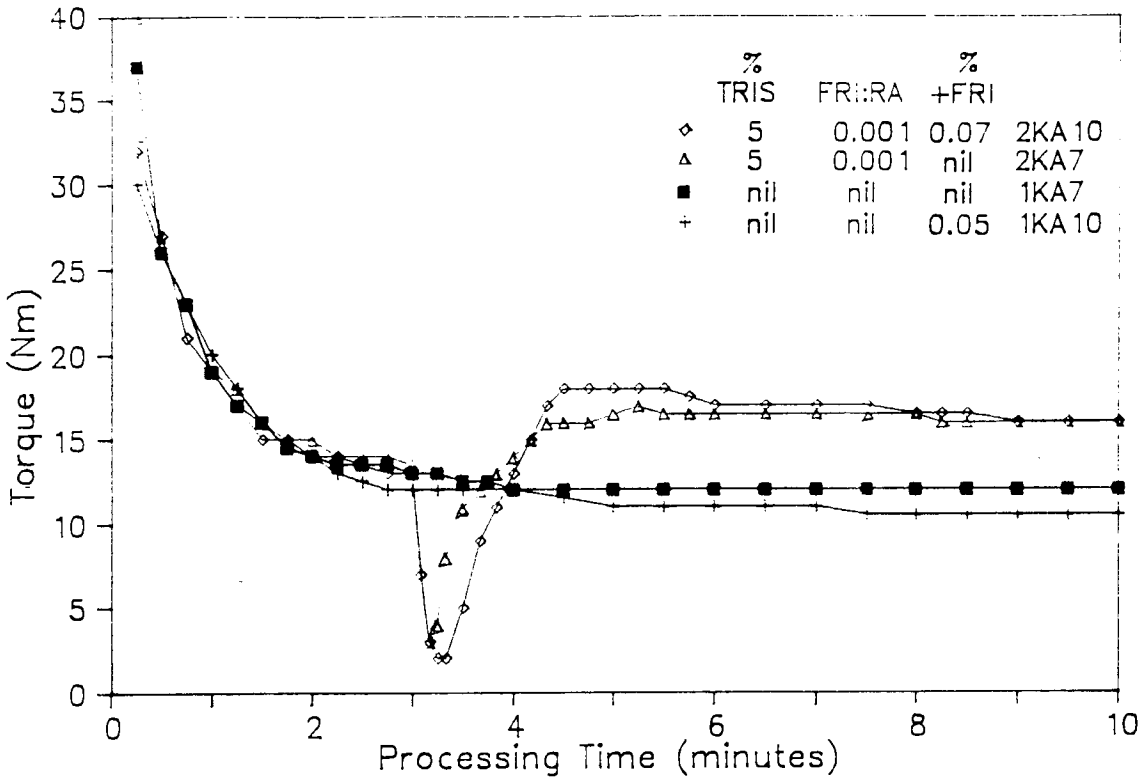
(2KA7) and continued to an even greater torque peak than the optimum DVB (2KA8). However, decay was considerable, bringing the final level to just below those of DVB and TRIS separately.

Table 5.3 **Compositions and torque behaviour of 70/30 PS (H311)/EPDM (V2504) blends reactively processed with nominally 5% TRIS, DVB or mixed reactive agent (nominally 2.5% TRIS at 0.001 mole ratio FRI:RA plus 2.5% DVB at 0.01 mole ratio FRI:RA) additions at various FRI:RA ratios, incorporating pre-addition of peroxide initiator (Trigonox 101) and controls processed under standard conditions.**

	Composition					Torque Behaviour			
Sample Cell	RA type	RA & FRI (% w/w) target	RA & FRI (% w/w) actual	FRI:RA molar molar	+ FRI (% w/w)	T_3 (Nm)	Peak (Nm)	Peak (min)	T_{10} (Nm)
1KA7	none	nil		nil	nil	13	none		12
1KA10	none	nil		nil	0.05	12	none		10.5
2KA7	TRIS	5.0	4.91	0.001	nil	13.5	17	5.25	16
2KA10	TRIS	5.0	5.14	0.001	0.07	13	18	4.5	16
2KA8	DVB	5.0	5.20	0.01	nil	14	18	5.25	16.5
3KA10	DVB	5.0	5.63	0.01	0.07	12	16	4.75	15
6KA10	TRIS + DVB	2.5 2.5		0.001 0.01	nil	12.5	14.5	5.25	14
7KA10	TRIS + DVB	2.5 2.5		0.001 0.01	0.06	12.5	19	4.8	15.5

Figure 5.3 **Torque behaviour of 70/30 PS/EPDM reactively processed blends with TRIS or DVB additions at different FRI:RA molar ratios, incorporating pre-addition of peroxide initiator (Trigonox 101) and controls under standard conditions.**

a) 5% TRIS additions.



b) 5% DVB additions.

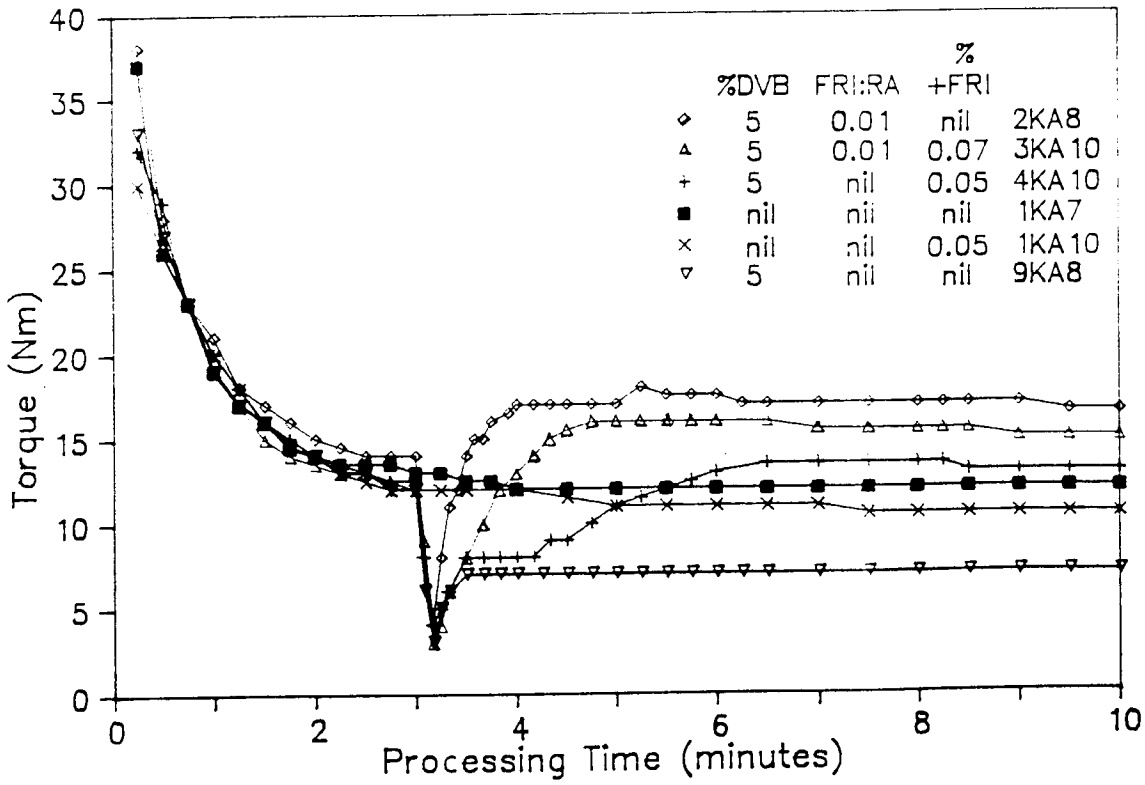
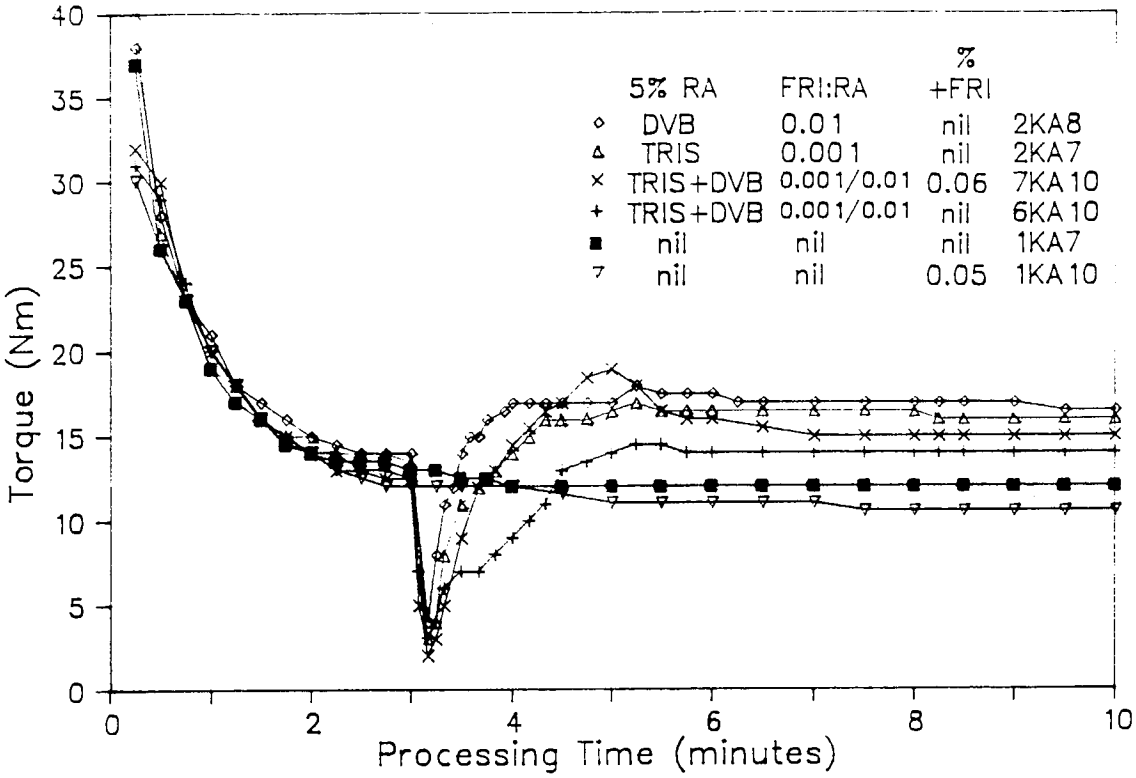


Figure 5.4 **Torque behaviour of 70/30 PS/EPDM reactively processed blends with mixed reactive agent addition (TRIS+DVB) and incorporating pre-addition of peroxide initiator (Trigonox 101) and controls processed under standard conditions.**



5.2.2 Tensile Properties of PS/EPDM Blends Reactively Processed with TRIS and DVB Interlinking Agents.

A series of key PS/EPDM blends from the reactive processing studies with TRIS or DVB and controls were selected for analysis to determine the possible physical and chemical effects of the two different interlinking agents at various reactive agent and free radical initiator formulations (Table 5.4). Measurement of tensile properties, examination of fracture surface morphologies and a scheme of solvent extraction were carried out on pressed films of each sample.

Table 5.4 **Compositions and torque behaviour of key 70/30 PS (H311) / EPDM (V2504) blends reactively processed with nominally 5% TRIS or DVB additions at various FRI:RA ratios, or mixed reactive agent additions, incorporating pre-addition of peroxide initiator (Trigonox 101) and controls processed under standard conditions.**

	Composition					Torque Behaviour			
Sample Cell	RA type	RA & FRI (% w/w) target	RA & FRI (% w/w) actual	FRI:RA molar molar	+ FRI (% w/w)	T_3 (Nm)	Peak (Nm)	Peak (min)	T_{10} (Nm)
1KA7	none	nil		nil	nil	13	none		12
4KA7	TRIS	5.0	4.99	nil	nil	13	14	5.5	14
2KA7	TRIS	5.0	4.91	0.001	nil	13.5	17	5.25	16
3KA7	TRIS	5.0	5.02	0.01	nil	12	16	4.75	14
2KA10	TRIS	5.0	5.14	0.001	0.07	13	18	4.5	16
5KA8	DVB	5.0	5.49	0.001	nil	14	14	6.25	14
2KA8	DVB	5.0	5.20	0.01	nil	14	18	5.25	16.5
3KA10	DVB	5.0	5.63	0.01	0.07	12	16	4.75	15
6KA10	TRIS + DVB	2.5 2.5		0.001 0.01	nil	12.5	14.5	5.25	14
7KA10	TRIS + DVB	2.5 2.5		0.001 0.01	0.06	12.5	19	4.8	15.5

Initial measurement of tensile properties was problematic, with large variations from replicates of the same sample. This was traced to the poor quality of the pressed films, having unacceptable thickness variation over short lengths. An improved method of compression moulding was developed, using card templates to produce more even films (Section 2.3). Reference was also made to ASTM D 882-83 (Tensile Properties of Thin Plastic Sheeting) for guidance on suitable test piece geometry and testing conditions (as detailed in Section 2.4) ; most of the key PS/EPDM test and control cells subsequently measured gave acceptable deviations about the sample mean value (Table 5.5). Once confidence was gained in this method, samples processed towards the end of the programme had tensile measurements made on single specimens only.

The tensile properties of the physical 70/30 PS/EPDM blend (1KA7) were poor ; extension to break was below 2% and tensile strength was considerably lower than the PS component alone would be expected to give (around 50 MPa), however a distinct yield point prior to ultimate failure was realised from analysis of the stress-strain curve. Changes in the tensile properties of reactively processed blends were differentiated, according to the RA & FRI formulations employed, though these were on a relatively minor scale rather than any orders of magnitude difference. The most telling change was in the mode of failure for reactive blends, which all gave brittle fracture, with no discernable yield point. Two exceptions were from DVB at low initiator concentration (5KA8) and the addition of TRIS without initiator (4KA7) - neither showed any great gain in ultimate extension, but yield points were distinguishable. This latter cell (4KA7) was the most outstanding of all compositions - yield failure, elongation just higher than the control physical blend (1KA7) and the highest tensile strength and modulus of all cells, though improvements over control levels were no more than 10%.

Table 5.5 **Tensile properties of pressed films from key 70/30 PS/EPDM reactively processed blends and controls (as detailed in Table 5.4) using parallel-sided test pieces nominally 150 x 6 x 0.60mm at a gage length of 100mm and a strain rate of 0.1min^{-1} in an Instron Model 4301 Testing Station.**

Sample Cell	Extension to yield (%)		Extension to break (%)		Tensile Strength (MPa)		Modulus (MPa)		Toughness Factor (x100 MPa)	
	mean	std	mean	std	mean	std	mean	std	mean	std
1KA7	1.4	0.1	1.5	0.1	9.2	1.3	940	50	9.0	1.3
4KA7	1.7	0.1	1.9	0.3	12.2	0.7	1090	50	15.9	3.7
2KA7	no yield		1.1	0.2	8.0	1.6	840	70	5.0	2.1
3KA7	no yield		1.1	0.2	8.3	1.3	930	80	5.0	1.6
2KA10	no yield		1.9	-	10.7	-	640	-	11.6	-
5KA8	1.4	0.3	1.5	0.4	9.6	1.7	890	100	9.3	5.2
2KA8	no yield		1.5	0.3	11.5	1.2	940	60	9.8	2.9
3KA10	no yield		1.8	-	7.8	-	530	-	8.4	-
6KA10	no yield		1.9	-	11.1	-	730	-	12.1	-
7KA10	no yield		2.8	-	9.8	-	550	-	17.8	-

The only significant increase in extensibility was for mixed reactive agent combined with FRI pre-addition (7KA10) ; there was a 50% improvement above the control level, but this only resulted in an ultimate elongation below 3% This had a greater impact on the toughness factor (an integrated value of total energy to break per unit volume of test piece) of this cell (7KA10) which was the highest of the series at almost double the control value. On the negative side, breaking strain decreased in both cells with additions of TRIS & FRI (2KA7 & 3KA7), which thus caused reduced toughness factors. Control tensile strength was maintained by all reactive mixtures with certain gains by DVB at the higher FRI:RA ratio (2KA8) and TRIS alone as highlighted before (4KA7). 4KA7 was also the only cell to yield higher modulus than the controls ; reductions were more common, as found for all cells with initiator pre-addition or mixed reactive agents.

5.2.3 Morphology of PS/EPDM Blends Reactively Processed with TRIS and DVB Interlinking Agents.

Fractured tensile test pieces were viewed across the failure surface over a range of magnifications in the scanning electron microscope after suitable preparation (Section 2.5). At low magnification (x150) the whole width of the specimen could be viewed to give an overall indication of the microphase structure and locus of failure. The physical blend (1KA7) gave a very uneven fracture surface, where apparantly large planar domains had pulled out and away from each other to different extents along the width of the test piece. Samples from TRIS cells had a similar disjointed lamellae-like appearance, with some reduction in phase size. DVB caused much greater reduction in the fineness of dispersion and gave very level failure across the fracture surface. At higher magnification (x1500) more detail of the morphology could be obtained. It was obvious that the physical blend (1KA7) did not provide a simple spherical dispersed phase in a continuous matrix so often modelled in the literature as a typical elastomer/thermoplastic blend - the EPDM and PS in this case both existed as semi-continuous planar domains (Figure 5.5). This domain geometry made it impossible to accurately quantify the phase sizes, which were of the order of 10 to 20 microns or larger and had smooth phase interfaces.

Morphology was altered by reactive processing of the blend with TRIS to different extents depending on initiator concentration. At the highest FRI:RA ratio (3KA7) the structure was very similar to the physical blend. There was obvious brittle failure of the semi-continuous PS phase and poor adhesion to the elongated planes of the softer phase (Figure 5.6). Intermediate FRI:RA (2KA7) produced a more discrete dispersed second phase with considerable reduction in phase size (1 to 5 microns) and a more even texture to the fracture surface (Figure 5.7). TRIS alone gave less of a reduction in phase size and

did not disperse the second phase as well, though interfacial texture was considerably rougher (Figure 5.8).

DVB produced more substantial changes in morphology, the PS matrix was much finer and the dispersed phase was considerably smaller (at the sub-micron level), independent of initiator concentration ; both 0.001 and 0.01 FRI:RA molar ratios had similar effect (5KA8 & 2KA8 - Figures 5.9 & 5.10).

The effect of FRI pre-addition was distinctly different for TRIS and DVB. For the triacrylate interlinking agent (combined with 0.001 FRI:RA molar ratio - 2KA10) the second phase was dispersed with many domains as round-ended cigar-shaped inclusions. These were quite distinct, being of a larger size (about 5 microns) than much of the remaining dispersed phase (below 1 to 2 microns) and having generally low adhesion to the fractured matrix, as seen by particle pull-out (Figure 5.11a & 5.11b). With DVB and FRI pre-treatment (3KA10) no such inclusions were visible and morphology was closer to that expected for straightforward DVB addition, though the matrix appeared to be more robust (Figures 5.12a & 5.12b).

The use of mixed reactive agents produced mixed morphologies within the same specimen. 6KA10 (TRIS + DVB at optimum FRI:RA's) gave an overall appearance of reduced phase size intermediate to that from TRIS or DVB separately, though there were some large domains with extended, smooth interfaces (Figures 5.13a & 5.13b). In the case with FRI pre-addition (7KA10 - Figures 5.14a & 5.14b) the matrix and dispersion was similar, if slightly coarser, to DVB separately under comparable conditions (3KA10), with occasional larger domains having smooth interfaces similar in size and shape to the inclusions found with TRIS separately under similar conditions (2KA10).

Figure 5.5 **View of fracture surface from tensile test using scanning electron microscopy to show internal structure of 70/30 PS (Huntsman 311) / EPDM (Vistalon 2504) physical blend (1KA7).**

Figure 5.6 **View of fracture surface from tensile test using scanning electron microscopy to show internal structure of 70/30 PS (Huntsman 311)/EPDM (Vistalon 2504) blend (3KA7) reactively processed with 5% TRIS addition at 0.01 FRI:RA molar ratio.**

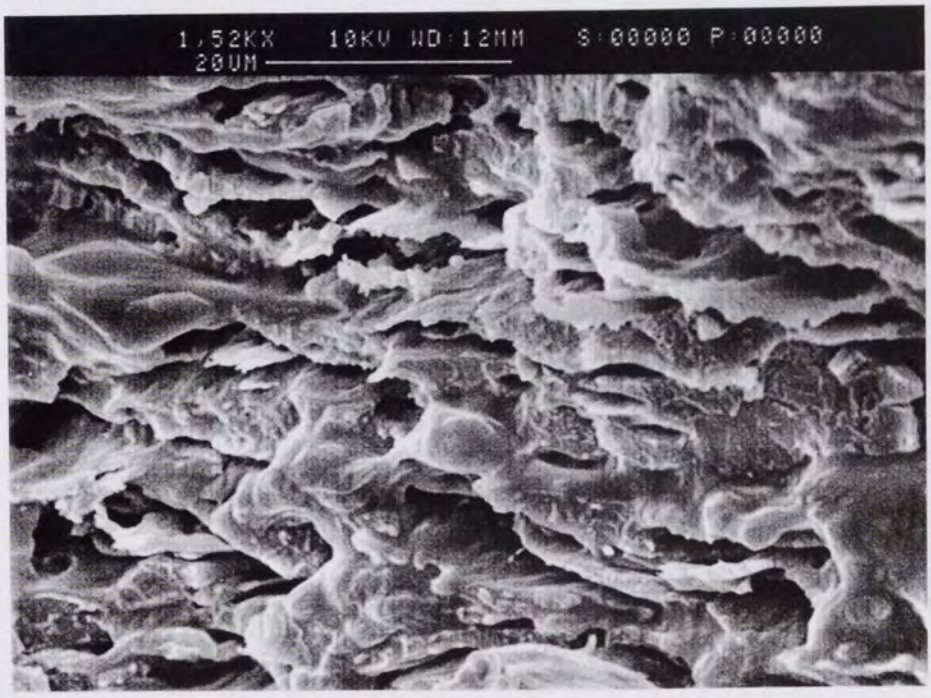


Figure 5.7 **View of fracture surface from tensile test using scanning electron microscopy to show internal structure of 70/30 PS (Huntsman 311) / EPDM (Vistalon 2504) blend (2KA7) reactively processed with 5% TRIS addition at 0.001 FRI:RA mole ratio.**

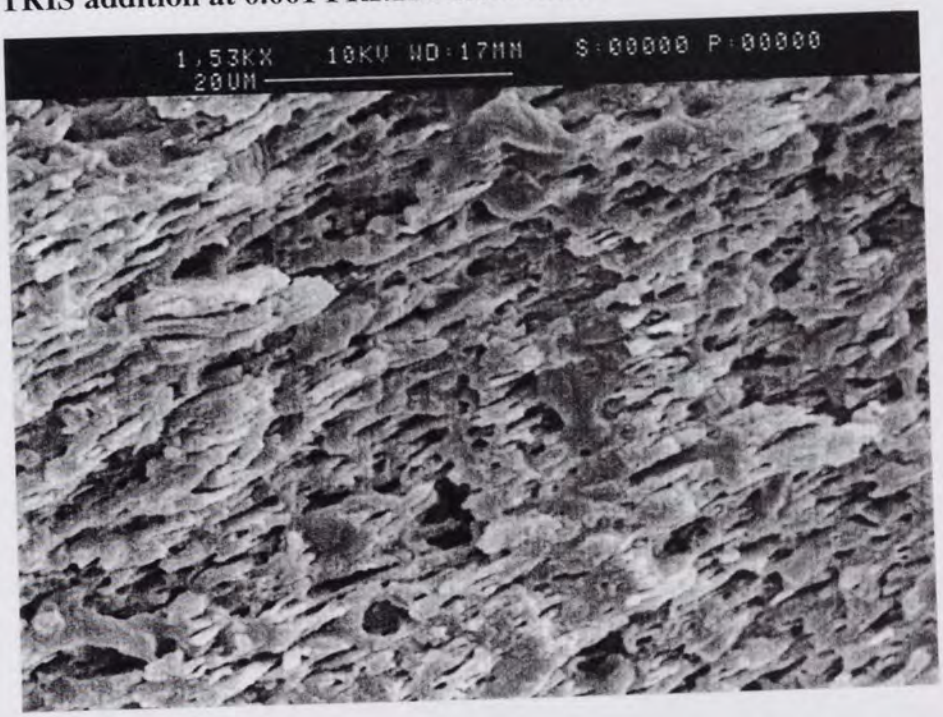


Figure 5.8 **View of fracture surface from tensile test using scanning electron microscopy to show internal structure of 70/30 PS (Huntsman 311) / EPDM (Vistalon 2504) blend (4KA7) reactively processed with 5% TRIS addition and no FRI.**

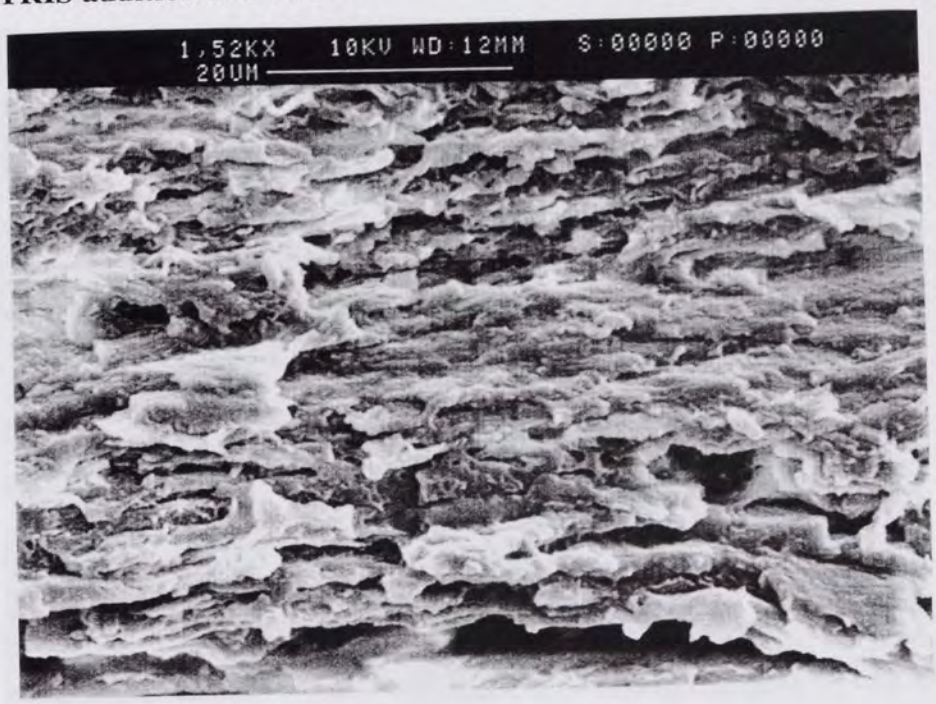


Figure 5.9 **View of fracture surface from tensile test using scanning electron microscopy to show internal structure of 70/30 PS (Huntsman 311) / EPDM (Vistalon 2504) blend (5KA8) reactively processed with 5% DVB addition at 0.001 FRI:RA mole ratio.**

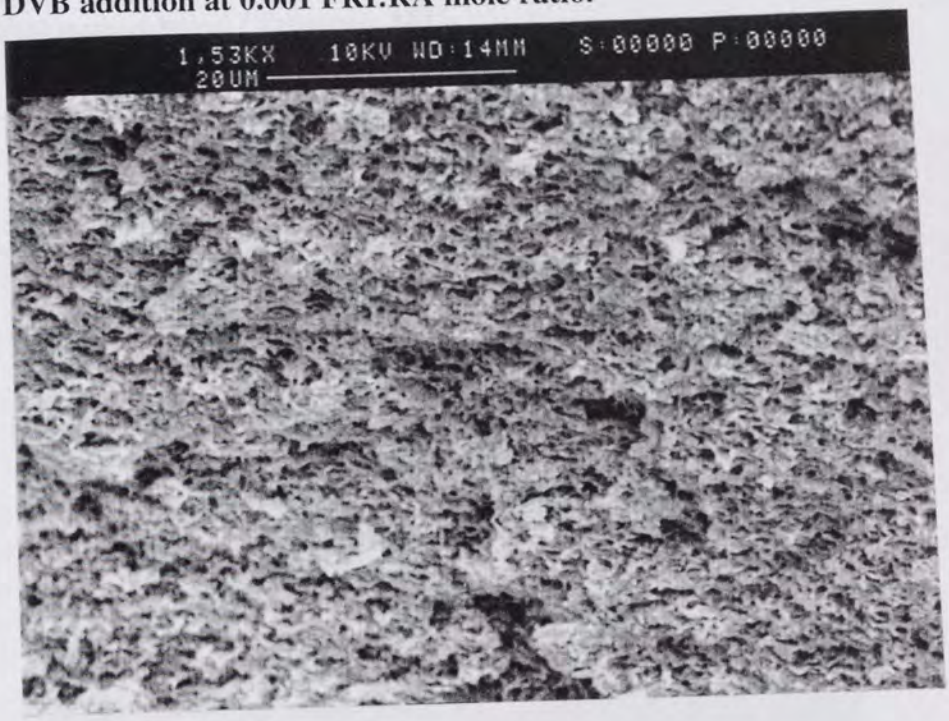


Figure 5.10 **View of fracture surface from tensile test using scanning electron microscopy to show internal structure of 70/30 PS (Huntsman 311) / EPDM (Vistalon 2504) blend (2KA8) reactively processed with 5% DVB addition at 0.01 FRI:RA mole ratio.**

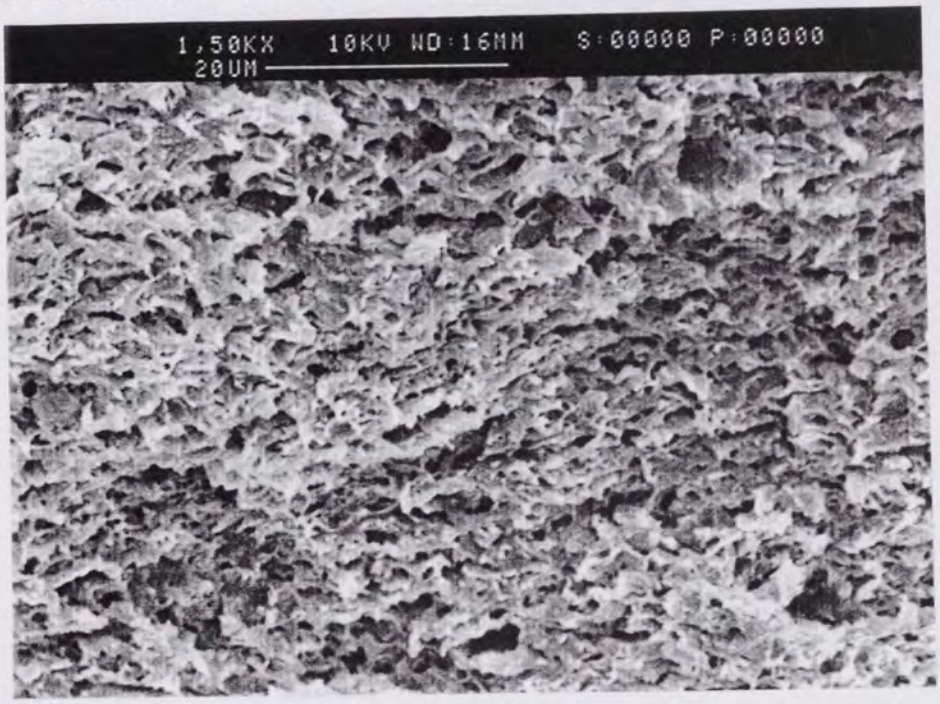
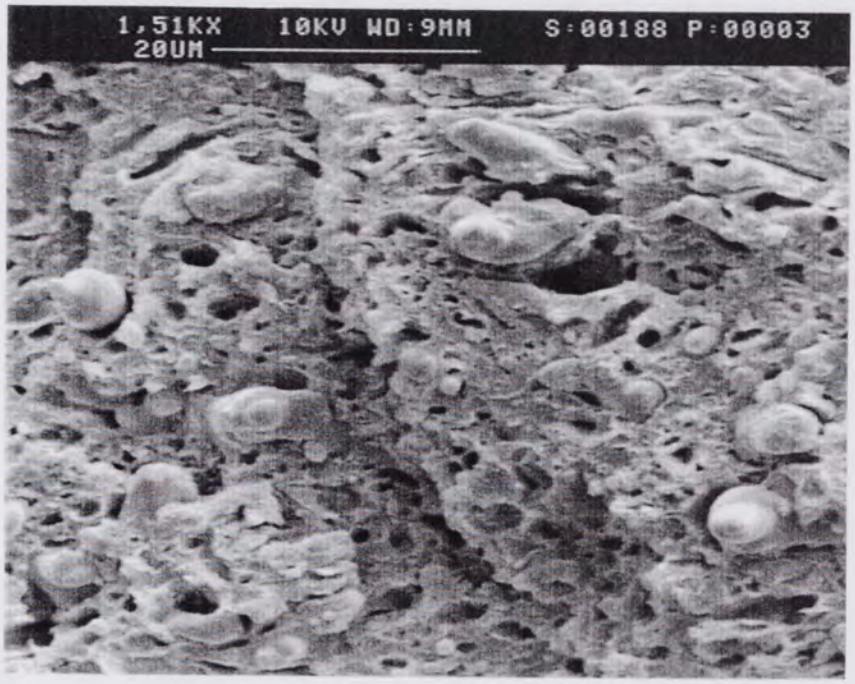


Figure 5.11 **View of fracture surface from tensile test using scanning electron microscopy to show internal structure of 70/30 PS (Huntsman 311) / EPDM (Vistalon2504) blend (2KA10) reactively processed with 5% TRIS addition at 0.001 FRI:RA mole ratio incorporating peroxide FRI pre-addition (Trigonox 101).**

a) low magnification



b) high magnification

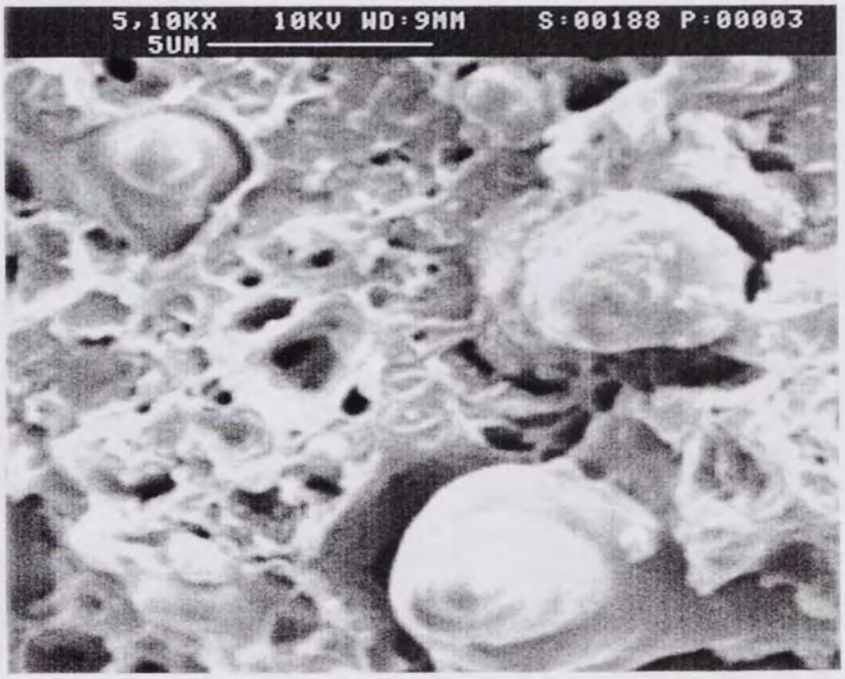
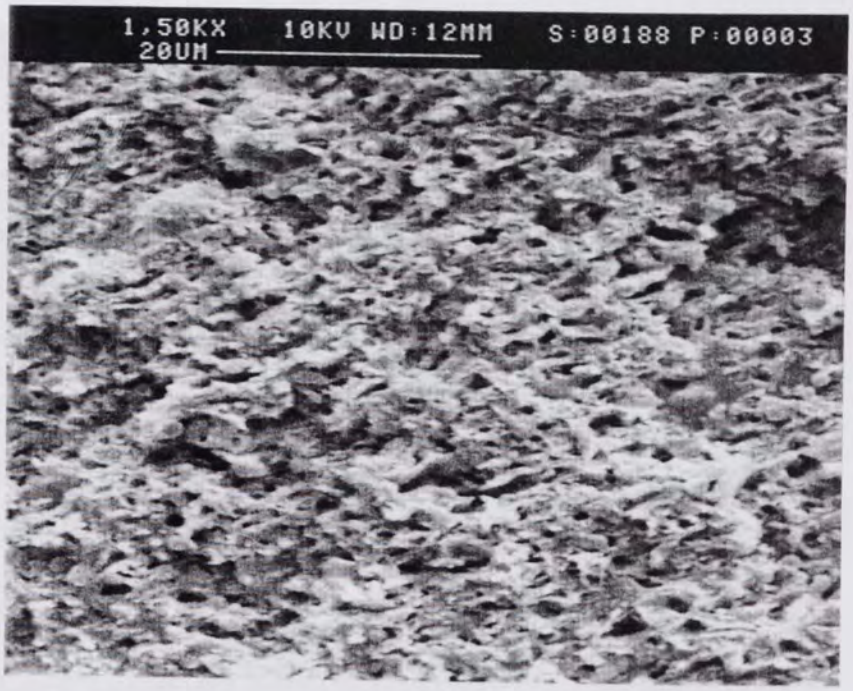


Figure 5.12 **View of fracture surface from tensile test using scanning electron microscopy to show internal structure of 70/30 PS (Huntsman 311) / EPDM (Vistalon 2504) blend (3KA10) reactively processed with 5% DVB addition at 0.01 FRI:RA molar ratio incorporating peroxide FRI pre-addition (Trigonox 101).**

a) low magnification



b) high magnification

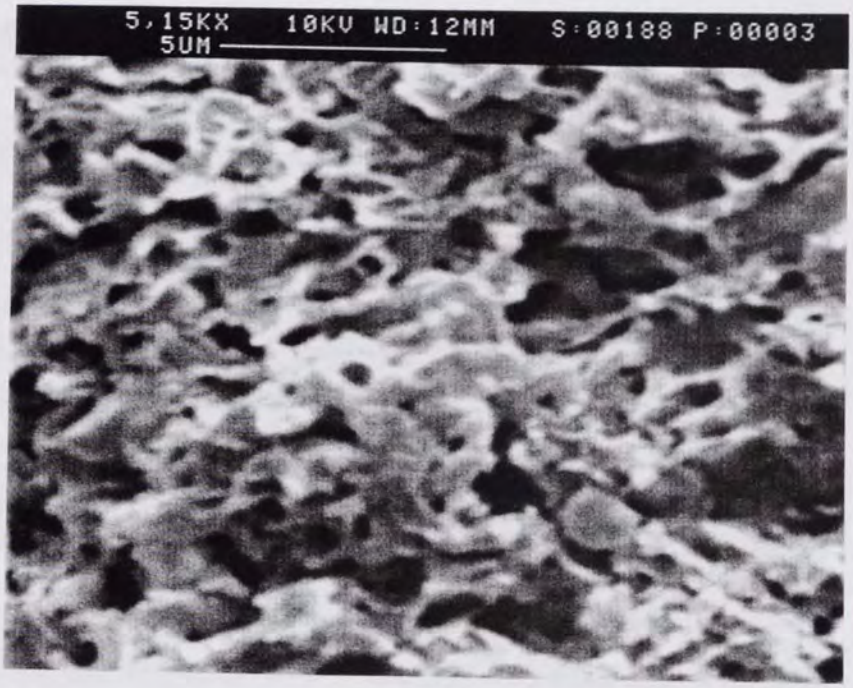
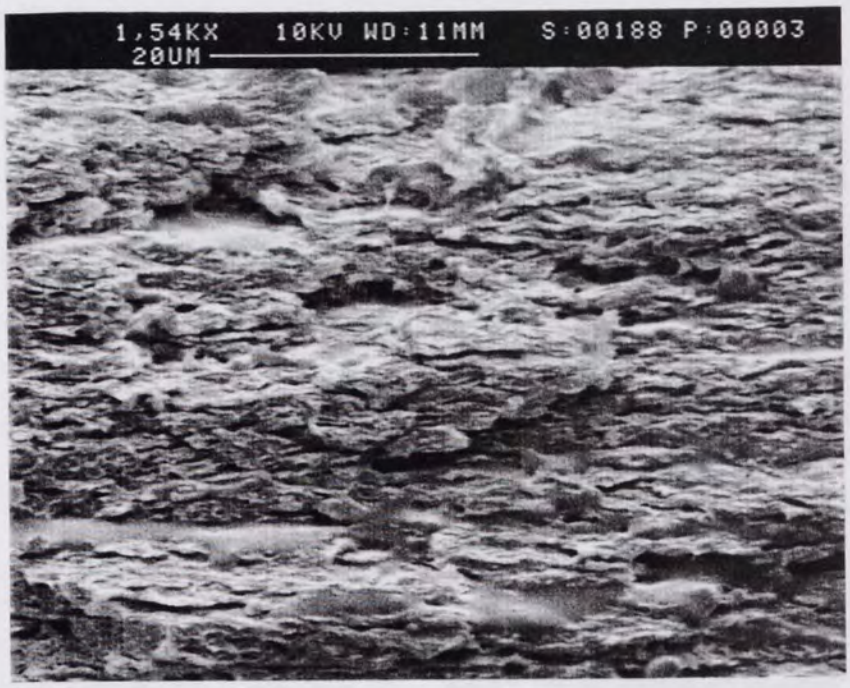


Figure 5.13 **View of fracture surface from tensile test using scanning electron microscopy to show internal structure of 70/30 PS (Huntsman 311) / EPDM (Vistalon 2504) blend (6KA10) reactively processed with 5% mixed reactive agent addition (nominally 2.5% TRIS at 0.001 FRI:RA molar ratio and 2.5% DVB at 0.01 FRI:RA molar ratio).**

a) low magnification



b) high magnification

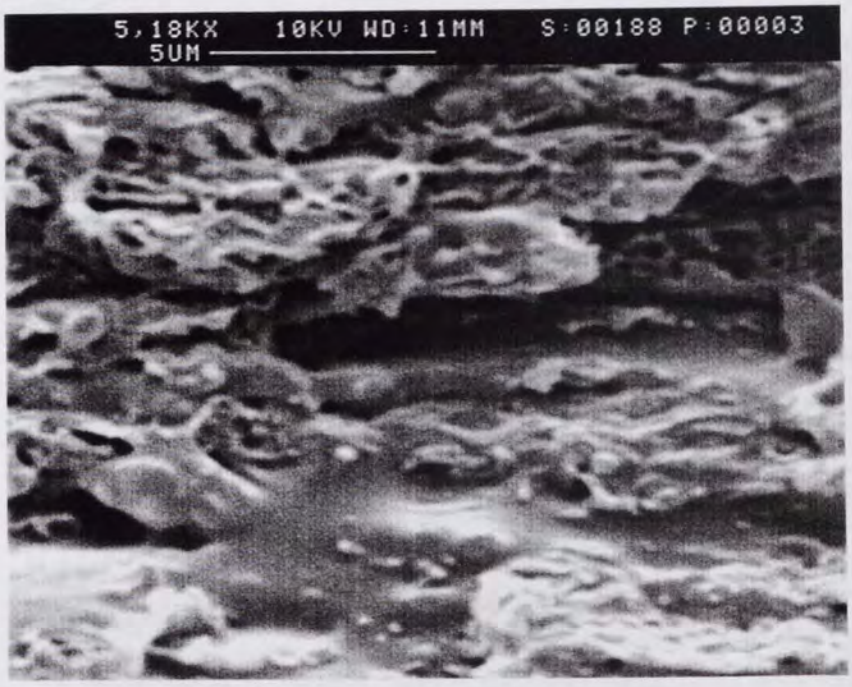
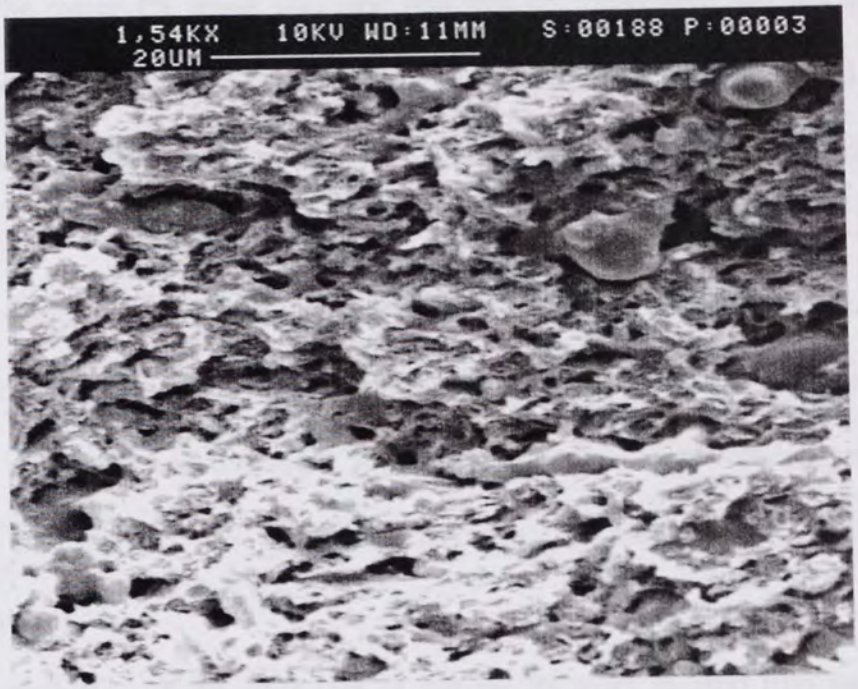
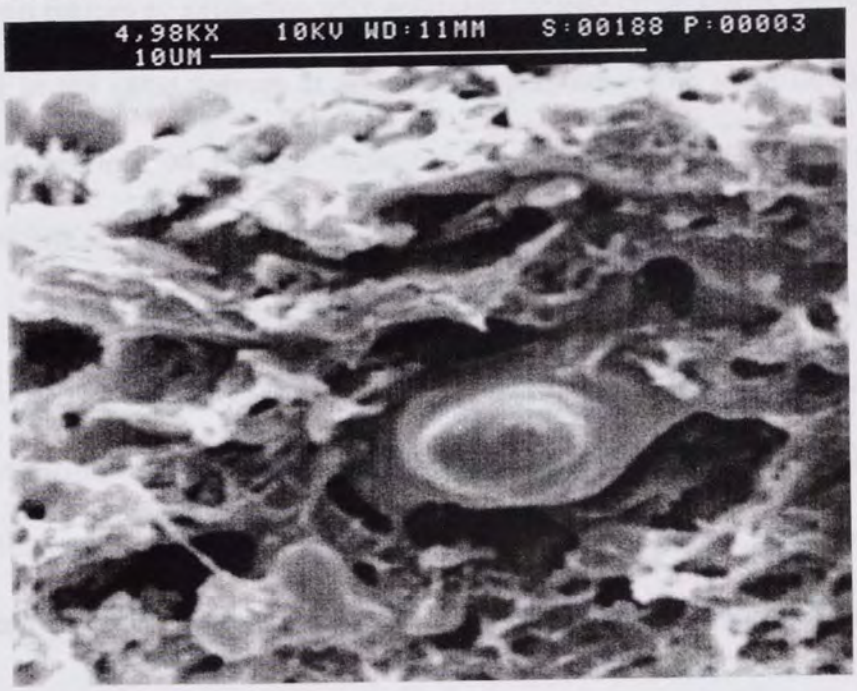


Figure 5.14 **View of fracture surface from tensile test using scanning electron microscopy to show internal structure of 70/30 PS (Huntsman 311) / EPDM (Vistalon 2504) blend (7KA10) reactively processed with 5% mixed reactive agent addition (nominally 2.5% TRIS at 0.001 FRI:RA molar ratio and 2.5% DVB at 0.01 FRI:RA molar ratio) with Trigonox 101 FRI pre-addition.**

a) low magnification



b) high magnification



5.2.4 Solvent Extraction of PS/EPDM Blends Reactively Processed with TRIS and DVB Interlinking Agents.

A double-pass method of solvent extraction was devised to separate and assay the components of reactively processed blends, especially any insoluble fraction (as detailed in Section 2.6). The major PS phase was first removed by exhaustive Soxhlet extraction using dichloromethane, previously shown to be a good solvent for this component (Section 4.2.5). EPDM was found to be substantially insoluble in refluxing dichloromethane, but was swollen on standing at room temperature over a period of several days. Several solvents were evaluated for EPDM ; hexane, toluene, decalin or tetrahydrofuran under reflux did not dissolve samples of the elastomer over a 60 minute period without extreme gel formation. After standing overnight at room temperature, only toluene produced a mobile gel-free solution and was therefore selected as the second pass solvent in the extraction scheme.

After determination of the mass loss of soluble PS from pressed film samples by dichloromethane extraction, the remaining material was returned to the Soxhlet apparatus and subjected to two periods of extraction with refluxing toluene separated by an overnight period of soaking in the same solvent at ambient temperature. The mass of insoluble residue was found and loss on toluene extraction attributed to soluble EPDM. Two additional 70/3 PS/EPDM blends to the previously selected key test and control cells (Table 5.4) were included in this analysis, these were 1KA10 (no RA, 0.05% FRI pre-addition) and 9KA8 (5% DVB, no FRI). The proportions of soluble fractions and insoluble residue determined by extraction are given in Table 5.6 for all cells analysed.

As seen with modified PS when extracted with dichloromethane (Section 4.2.5), certain blend samples became extremely swollen during extraction (Table 5.6). This

caused some of the swollen material to be lost from the Soxhlet, resulting in an indeterminate over-estimation of soluble PS.

The effects of interlinking agent addition were dramatic compared to the physical blend and control with FRI pre-addition (1KA7 & 1KA10), which gave minimal insoluble gel in both cases. All reactively processed blends yielded major gel fractions (above 14%), except for DVB without initiator (9KA8) at below half this amount. Highest gel contents were obtained from blends having DVB addition at high FRI:RA ratio (2KA8) and the TRIS + DVB mixed interlinking agents with initiator pre-addition (7KA10), both giving practically 21% residual gel, though with such extreme swelling the latter may have been under-estimated due to losses during extraction.

Table 5.6 **Sequential solvent extraction of pressed films from key 70/30 PS/EPDM reactively processed blends and controls according to Scheme 2.4 using dichloromethane for soluble PS and toluene for soluble EPDM.**

	Composition				Extraction			
Sample Cell	RA type	Target RA % w/w	FRI:RA molar ratio	+ FRI % w/w	swelling with dcm	Soluble PS % w/w	Soluble EPDM % w/w	Insoluble gel % w/w
1KA7	none	nil	nil	nil	none	73.0	26.7	0.3
1KA10	none	nil	nil	0.05	none	75.4	24.3	0.3
4KA7	TRIS	5	nil	nil	none	73.5	12.1	14.4
2KA7	TRIS	5	0.001	nil	none	72.1	11.7	16.2
3KA7	TRIS	5	0.01	nil	none	70.6	12.0	17.4
2KA10	TRIS	5	0.001	0.07	extreme	62.5	22.4	15.1
9KA8	DVB	5	nil	nil	none	64.7	28.4	6.9
5KA8	DVB	5	0.001	nil	slight	54.6	28.9	16.5
2KA8	DVB	5	0.01	nil	none	70.5	8.6	20.9
3KA10	DVB	5	0.01	0.07	extreme	72.2	9.3	18.5
6KA10	TRIS + DVB	2.5 2.5	0.001 0.01	nil	extreme	74.9	9.8	15.3
7KA10	TRIS + DVB	2.5 2.5	0.001 0.01	0.06	extreme	66.0	13.3	20.7

Although controls (1KA7 & 1KA10) showed full dissolution of both PS and EPDM fractions, after the first (dichloromethane) extraction weight loss exceeded the 70% value expected from the exact 70/30 PS/EPDM blends prepared. This could have been due to slight compositional variation of the sample chosen from the bulk of material processed, or possibly slight solubility of EPDM from the film specimen. It was however quite clear which cells had substantially lower soluble PS than controls - TRIS or DVB additions at low initiator concentrations (2KA7 & 5KA8), DVB without initiator (9KA8) and the mixed reactive agent package incorporating FRI pre-addition (7KA10). For EPDM the converse was found in that for the majority of cases solubility was considerably lower than in controls, suggesting gel to consist principally of insoluble EPDM. Exceptions to this had soluble EPDM close to or higher than control values ; these cells had also shown low PS loses - TRIS or DVB additions at low FRI:RA ratios (2KA7 & 5KA8) and DVB without FRI (9KA8), suggesting gel in these cases to be principally, or exclusively, insoluble PS. The final cell (7KA10 - mixed reactive agent package incorporating FRI pre-addition) was thus the only condition under which gel appeared to be composed of high proportions of both PS and EPDM.

From the differences in component solubilities compared to control values a means of estimating the composition of the insoluble gel fraction was derived. If the loss on extraction of PS for controls was assigned a value of 75% then for any lower loss the difference (ie. control - result) would be the amount of PS remaining in the insoluble residue. The EPDM content of the gel would similarly be given from the difference between a 25% control value less the measured soluble portion. The combined sum of these two values should equal the measured insoluble gel content of the blend, and thus allowing the percentage PS and EPDM contributions to the insoluble gel to be estimated

(Table 5.7). It was realised that becauseof the errors in measurement and losses of swollen gel during extraction, in some cases, this did not give an absolute determination of composition. Nevertheless in the absence of any direct analysis of residual fractions, then this could provide a useful indication of PS and EPDM contribution to insoluble gel, from which it was hoped to be able to deduce most probable routes of reaction in blends reactively processed with interlinking agents (see Section 5.3).

Table 5.7 **Estimated insoluble gel compositions by differences in soluble PS and EPDM portions to control values for key 70/30 PS/EPDM reactively processed blends (from Table 5.6).**

	Extraction soluble portions (%w/w)		Insoluble portions (control value - soluble portion)		Total insoluble gel %	Estimated gel composition (% of insoluble gel)	
	PS Sp	EPDM Se	PS 75-Sp	EPDM 25-Se		PS	EPDM
4KA7	73.5	12.1	1.5	12.9	14.4	10.4	89.6
2KA7	72.1	11.7	2.9	13.3	16.2	17.9	82.1
3KA7	70.6	12.0	4.4	13.0	17.4	25.3	74.7
2KA10	62.5	22.4	12.5	2.6	15.1	82.8	17.2
9KA8	64.7	28.4	10.3	(-3.4)	6.9	100	0
5KA8	54.6	28.9	20.4	(-3.4)	16.5	100	0
2KA8	70.5	8.6	4.5	16.4	20.9	21.5	78.5
3KA10	72.2	9.3	2.8	15.7	18.5	15.1	84.9
6KA10	74.9	9.8	0.1	15.2	15.3	0.7	99.3
7KA10	66.0	13.3	9.0	11.7	20.7	45.0	55.0

5.2.5 FT-IR Analysis of Reactively Processed PS/EPDM Blends and Extraction Residues.

All PS/EPDM blends prepared were opaque and it was thus recognised that clear infra-red spectra would be difficult to obtain in transmission mode unless thin enough films to allow sufficient passage IR radiation for absorptions to be resolved. A modified technique of pressing was attempted (0.1g of previously prepared blend film or 0.06g of extraction residue between Cellophane films and steel plates in the DANIELS PRESS at 180°C with 8 minutes pre-heating under gradually increasing pressure until the final application of 110 kg/cm^2 and subsequent cooling) which gave thin (<0.1 mm), but still partially opaque, films from which transmission spectra were obtained that were suitable for assessment of the value of FT-IR analysis of PS/EPDM blends.

A complete spectrum for the thin film of a control 70/30 PS/EPDM blend (1KA7) is given in Figure 5.15 and may be compared to spectra for the component polymers as thicker pressed films (0.2-0.3 mm thick) ; Huntsman 311 PS in Figure 4.9 (Section 4.2.6) and Vistalon 2504 EPDM in Figure 5.16. From Figure 5.16 the 1378, 1156 and 720 cm^{-1} fingerprint regions used in the ASTM infra-red method for the determination of ethylene units in EPM and EPDM (D3900-86[156]) were obvious and the presence of ENB termonomer could also be confirmed by the 1688 and 810 cm^{-1} bands[131] (F & G ; Table 5.8). Principle absorptions for the 1KA7 blend are detailed in Table 5.9 along with probable functional group assignments and likely origin. From this analysis it was apparent that in thin films of the 70/30 PS/EPDM blends differentiation of the characteristics of PS and EPDM components was not straightforward due to substantial overlap of EPDM fingerprint absorptions with strong PS bands (especially with EPDM as the minor component). Similar reasoning precluded identification of EPDM diene units in the blend. Thus without considerable method development, possibly involving subtraction

Figure 5.15 **FT-IR spectrum of 70/30 PS/EPDM control blend (1KA7) from a thin pressed film.**

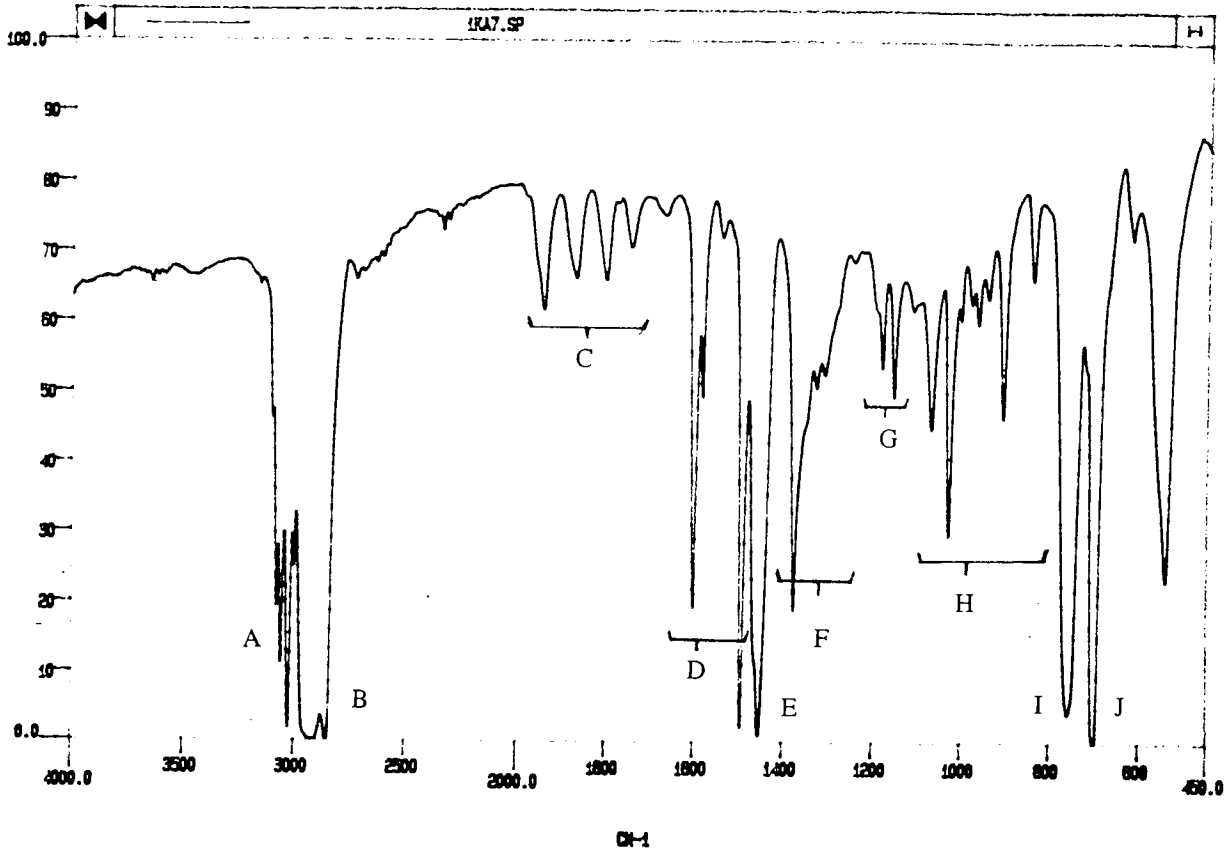
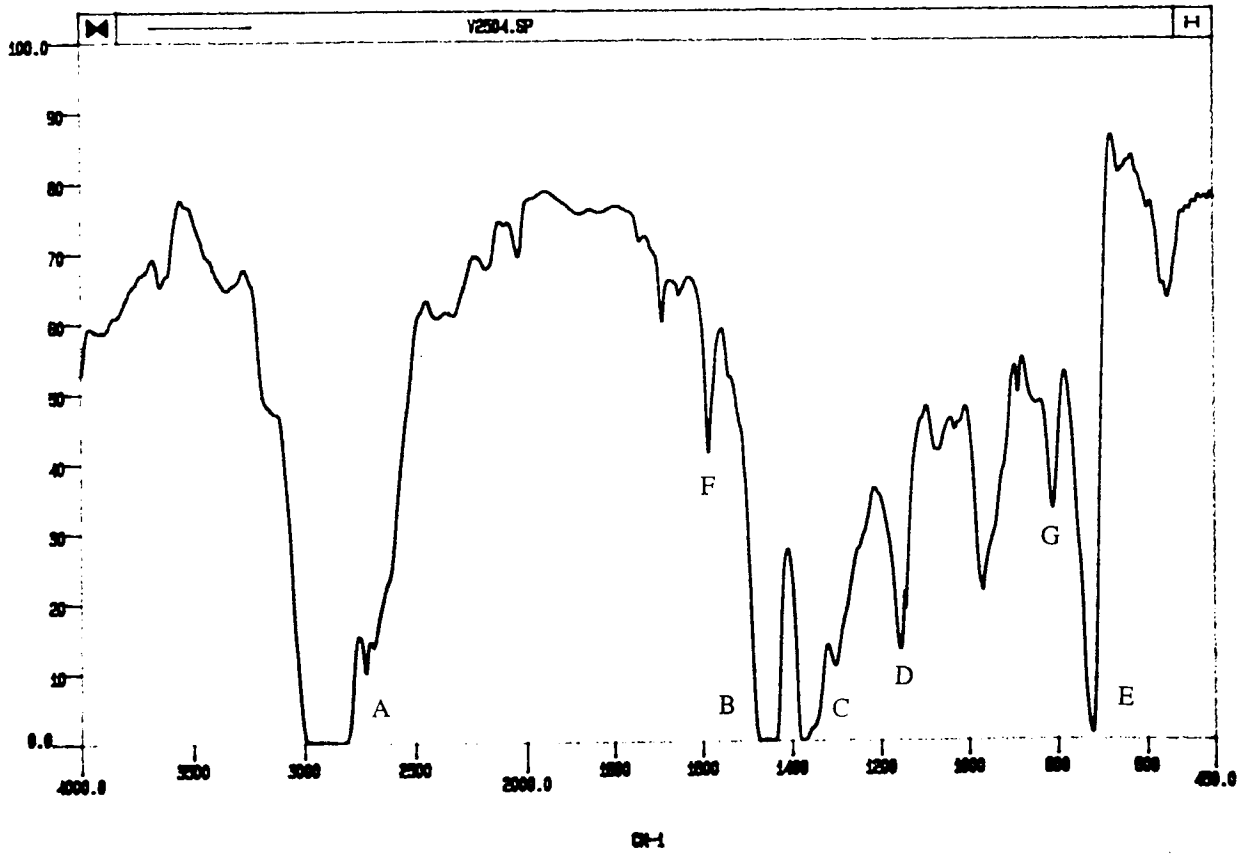


Figure 5.16 **FT-IR spectrum of Vistalon 2504 EPDM (0.3mm thick pressed film).**



of PS and EPDM absorptions corrected for film thickness and blend composition, direct quantification of PS or EPDM from the spectra obtained was not possible. Nevertheless some qualititative inferences could be made from the spectra of key reactively processed PS/EPDM blends and insoluble residues from solvent extraction (Scheme 2.4 Section 2.6).

For 2KA7 reactively processed 70/30 PS/EPDM blend with a 5% TRIS addition at 0.001 FRI:RA ratio all components were distinct in the FT-IR spectrum (Figure 5.17a) ; PS and EPDM showed similar overlap as in the inert blend (1KA7 - Figure 5.15) and grafted (polymerised) TRIS was easily discernible through strong carbonyl absorbance at 1739 cm^{-1} (shifted from a 1729 cm^{-1} position as for an unsaturated carbonyl in unreacted TRIS {Table4.13, Figure 4.10, Section 4.2.7). The gel residue of this cell from solvent extraction gave very low IR transmission due to the opacity of even a very thin pressed film of this fraction (Figure 5.17b). However, binding of TRIS into this insoluble gel was clearly shown by the very strong saturated carbonyl absorption (1740 cm^{-1}).

Table 5.8 **Major absorption bands and probable functional assignments in the infra-red spectrum of Vistalon 2504 EPDM (Figure 5.16).**

	Peak (cm^{-1})	Intensity	Assignment
A	below 3000	very strong (unresolved)	aliphatic methyl and methylene C-H stretching
B	1460	very strong (unresolved)	methylene symmetrical (scissoring) C-H bending
C	1378	very strong (unresolved)	methyl C-H bending
D	1156	strong	methyl C-H bending
E	720	very strong	methylene sequences
F	1688	medium	diene C=C stretching
G	810	medium	diene out-of-plane C-H bending

Table 5.9 **Major absorption bands and probable functional assignments in the IR spectrum of 1KA7 70/30 PS/EPDM control blend (Figure 5.15).**

	Peak (cm^{-1})	Intensity	Assignment
A	3082, 3060 3026, 3001	strong and sharp	PS aromatic C-H stretching
B	2913, 2852	very strong (unresolved)	PS + EPDM aliphatic C-H stretching
C	1943, 1871 1083, 1746 1668	medium to weak	PS combination and overtone bands for mono-substituted benzene ring
D	1601, 1583 1541, 1493	strong	PS aromatic C=C stretching
E	1453 + shoulder	strong	PS + EPDM methylene C-H bending
F	1377, 1329	strong	EPDM methyl + PS methylene C-H bending
G	1182, 1155	medium	PS aromatic + EPDM methyl C-H bending
H	1069, 1029 907,842	medium	PS + EPDM skeletal aliphatic C-C stretching
I	758	very strong	PS aromatic C-H bending
J	698 (+ 720)	very strong (unresolved)	PS aromatic C-H bending + EPDM methylene sequences

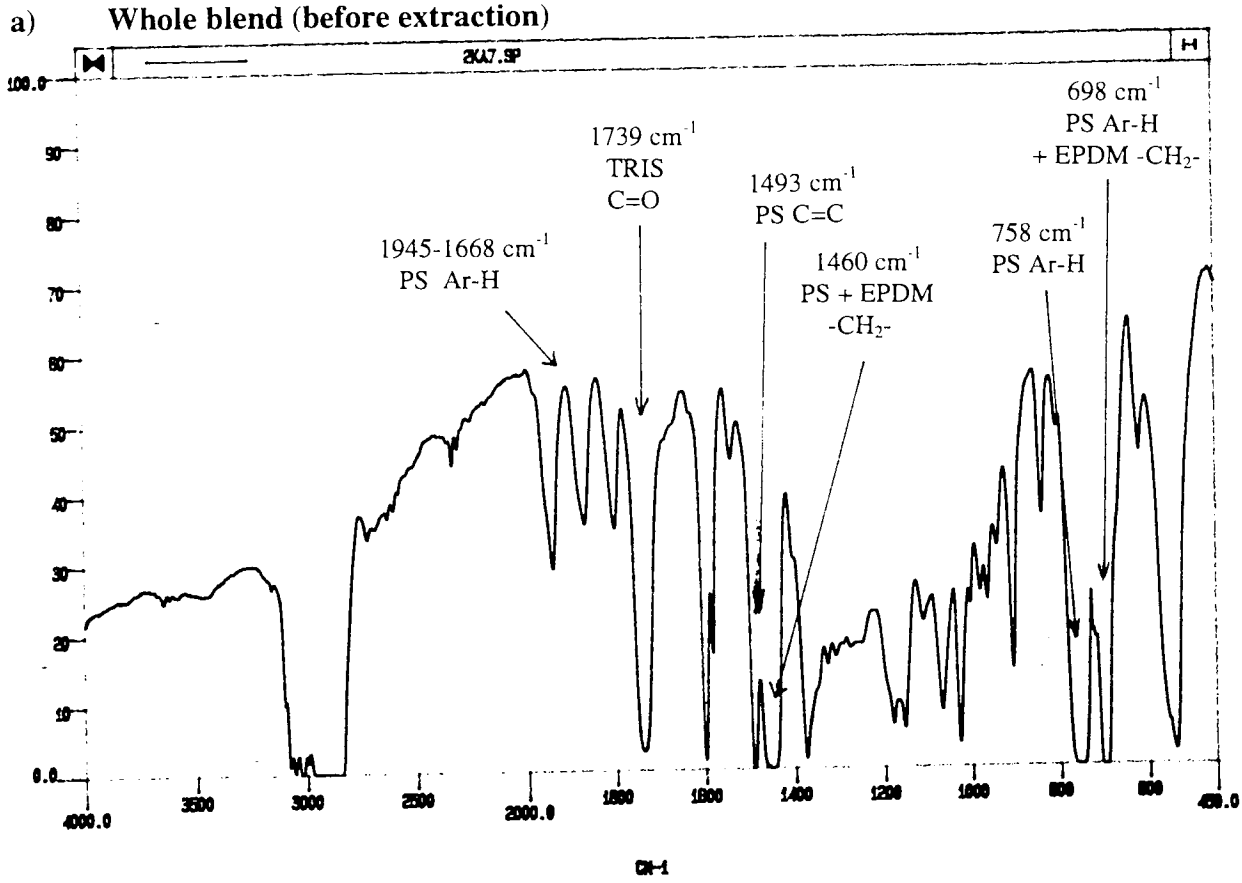
A PS contribution was apparent (1940-1670 cm^{-1}), but absorptions were significantly weaker, and compensated for by the EPDM component ; shown by strong, unresolved absorbance around 1460 cm^{-1} from methylene units and distinct separation of a 720 cm^{-1} band for EPDM methylene sequences from weaker PS absorbance in this region. Thus the presence of both blend and reactive agent components was shown in the 2KA7 gel, with suggestion of increased EPDM content.

Another key reactively processed 70/30 PS/EPDM blend cell analysed was 7KA10 (2.5% TRIS at 0.001 FRI:RA + 2.5% DVB at 0.01 FRI:RA with initiator pre-addition). A clear IR spectrum was obtained for the whole composition as a pressed thin film (Figure 5.18a) in which there was typical PS and EPDM overlap, as per the 1KA7 inert blend. The TRIS carbonyl peak (1739 cm^{-1}) in 7KA10 was much reduced compared to 2KA7 (Figure 5.17a) as expected for a 2.5% rather than 5% addition and DVB characteristics were not discernible (not surprising since 5% additions in PS alone had proved difficult to resolve - Section 4.2.8).

The residue from 7KA10 also gave a fairly clear spectrum (Figure 5.18b), with several interesting features. The presence of TRIS in this gel was obvious from the very strong carbonyl absorbance (1740 cm^{-1}), the intensity of which relative the remainder of the spectrum suggested an increased concentration of TRIS in this fraction compared to the entire blend and thus a high degree of incorporation in the gel phase (ie from 2.5% TRIS in the entire blend, with the insoluble gel portion over 20% for this blend {Section 5.2.4}, if there was total TRIS incorporation in gel, then the level of TRIS in this fraction would be in excess of 12%). There was also a clear presence of PS in the gel from 7KA10 as shown by the aromatic overtone bands (1940-1670 cm^{-1}) and others. EPDM was also well represented and, as with the residue of 2KA7, absorbance from methylene sequences was resolvable at 720 cm^{-1} as a shoulder on a strong PS aromatic C-H peak at 698 cm^{-1}. This again suggested a relative gain in EPDM content of the gel fraction, perhaps above the 30% level in the processed blend (for which the 720cm^{-1} peak was not distinguishable due to PS overlap), but not as high as in 2KA7 (in which the 720 cm^{-1} peak was more distinct). Thus even though the FT-IR technique used was not optimal and unable to fully separate PS and EPDM, the "interpolymer" nature of gel fractions was clearly indicated.

Figure 5.17 **FT-IR spectrum of reactively processed 70/30 PS/EPDM (2KA7) with 5% TRIS addition at 0.001 FRI:RA ratio, as a thin pressed film.**

a) **Whole blend (before extraction)**



b) **Gel portion (from solvent extraction).**

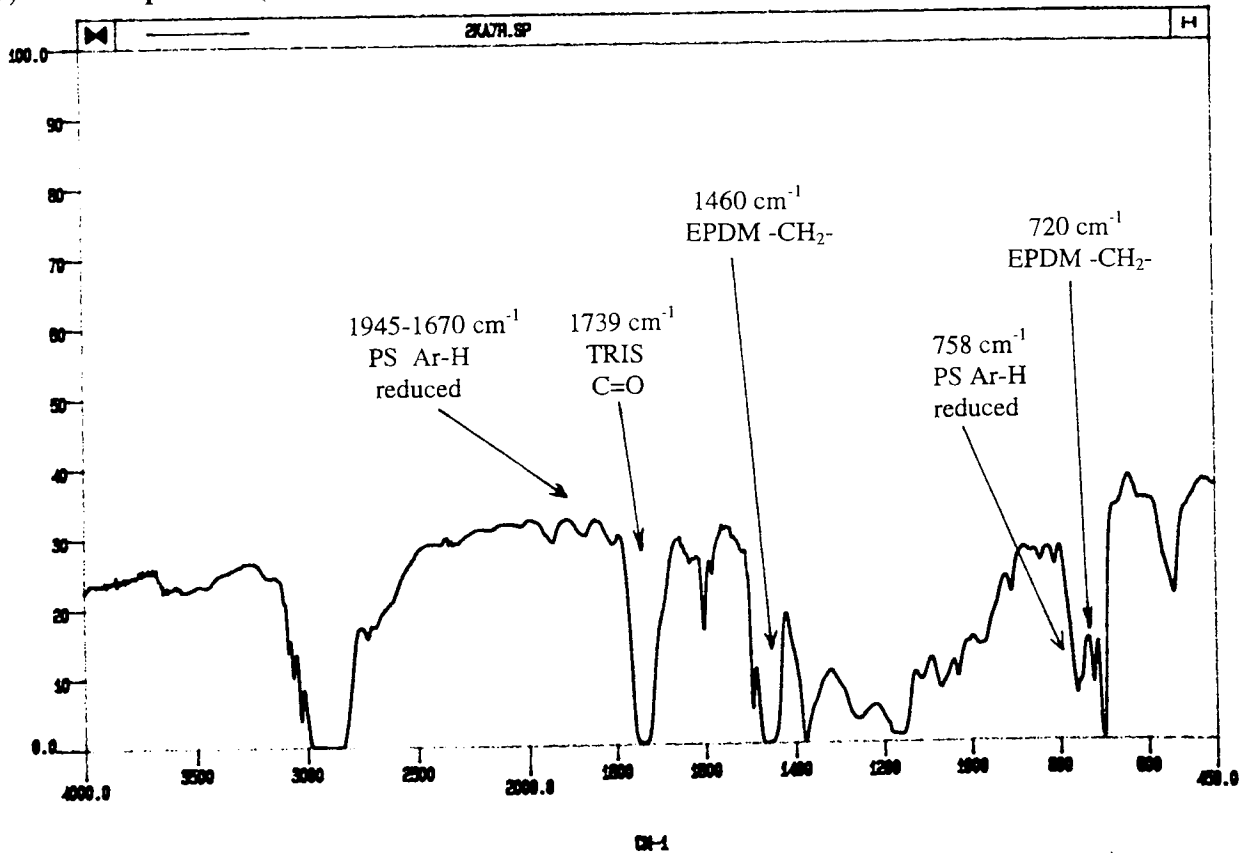
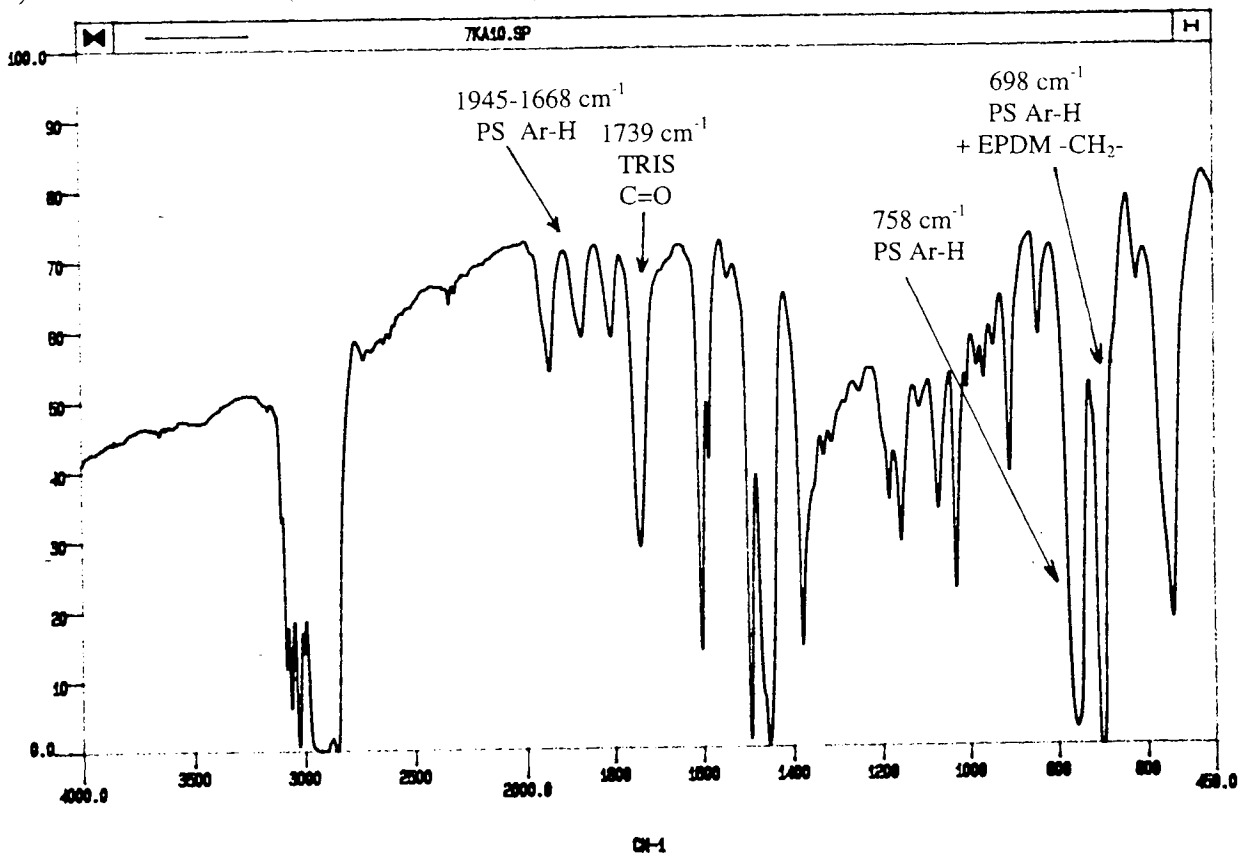
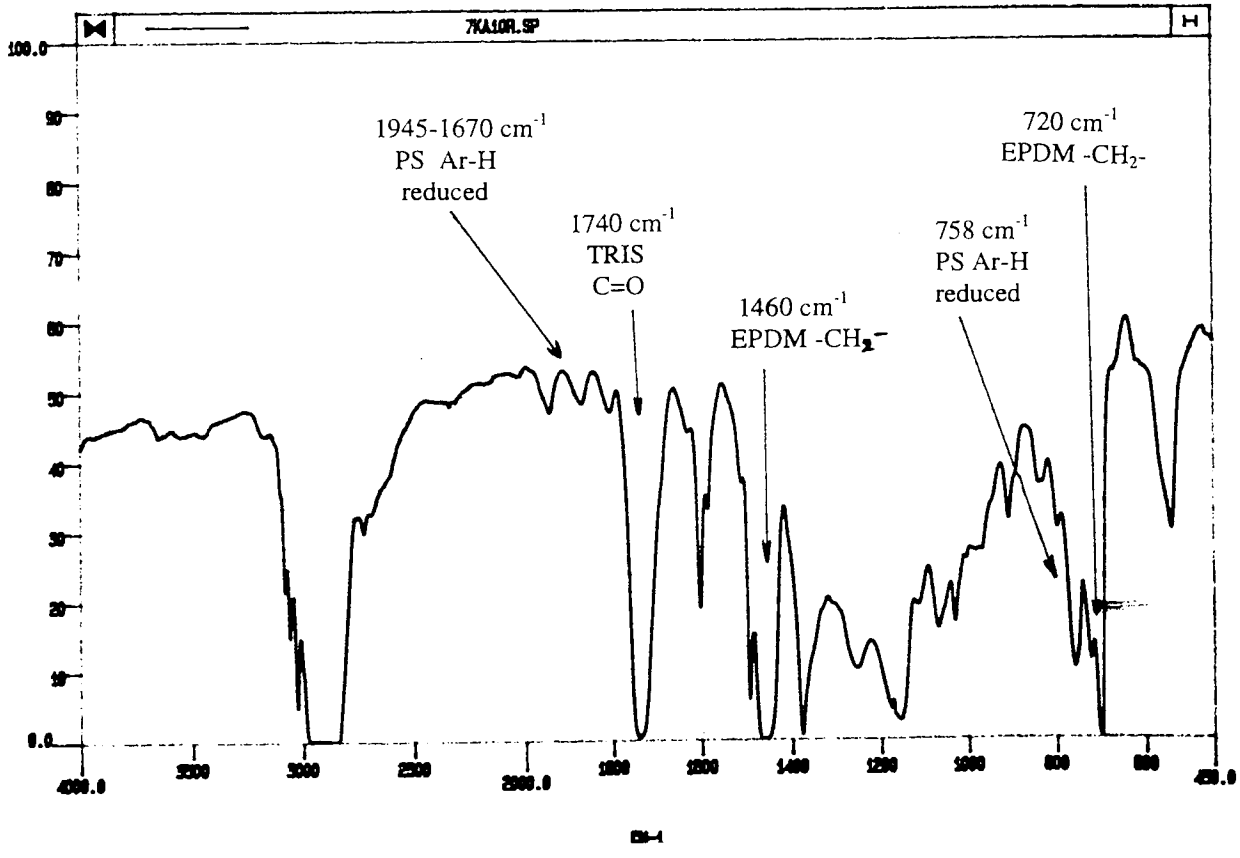


Figure 5.18 **FT-IR spectrum of reactively processed 70/30 PS/EPDM (7KA10) with mixed reactive agent addition (2.5% TRIS at 0.001 FRI:RA + 2.5% DVB at 0.01 FRI:RA) and FRI pre-addtion, as a thin pressed film.**

a) **Whole blend (before extraction)**



b) **Gel portion (from solvent extraction).**



5.2.6 Thermal Analysis (DSC) of Reactively Processed PS/EPDM Blends and Extraction Residues.

Differential Scanning Calorimetry (DSC) was carried out on a selective number of samples from key reactively processed 70/30 PS/EPDM blends (Table 5.4), PS & EPDM controls and insoluble residues from solvent extraction analysis (Section 5.2.4), examining a temperature range from -100 to +150°C according to the routine detailed in Section 2.10. Between this range it was possible to identify both EPDM and PS glass transition temperatures, and although changes in the heat capacity were often not large enough for either component transition to be particularly distinct, accurate values of Tg were obtained from peak maxima in the first derivative curves obtainable through the PERKIN-ELMER DSC7 software (Table 5.10). In the blends PS produced the more noticeable inflexion in the heat flow curve (at around 100°C) and hence a larger peak in the first derivative curve (Figure 5.19 - 2KA7), presumably due to its presence as the major component at a 70% by weight level. Comparison of complete DSC scans for all samples is given in Figure 5.20.

The Tg of unprocessed EPDM (from a pressed film sample) was -53.3°C (V2504 - Table 5.10) which gave good agreement with that of the EPDM component in an inert blend (-52.9°C : 1KA7). However in reactively processed blends with simple addition of TRIS or DVB intimate with FRI (2KA7 & 5KA8), the EPDM Tg was raised by 1-2°C. This was not quite as great for that achieved by 5% TRIS at 0.001 FRI:RA to EPDM alone (4KA4 : EPDM Tg shifted to -49.6°C ; over 3° rise vs unprocessed V2504 EPDM). Also in both 2KA7 & 5KA8, PS glass transitions in the whole blends were increased similarly above that measured in the 1KA7 inert blend (Table 5.10). An additional feature was found for the DVB addition (5KA8) with what appeared to be a second, low magnitude transition at 116.3°C just above that of the PS component (Figure 5.20). This suggested the

Table 5.10 **Glass transition temperatures of PS and EPDM components in blends, controls (Table 5.4) and insoluble gel fractions from solvent extraction (Scheme 2.4) using DSC (10mg sample, -100 to 150°C at 10°C / minute).**

Cell	Component Tg (°C)					
	EPDM			PS		
	whole blend	gel fraction	(whole - gel)	whole blend	gel fraction	(whole - gel)
1KA7	-52.9	no gel	/	101.6	no gel	/
2KA7	-51.8	-50.8	+ 1.0	104.3	108.0	+ 3.7
2KA10	- 54.8	-48.9	+ 5.9	102.8	no PS Tg	/
5KA8	- 50.7	- 49.7 (very minor)	+ 1.0	104.9 & 116.3	108.8	+ 3.9
7KA10	- 54.8	-48.7	+ 6.1	99.1	no PS Tg	/
V2504[1]	- 53.3					
4KA4[2]	- 49.3					

Notes : 1 - V2504 = pressed film of unprocessed Vistalon 2504 EPDM
2 - 4KA4 = reactively processed Vistalon 2505 with 5% TRIS at 0.001 FRI:RA

Figure 5.19 **Normalised DSC curve for reactively processed 70/30 PS/EPDM blend with 5% TRIS addition at 0.001 FRI:RA molar ratio (2KA7).**

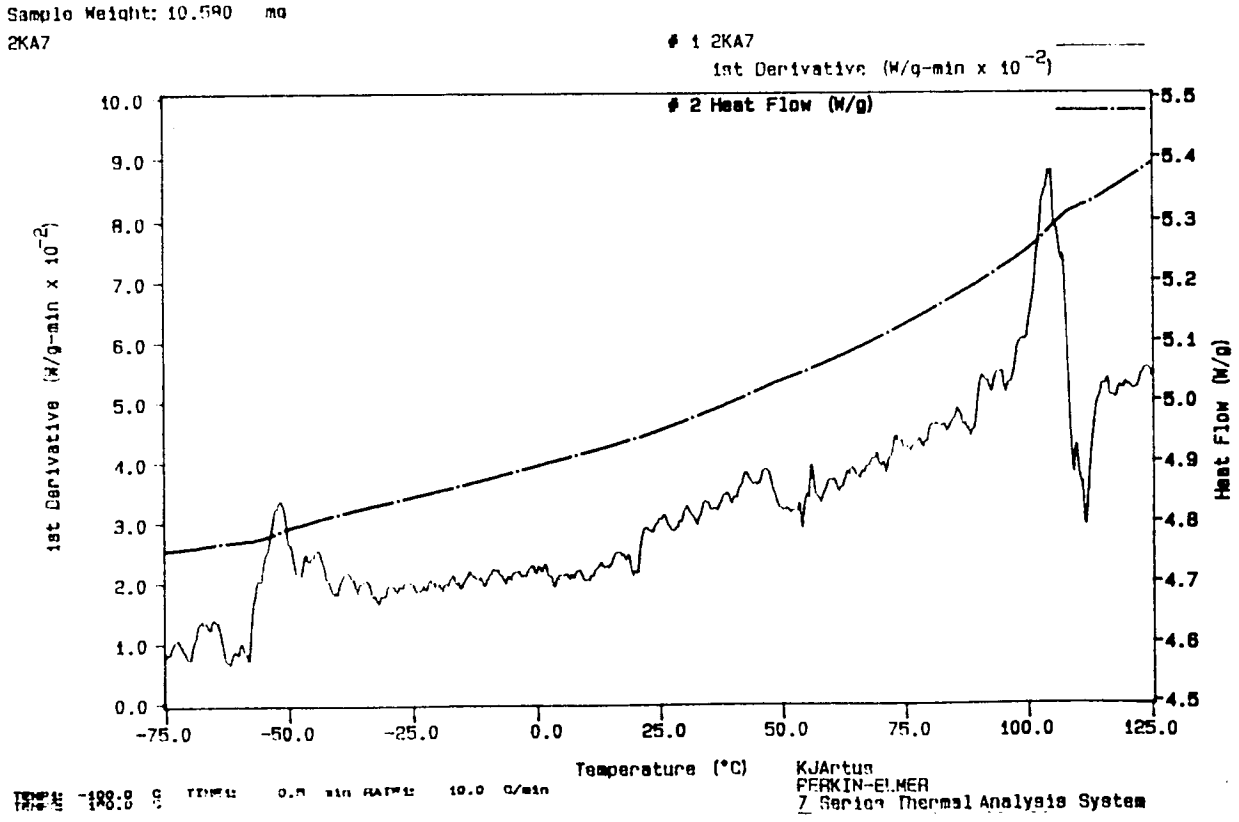
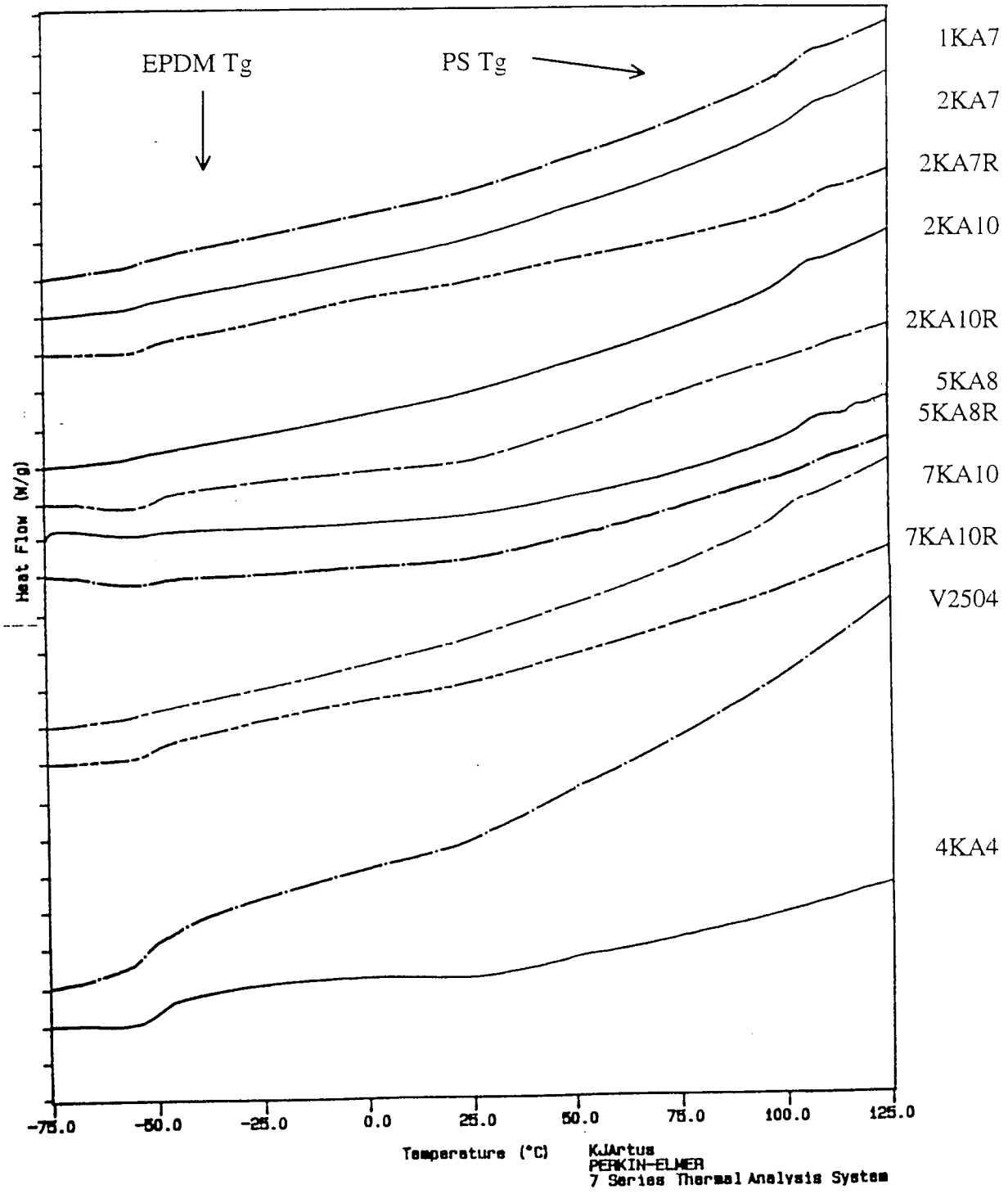
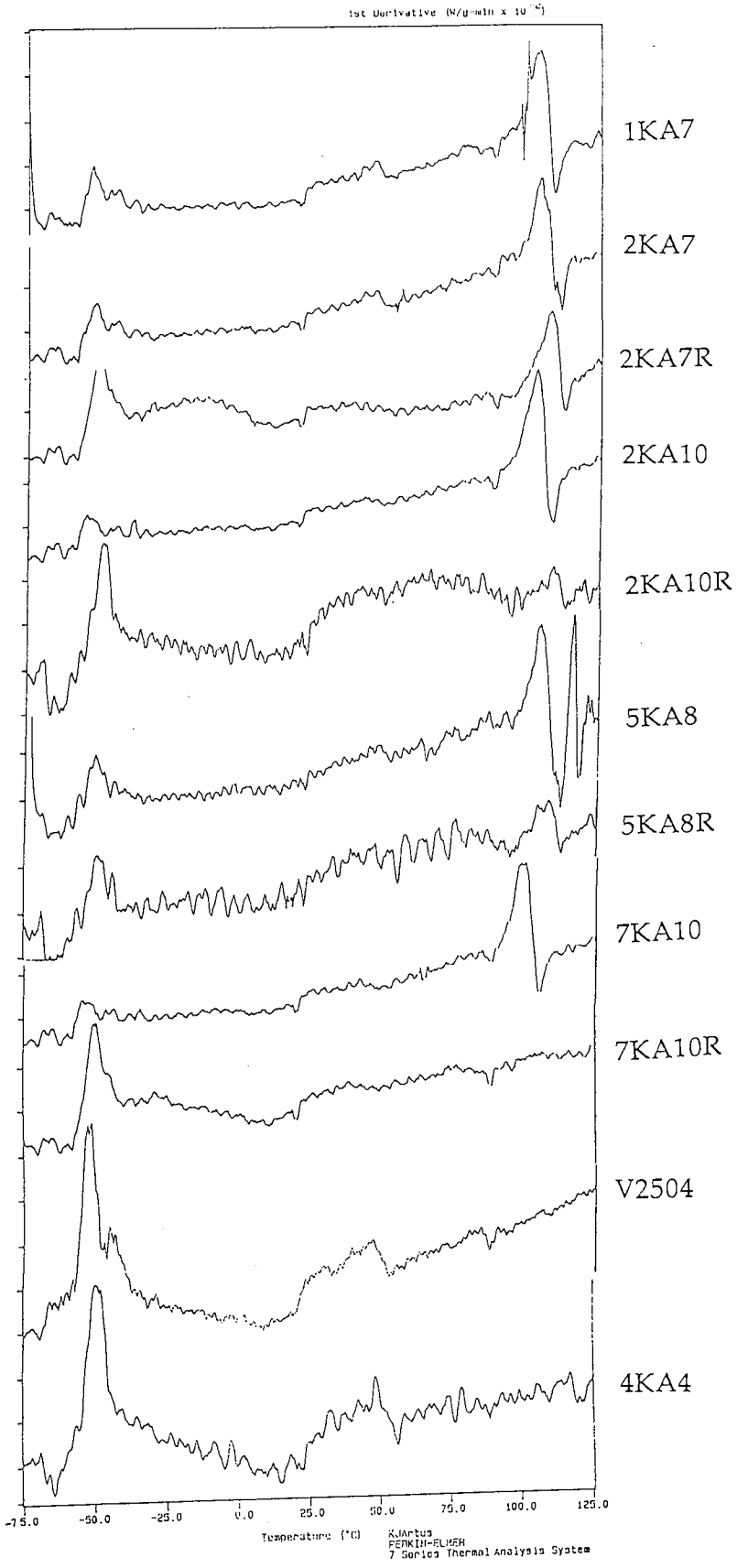


Figure 5.20 **Normalised DSC curves for reactively processed 70/30 PS/EPDM blends, gel fractions from solvent extraction ("R" suffix), controls and V2504 EPDM (10 mg samples, - 100 to 150°C at 10° per minute)**



Section 5.2.6

Figure 5.20b First derivative DSC curves for reactively processed 70/30 PS/EPDM blends, gel fractions from solvent extraction ("R" suffix), controls and V2504 EPDM (10 mg samples, -100 to 150°C at 10° per minute)



possibility of a small fraction of raised MW or partially cross-linked PS under the influence of DVB. Further behaviour of 2KA7 and 5KA8 were similar in that for the gel fractions analysed EPDM Tg's were both 1° higher than in the whole blends, to approach that of EPDM alone reactively processed with TRIS & FRI (4KA4 - Table 5.10). However in 5KA8 gel residue the EPDM transition was very weak (only a small difference in heat flow before and after Tg) suggesting only a low concentration of EPDM in the 5KA8 gel. Change in the PS Tg's for gel from 2KA7 and 5KA8 were also near identical, with a significant almost 4° rise to 108.0 and 108.8°C respectively in each case, though there was no indication of any second transition in the 5KA8 gel fraction.

The transition behaviour of PS and EPDM components in reactively processed blends incorporating initiator pre-addition were very different to simple RA/FRI additions, but for both TRIS and mixed reactive agent the pattern of changes was nearly identical (2KA10 & 7KA10 : Table 5.10). In the whole blends EPDM Tg's were the same for 2KA10 and 7KA10 at -54.8°C which was lower than EPDM in the inert blend (1KA7) and the unprocessed material (by 1.5°C which may just have been at the limit of significance). However in both gel fractions the EPDM transition was significantly increased in both the magnitude and measured temperature by around 6°C to slightly higher values than the reactively processed EPDM with 5% TRIS (4KA4). An even more pronounced effect in both these gel fractions was the total absence of any PS transition (up to the 150°C final test temperature - Figure 5.20), which was confirmed by replicate testing of fresh samples. In whole blends PS Tg's in 2KA10 and 7KA10 were apparent and lower than for PS in the inert blend, most particularly in 7KA10 (100.6 and 98.3°C respectively vs 101.6°C). Such reduction in the Tg of an amorphous glassy phase (the PS) by a lower Tg rubbery component may be the result of partial miscibilisation of the blend, presumably

concentrated in the interfacial regions. It was precisely these interfacial regions that sequential solvent extraction was intended to capture, with the assumption that cross-reacted interpolymer product would be insoluble in selective solvents for both phases. On the basis that both PS and EPDM were present in the insoluble portions of 2KA10 and 7KA10 (by the calculation of gel composition from extraction analysis {Table 5.8, Section 5.2.4} and confirmed by FT-IR analysis of 7KA10 gel {Section 5.2.5}) then the absence of PS Tg by DSC in these portions was likely to be associated with the molecular form of the interpolymer product.

Numerous theories and models can be applied to account for the compositional dependence of the glass transition in fully miscible blend systems.[19, 157] However, whilst it is generally accepted that in partially miscible (or compatibilised) blends, component transitions will be shifted and probably broadened (making accurate measurement more difficult) compared to their position in a fully immiscible condition, understanding and hence qualification of these shifts is still under development. Several factors may influence component Tg adjustments in compatibilised blends, particularly domain size and interfacial structure/compositional effects,[157] accounting for the very mixed nature of these systems. In the current case with further factors associated with the reactive processing aspect of the adopted approach, the strict application of present theories is probably very questionable. Nevertheless changes in the thermal behaviour of the PS/EPDM blends analysed were believed to be manifestations of partial miscibilisation of immiscible blend components by the in-situ formation of interpolymer products from the reactive processing routes employed. It was therefore hoped that this compatibilisation believed to have been effected could be related to possible changes in the physical characteristics of these blends (Section 5.3.3).

5.3 DISCUSSIONS.

From the studies on individual polymer modifications (Chapter 4), several strategies were conceived with the aim of enhancing interpolymer yield in 70/30 PS/EPDM blends by specifically targetting the less favourable reaction of the polystyrene component. The different schemes examined were ;

i. - variation of initiator concentration, firstly with TRIS addition and then with the divinylbenzene reactive agent ;

ii. - the use of peroxide initiator pre-addition to the PS prior to blending with the EPDM and either TRIS or DVB addition ;

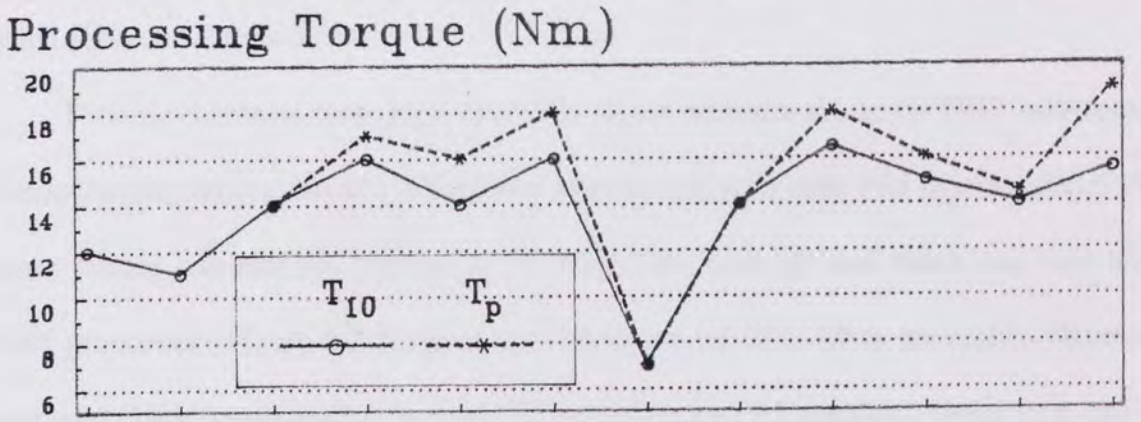
iii. - combined TRIS & DVB additions at optimum initiator contents, with and without FRI pre-treatment.

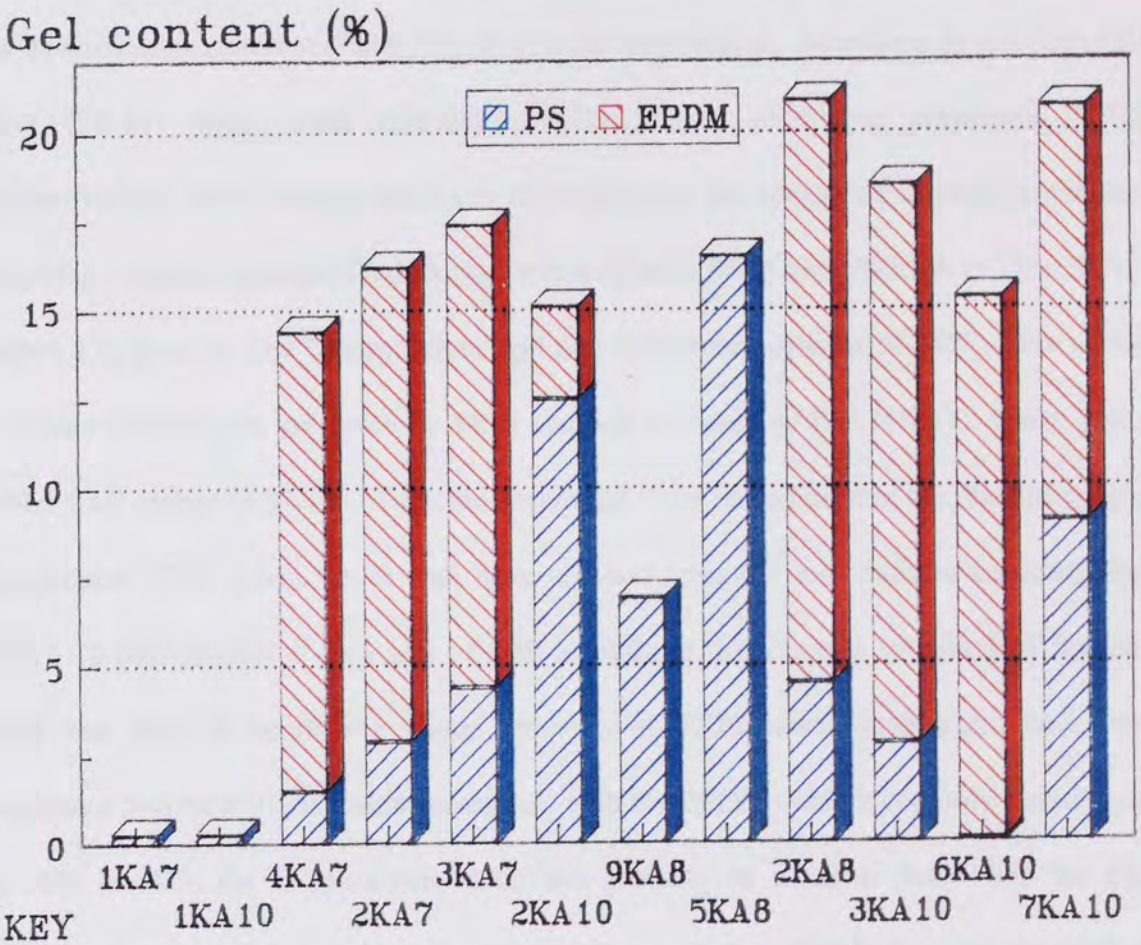
From examination of blend torque behavior, coupled with the results of extraction analysis, and learning from component reactive processing, understanding about the ongoing reaction pathways was developed, allowing the merits of different approaches to be judged. The relevant data from all strategies are shown graphically in Figure 5.21.

5.3.1 Optimisation of PS/EPDM Reactive Blending using TRIS Interlinking Agent.

For simple addition of triacrylate interlinking agent at different initiator concentrations in PS/EPDM blends, the maximum torque response was given at low FRI:RA molar ratio (2KA7). This was the same behavior as for EPDM alone with an identical addition (4KA4, Section 4.2.3), suggesting preferential reaction in the blend with the elastomer. This contrasted with PS, in which the largest torque rise resulted from the highest FRI:RA ratio (3KA5), though this was shown to be because of a predominance of TRIS self-polymerisation, rather than any improvement in modification effectiveness, resulting in a heavy loading of solids which was believed to be the main cause of the

Figure 5.21 **Analysis of processing torques and gel content / compositions for key reactively processed 70/30 PS (H311)/EPDM (V2504) blends & controls.**





KEY

	1KA7	1KA10	4KA7	2KA7	3KA7	2KA10	9KA8	5KA8	2KA8	3KA10	6KA10	7KA10
RA (5%)	nil	nil	TRIS	TRIS	TRIS	TRIS	DVB	DVB	DVB	DVB	TRIS +DVB	TRIS +DVB
FRI:RA (molar ratio)	nil	nil	nil	0.001	0.01	0.001	nil	0.001	0.01	0.01	0.001 /0.01	0.001 /0.01
+ FRI (%)	nil	0.05	nil	nil	nil	0.07	nil	nil	nil	0.07	nil	0.06

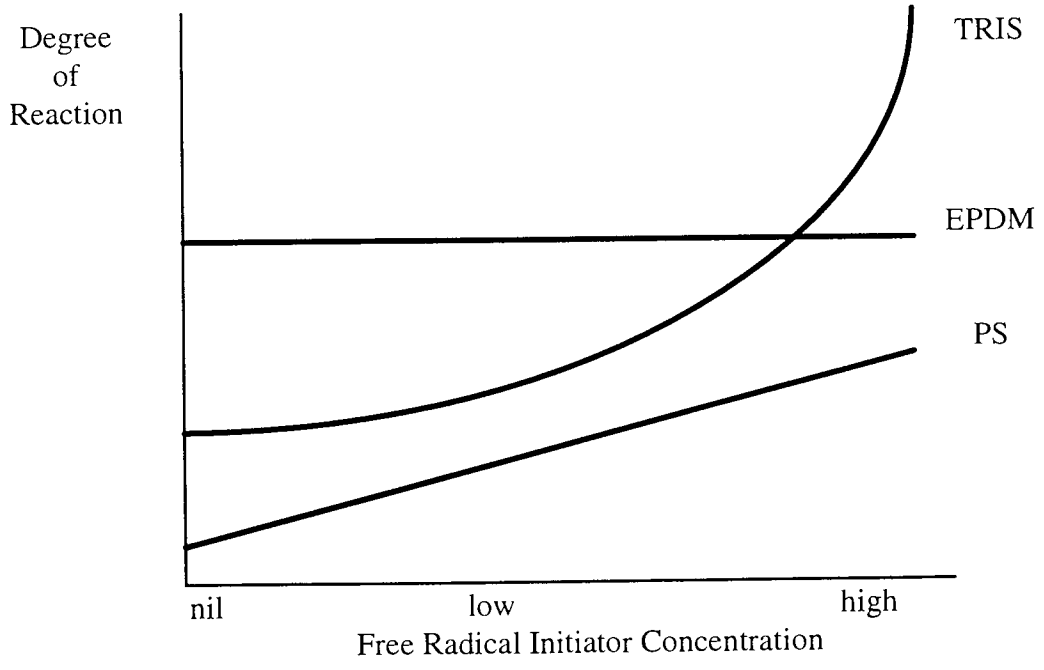
torque gain in PS (Section 4.3.2.1). The premise of limited PS reaction, in the blend also, even at high FRI concentration, was further supported by gel composition data (Table 5.7 Section 5.2.4 and Figure 5.21).

Total gel contents were high (14-17%) in all blends with direct TRIS additions, quite unlike the physical blend (1KA7), and increased slightly with FRI concentration. A distinct feature was that the fraction of PS within the total gel was much less than the EPDM proportion (Figure 5.21), rising to a maximum of 25% PS at the higher FRI:RA molar ratio (3KA7) ; supporting favored EPDM and limited PS reactions, though the latter was nevertheless improved slightly by raising initiator content. Moreover, in this high FRI blend (3KA7) there were significant solids, again indicating substantial TRIS polymerisation, which would also have contributed to the measured insolubles content. Assuming a similar amount of solids was produced as in PS at high FRI:RA (>3% : 3KA5, Table 4.11), then the true "interpolymer" gel may have been lower at 14-15%. This would have been closer to the gel given by TRIS addition without any FRI (4KA7), which had a similar final torque to 3KA7. Thus the maximum "true" interpolymer gel, excluding any polymerised TRIS solids, could well have resulted from the low initiator concentration (2KA7 : 0.001 FRI:RA = 16% gel). FT-IR analysis of this fraction (Figure 5.17 Section 5.2.5) was able to confirm a major presence of TRIS interlinking agent and both component polymers in the insoluble residue, with the EPDM content certainly higher than the 30% level in the as-processed blend and probably at a higher level than the PS, supporting compositional evidence from extraction analysis. 2KA7 also gave the highest torque response of this series and indeed for simple addition of TRIS to PS alone, low initiator concentration had been found to produce optimum grafting without significant TRIS self-reaction (2KA5 - Table 4.21, Section 4.3.2.1).

A key factor in determining the outcome of reactive blending PS and EPDM using TRIS interlinking agent thus appeared to be the effect of initiator concentration upon the relative degree of reaction of each component. A model for this effect could be visualised (Figure 5.22), which considering the routes for TRIS polymerisation (Scheme 4.3), TRIS reaction with PS (Scheme 4.4) and TRIS reaction with EPDM (Scheme 3.2), was believed to have a strong foundation.

For TRIS addition without any peroxide initiator, radical formation would only have been possible by thermal or mechanochemical inducement, obviously limiting the availability of reactive acrylate radicals. The most likely routes for reaction of initiated TRIS under these conditions would have been addition to free unsaturation in the EPDM (Scheme 3.2) and to a lesser extent self-polymerisation. This limited resource of acrylate radicals and absence of peroxide initiator would have had a particularly negative impact upon the generation of polystyryl radicals, believed to be critical in PS reaction (Section

Figure 5.22 **Proposed model of the effect of free radical initiator concentration on the degree of reaction of each component in PS/EPDM blends reactively processed with TRIS interlinking agent.**



4.3.1). This rationale fits well with the extraction results for this blend (4KA7, no FRI), which showed that the significant fraction of insoluble gel (14%) was comprised of a very minor PS portion and a 90% contribution from EPDM (Figure 5.21), presumably via the cross-linking of TRIS adducts (Scheme 3.2). Also in this blend, although there was no direct evidence to discount interlinking agent self-reaction, for PS alone under similar conditions (4KA6) TRIS polymerisation was minimal and indeed a large fraction remained unreacted after processing (Table 4.21; Section 4.3.2.1). Thus although addition without initiator was not conducive to reaction of TRIS and PS components, EPDM reactivity was unaffected, hence the starting positions of the curves in Figure 5.22.

At high initiator concentration there was a massive increase in TRIS polymerisation, as seen by the level of solids in both blend and PS cells (3KA7 and 3KA5), and estimated in the latter to account for more than 60% of the TRIS addition (Table 4.21). Such extensive polymerisation of the triacrylate monomer at high peroxide content was possible from initiation and reaction of each of the three equivalent acrylate end groups per TRIS molecule and branch growth from each alpha-carbon site after abstraction of labile tertiary hydrogens by further radical initiation (resulting in **XVIII** ; page 187). Considering the EPDM contribution to insoluble gel, there appeared to be no increase in the proportion reacted at high peroxide content compared with blends having less than or even zero FRI ; implying that the degree of EPDM reaction in blends was not dependent on initiator concentration (Figure 5.22). The basis for this may have been that EPDM reaction was limited by the low level of pendant unsaturation provided by the minor amount of diene monomer in the terpolymer (around 4% - Section 2.1). Even without any initiator, substantial EPDM reaction was indicated by torque gains (Section 4.2.3), perhaps due to almost complete saturation of available functional centers.

Appropriate analysis of the reactively processed EPDM products may have allowed confirmation of this.

In contrast, a high FRI:RA level was thought to encourage PS reaction by improving polystyryl radical generation due to both the added peroxide directly and the increased presence of initiated acrylate moieties (Scheme 4.4). Evidence for this in the blends was from increased PS incorporation in the interpolymer gel fractions as FRI content was raised, hence linking the degree of PS reaction to initiator concentration (Figure 5.22). However, no overall benefit was gained from enhanced reaction of PS at the highest FRI:RA level due to the predominance of TRIS self-polymerisation. This was shown by the solids loading in 3KA7 (Section 5.2.1.1), which compromised interpolymer yield. "Best effort" interpolymer gel was thus achieved at intermediate initiator concentration (2KA7), as reasoned earlier in this discussion, an identical relationship to that found for the level of TRIS grafting in PS alone (Table 4.21 Section 4.3.2.1). However, DSC analysis of this fraction (Section 5.2.6) showed both PS and EPDM component Tg's to be raised, in accordance with homopolymer modifications, hence "within-phase" rather than substantial "between-phase" grafting was indicated. This was nevertheless the most positive result for simple TRIS/FRI addition to blends and was believed to arise from a balanced position between improved PS initiation, minimal TRIS polymerisation and facile grafting with the EPDM, encouraging reaction of all components and some limited formation of the desired interpolymer.

Thus an important concept, in the application of interlinking agents for the reactive processing of polymer blends, was that optimisation of targetted interpolymer formation should be achieved under conditions which equalise differing component reactivities and avoid triggering excessive competitive processes.

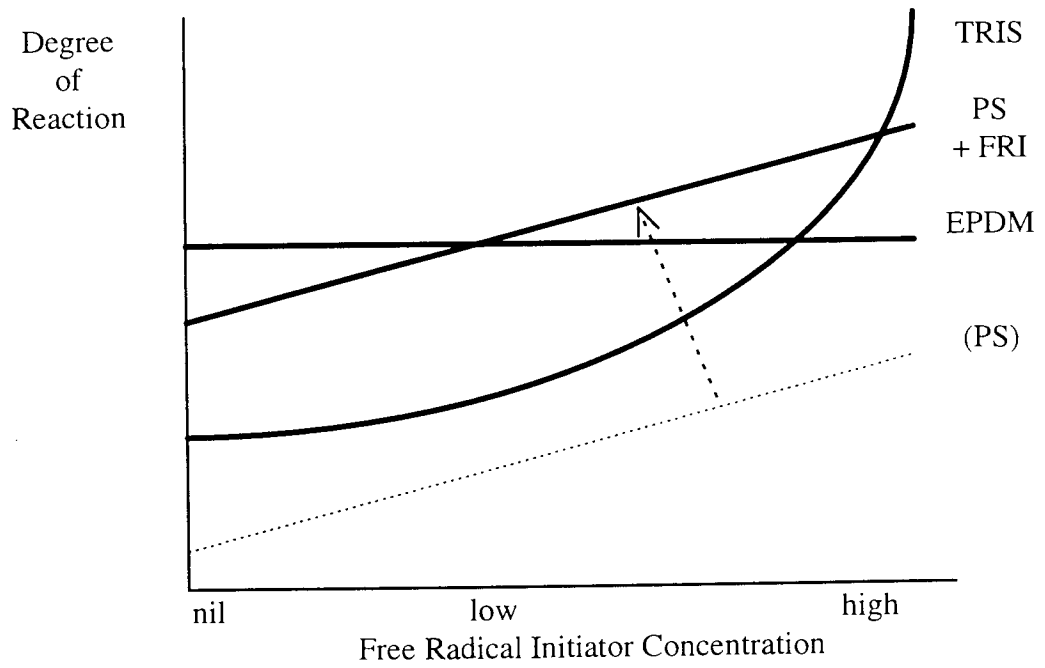
Two cases from the literature on PS blends add further weight to this argument. Pukanszky et al found that Lewis Acid catalysed mechanochemical grafting between PS and EPDM could be optimised according to the structure and diene content of the EPDM,[117] by minimising competitive degradation and cross-linking reactions, and that high Lewis Acid addition favoured grafting due to enhanced PS reaction.[118] Also, Rudin and Teh[123] explored the concept of "within phase" versus "across phase" reaction in PS/PE blends with dicumyl peroxide/TAIC (triallyl isocyanurate) additions, spotting a preference for PE-PE cross-linking at low initiator additions. However, although "across phase" grafting was confirmed at high TAIC, massive PS degradation was also suggested, but ignored even though high peroxide additions had been used, adversely affecting blend properties. Thus in this case there had been a serious imbalance between enhanced interpolymer reaction and competitive, disadvantageous degradation.

The strategy of improving PS reactivity in-situ by peroxide-initiated polystyryl radical formation, using FRI pre-addition, had been found to be successful in raising TRIS grafting to PS alone (3KA6 & 5KA6 - Table 4.21, Section 4.3.2.1). Application of this scheme in PS/EPDM blends was also most satisfactory ; high peak and final torques indicated the occurrence of substantial reactive events in this cell and although total gel content may not have increased, the proportions of PS and EPDM in the interpolymer were reversed, so that the PS contribution was an astonishing 80% (2KA10 - Figure 5.21). However, a by-product of FRI pre-addition was the possibility of PS cross-linking, as indicated by the extreme swelling during dichloromethane extraction (Table 5.6) and may have caused an indeterminate under-estimation of the total gel level due to losses by swelling during extraction. Furthermore, thermal analysis of 2KA10 residue (Section 5.2.6) revealed a significant rise in the EPDM portion Tg and absence of any transition

from PS, which was taken as a good indication of effective cross-reaction between PS and EPDM to the extent that the substantial PS content must have been efficiently grafted throughout interpolymer as micro-domains below the scale at which an independent glass transition would be discernible by DSC.[157]

This net positive effect fitted well with the model proposed earlier, by considering the degree of PS reaction to be shifted upwards on initiator pre-addition (Figure 5.23). A possible mechanism for this shift was that the polystyryl macro-radicals generated during pre-mixing were available for increased cross reaction with EPDM and active unsaturation in added TRIS, thus reducing the significance of acrylate radical reactions. Further improvement in interpolymer formation could be predicted by reference to the adjusted model and the results of modification analysis in PS alone ; at lower or even zero FRI intimate with TRIS addition the efficiency of useful interlinking agent grafting to polymer could be maximised by eliminating self-polymerisation (cf PS : 3KA6 - Table 4.21). With

Figure 5.23 Proposed model of FRI pre-addition on the degree of PS reaction in PS/EPDM blends reactively processed with TRIS interlinking agent.



hindsight the importance of such a test cell in confirming the initiator pre-addition shift factor in a blend is obvious, but during the processing phase was not considered to offer this opportunity. Another area for further development would be in limiting the extent of PS cross-linking by this approach, perhaps by optimising the relative timings of initiator and interlinking agent additions, which may be simpler using a larger scale, versatile twin-screw extruder for blend processing.[1-3]

5.3.2 Optimisation of PS/EPDM Reactive Blending using DVB and TRIS+DVB Interlinking Agents.

The alternative, divinylbenzene reactive agent was found to produce quite contrasting results to the triacrylate modifier in PS/EPDM blends, but understanding of the mechanisms involved was consistent with previous developments. The pattern of considerable torque changes, from well below to much higher than control levels, according to initiator concentration in the DVB additions, was identical in both 70/30 PS/EPDM and 100% PS test cells (Figures 5.2 and 4.4). However, only limited insight into reaction outcome could be obtained from the PS study. A possible affinity between PS and DVB was inferred, but only from torque behavior having the largest range of torque changes with FRI content, since the structural similarity of the aromatic reactive agent and PS polymer prevented qualification of modification effectiveness (Section 4.3.2.2). This was not so in blends, for which extraction analysis confirmed reaction of PS on DVB addition.

A positive link was shown for the gel content and torque level dependence on initiator concentration in these blends, though of more interest were the corresponding gel compositions (Figure 5.21). At zero or low FRI:RA (9KA8 and 5KA8) insoluble gel appeared to have been formed almost totally from the PS component. DSC analysis of the 5KA8 gel fraction did show a weak EPDM transition, but there was a major presence of

PS and both Tg's were shifted to slightly higher temperatures indicating some degree of modification, though not necessarily "between-phase" interpolymer formation. At high initiator (2KA8 ; with the highest gel fraction of all cells) EPDM was in the ascendancy, limiting PS to a 21% contribution. This suggested that DVB reaction was more specific to PS at low degrees of initiation in the PS/EPDM blends, yet at higher levels reaction with EPDM became favourable.

The suitability of DVB for reaction with styrenic polymer was thought to be due to the chemical similarity of the modifier and PS. A measure of this was the adjacency of solubility parameters for PS and DVB (9.2 versus 10.8 $cal^{1/2}$ $cm^{3/2}$), the latter estimated using Small's method.[150] This predicted miscibility of DVB in PS. In blend/DVB mixtures, since the EPDM value was considerably lower (7.7 $cal^{1/2}$ $cm^{3/2}$), partition of DVB into the PS phase could be postulated. This could also help to explain the extreme plasticising effect for DVB addition without initiator to PS alone (by processing torques, Figure 4.4, and Tg measurement, Section 4.2.10, for 3KA8) and limited torque development in the 9KA8 blend (Figure 5.2 & 5.21), even though some reaction of PS was shown to have occurred by gel analysis (Table 5.6 and Figure 5.21) presumably via thermally generated DVB radicals (Section 4.3.1.3). With the introduction of low peroxide concentration, greater DVB initiation and hence within-phase PS reaction was caused, resulting in the higher yield of predominantly PS-containing gel (5KA8). DSC of 5KA8 did show some modification of the EPDM component in both the entire blend and a minor presence in the gel fraction (Section 5.2.6), but the major effect appeared to be in the PS phase ; Tg was raised in both the residue and blend, in which a significant second transition just above that of the PS was discernible. This may have been a partially cross-linked PS fraction responsible for slight swelling during extraction (Table 5.6).

For substantial reaction of EPDM at high FRI content (2KA8), the effect of DVB partition into the PS phase must have been negated. Since these conditions produced the greatest rate of post-addition torque rise (Figure 5.2), then kinetic factors may have been involved. One possible mechanism was that with sufficient peroxide the rate of radical initiation exceeded the rate of DVB diffusion into the PS phase, allowing competition between non-specific reactions, so that facile addition of initiated DVB to unsaturation in EPDM became the dominant process ; hence the high EPDM and reduced PS proportions in the considerable gel fraction (2KA8 - Figure 5.21). By following this reasoning, to redress the balance between EPDM and PS incorporation in the interpolymer gel, then perhaps an intermediate initiator concentration would have been more effective.

Effects of DVB self-reaction were not obvious even at this higher peroxide loading; the cross-link density of fully polymerised DVB, a difunctional reagent, would have been lower than that of the triacrylate modifier and may perhaps have remained miscible with the PS phase anyhow. Indeed in PS alone, even at high FRI:RA, there were no solids contamination and only around 10% was quantified as insoluble, fully networked product (Section 4.3.2.2). Other factors may also have been involved in preventing DVB-EPDM reaction below a critical degree of initiation (cf the limited torque gains of EPDM + DVB at low FRI:RA molar ratio ; 6KA8 - Section 4.2.4), such as the enhanced stability of benzylic radicals and partial ethyl substitution of the DVB (Section 4.3.1.3) or a competitive influence from EPDM main chain reaction via initiated ethylene and propylene units (Section 3.3.3.1).

The combination of DVB, as an effective PS modifier, and the use of peroxide pre-addition to PS in the blends was found to be disadvantageous compared to the best simple addition of DVB at high initiator level ; in 3KA10 torque functions, measured gel content and PS contribution were all lower than in 2KA8 (Figure 5.21). However, on extraction of

3KA10 extreme swelling was observed (Table 5.6), causing inestimable losses and thus invalidating the measured gel and PS contents. This indicated substantial interference by PS cross-linking on pre-initiation, seen previously to a lesser extent with TRIS (Section 5.3.1). With DVB though, raising PS reactivity further may have intensified cross-linking processes, hindering interpolymer formation.

It was apparent that for optimised interpolymer formation there was a need to unlock reaction of both polymers, but under conditions that would not also release excessive competitive processes. One attempt to achieve this was a combined addition package of TRIS+DVB reagents. The intention was to target in-situ modification of each polymer with favoured modifier, simultaneously with cross-reaction of the two interlinking agents. In the absence of initiator pre-addition, combined reagents produced similar gel and torque levels to TRIS alone, yet the insoluble fraction became almost entirely composed of EPDM (6KA10 - Figure 5.21). This suggested that the preferred reaction pathways from TRIS and DVB alone at the appropriate FRI contents (2KA7 & 2KA8), both involving EPDM, were amplified when combined, to the almost total exclusion of the minor PS reaction. Also this blend was also the only one without FRI pre-addition to swell during extraction (Table 5.6), perhaps due to a higher degree of DVB cross-linking by EPDM grafting and partial copolymerisation with trifunctional TRIS.

The use of both reactive agents with initiator pre-addition however, produced the highest yield of apparently near-optimum interpolymer (7KA10 - Figure 5.21). Torque functions were similarly high corresponding to the major changes caused by significant reaction within this blend. Further evidence of this was the extreme swelling during extraction (Table 5.6), such that the measured gel level may have been even higher if not for the losses caused by this behaviour, which was indicative of PS cross-linking.

Nevertheless, the most satisfying result for this cell was the near equal contribution of PS and EPDM in the interpolymer. This was confirmed, but not quantified, by infra-red analysis of 7KA10 gel (Figure 5.18a Section 5.2.5) which showed the significant presence of PS, EPDM and TRIS in this fraction. Furthermore the thermal behaviour of the whole blend and gel produced characteristic glass transition shifts, particularly in the gel with loss of the PS Tg (even though FT-IR confirmed its presence) and broadening of the EPDM Tg, that were indicative of substantial "between-phase" PS and EPDM grafting (Section 5.2.6). Almost balanced reaction of components thus appeared to have been achieved in this instance, in a fashion consistent with the understanding developed previously. In 6KA10 the failing of simple combined reactive agent addition had been exclusion of PS reaction, whereas by pre-initiation of the reluctant PS component its reactivity was raised sufficiently for appropriate modification (Figure 5.23) and hence interpolymer formation via interlinking agent with EPDM.

5.3.3 Evidence and Effects of the Compatibilisation of PS/EPDM Blends by Reactive Processing with Interlinking Agents.

Previous discussions have been concerned primarily with the progress and outcome of chemical events during the reactive processing of PS/EPDM blends with interlinking agents. However as yet, two equally important questions have not been fully resolved ;

i. - do different reaction outcomes actually influence the level of compatibility between the immiscible components of the blends ?

ii. - are there consequent improvements in physical characteristics of blends compatibilised by reactive processing ?

A principle measure of compatibility applied almost universally in polymer blend studies (see Sections 1.3 and 1.4) is the reduction in phase size upon compatibilisation. This results from the minimisation of interfacial energy by enhanced molecular interaction

at phase boundaries, which also raises the adhesion between otherwise weakly bonded dissimilar phases, contributing to potential improvements in physical properties.[19] Thus from morphological examination by SEM (Section 5.2.3), judgments on the relative compatibility of key reactively processed and control blends could be made (Table 5.11), support ascertained from blend thermal analysis (Section 5.2.6), and correlation attempted with resulting tensile properties (Section 5.2.2) and predominant reaction outcomes (Section 5.3.1 & 5.3.2).

For all reactively processed blends which yielded significant polymer modifications, morphology was indicative of increased blend compatibility to varying degrees depending on predominant reaction outcome (Table 5.11). However, in many cases this did not produce advantageous change in tensile properties ; thus factors other than the degree of compatibility must also be important. Two other factors also apparent from this work were blend morphology and the effects of competitive processes, acting either throughout the system as a whole or within one phase only and having a localised effect on the characteristics of that one component. All factors were evident in many of the blends, as exemplified in the following discussions.

1. **Morphology** - for 4KA7 (TRIS, nil FRI), with the facile EPDM reaction predominant over limited PS grafting, compatibility level was raised, but only to a limited extent, such that the semi-continuous morphology of the physical blend was maintained. Since this was an advantageous condition, offering a degree of load sharing by the interlocked component domains, enhanced by some further improvement in stress transfer across partially miscibilised phase boundaries, increased tensile properties were realised, producing the highest stress to break of all cells. A similar effect was shown in 6KA10 (mixed RAs) from the same reaction outcome. In contrast, for 2KA7 (TRIS, low

Table 5.11 **Correlation of blend compatibility (from morphology) with tensile properties and predominant reaction outcomes for key reactively processed and control 70/30 PS/EPDM blends.**

Sample Cell (RA, FRI:RA)	Morphology (Figure)	Compatibilty	Tensile Properties		Predominant Reaction Outcome
			Failure	Overall Performance	
1KA7 (inert)	semi-continuous large phases (5.5)	low	yield	baseline	none
4KA7 (TRIS nil FRI)	semi-continuous smaller phases (5.8)	limited gain	yield	improved, highest σ_b	major EPDM
2KA7 (TRIS 0.001)	fine dispersed phase in coarse matrix (5.7)	raised	brittle	reduced	interpolymer formation (high EPDM)
3KA7 (TRIS 0.01)	semi-continuous large phases + particles (5.6)	low	brittle	reduced	polymerisation of TRIS
2KA10 (TRIS 0.001 +FRI)	dispersed phase in coarse matrix + inclusions (5.11)	raised	brittle	ε_b and σ_b improved, E reduced	interpolymer formation (high PS) + PS cross-linking
5KA8 (DVB 0.001)	fine dispersed and matrix phases (5.9)	raised	yield	maintained	almost exclusively PS
2KA8 (DVB 0.01)	very fine dispersed and matrix phases (5.10)	highly raised	brittle	σ_b improved	interpolymer formation (high EPDM)
3KA10 (DVB 0.01 +FRI)	fine dispersed and matrix phases (5.12)	raised	brittle	neutral, E reduced	interpolymer formation (high EPDM) + PS cross-linking
6KA10 (mixed RA/FRI)	fine dispersed and matrix phases + semi-continuous regions (5.13)	limited gain	brittle	ε_b and σ_b improved, E reduced	major EPDM + suspected PS cross-linking
7KA10 (mixed RA/FRI + FRI)	fine dispersed and matrix phases + inclusions (5.14)	raised	brittle	improved, highest ε_b E reduced	interpolymer (high PS + EPDM) + PS cross-linking

Note : σ_b - stress to break ; ε_b - elongation to break ; E - tensile modulus

FRI:RA), with some interpolymer reaction effected, down-sizing and dispersion of the second phase resulted from raised compatibility. However, since morphology was no longer advantageous, irrespective of apparent miscibilisation, tensile performance was reduced, demonstrating the importance of the morphological factor in determining ultimate blend properties.

2. **Competitive effects across the whole system** - 3KA7 (TRIS high FRI:RA) was a prime example of this, where polymerisation of the TRIS was predominant, compatibility enhancement was not affected, and although a semi-continuous morphology was maintained tensiles were reduced, presumably due to stress concentration and failure from the presence of resulting polyTRIS solid particles.

3. **Within phase competitive effects** - in every case where cross-linking of PS was indicated, particularly with FRI pre-addition, tensile modulus was reduced (2,3,6 and 7KA10), suggesting that this outcome affected the properties of the matrix phase. However, significant grafting with the rubbery EPDM component in some of these cells may also have contributed to the reduced product stiffness, weakening this "within-phase" hypothesis. Perhaps better examples were 2KA7 (TRIS, low FRI:RA) and 5KA8 (DVB, low FRI:RA), since these were characterised by almost exclusive "within-phase" reaction. For 2KA7 EPDM reaction was predominant (shown as the major constituent of the gel fraction by extraction and FT-IR) and although modification of both components was shown by increased glass transitions in entire blend and gel portions these effects were believed to be localised within each phase rather than between. This was common to 5KA8, but in this case reaction was almost exclusively within the PS matrix. Near similar physical behaviour was seen for both 2KA7 and 5KA8 ; blend phase size was reduced, in accordance with raised compatibility but tensile properties were not advantageous, even for 5KA8 which showed yield failure presumably due to DVB modification of the PS.

4. **Compatibility level** did nevertheless have some positive influence on blend characteristics. One example was shown by the highly compatibilised 2KA8 (DVB, high FRI:RA) providing improved tensile performance over the less miscibilised 5KA8 (DVB, low FRI:RA). This was believed to have been achieved by the enhancement of interpolymer reaction in 2KA8, resulting in sufficiently increased interfacial adhesion to overcome the unfavourable dispersed-phase morphology with consequent improvement in bulk properties.

It appears that the most specific requirement for realising the potential physical benefits of blend compatibilisation by reactive processing was thus optimisation of "between-phase" interpolymer formation. In 2KA10 (TRIS, low FRI:RA, with FRI pre-addition) this was achieved through initiator pre-addition to the PS, enhancing reactivity of this otherwise quite inert component and increasing cross-reaction with EPDM to the extent that the insoluble gel portion, believed to contain a high level of PS (from extraction analysis) gave only a single Tg by DSC analysis, shifted upwards from the EPDM position. 7KA10 (mixed RA + FRI and FRI pre-addition) showed the exact same thermal behaviour, though was by far the "star" performer, producing the highest interpolymer gel content of near equal PS and EPDM composition (Table 5.7). Both 2KA10 and 7KA10 had improved tensile properties (except for modulus, due to elastomer grafting ?) as the result of increased compatibility shown by dispersed morphologies and component Tg shifts in whole blends. Indeed 7KA10 showed the highest elongation to break of all cells, suggesting increased interaction within the interfacial zone of this blend, realising the potential of effective compatibilisation by apparently optimum interpolymer formation.

The modification of blend miscibility by reactive blending and the importance of the above factors in determining the ultimate performance of resulting blends may be

further substantiated by reference to the relevant literature (Section 1.4), where examples consistent with the effects seen in the present work can be found. Morphology has also been found in other studies to have a particular influence, especially in attempting rubber toughening via reactive blending ; as with blends of oxazoline-containing PS and carboxylated acrylonitrile-butadiene rubber (Fowler and Baker[112]) in which, at high levels of reaction and apparent compatibilisation, the elastomeric phase size was reduced to below the optimum for improvement in impact properties.

Another effect, common with the present work, in PS/PE blends with triallyl isocyanurate reactive agent (TAIC - van Ballegooie and Rudin[112]), was the dominance of a two-phase co-continuous morphology on blend properties independent of the outcome of reactive processing for certain compositions.

The negative effects of competitive degradation of components have also been seen in the reactive processing of other blends, typically through the reduction of component molecular weight ; as with blends of polyamide 6/sulphonated PS[115] and for high additions of TAIC/dicumyl peroxide to PS/PE blends.[123] Another within-phase competitive effect was found by Cheng and Hwu[127] whereby unreacted styrene-maleic anhydride copolymer, added as a reactive compatibiliser, was believed to cause embrittlement of the polyamide 66 phase in blends with PS.

In many such cases it appears that the effects detailed above (and others) prevent guaranteed improvements in blend performance on compatibilisation by this route. However, suitably targetted reactive processes, in the absence of these competitive factors, can produce improved blend characteristics by enhanced miscibility. One instance of this was shown by Willis, Favis and Lunt[124] using blends of polystyrene-co-maleic anhydride and bromobutyl rubber, in which impact strength improvements were achieved only at high additions of dimethylaminoethanol reactive agent and believed to be solely due to

increased interfacial adhesion, without any morphological change, from high levels of specific co-reaction between components (Scheme 1.7, Section 1.4.4).

Findings of the present research are thus consistent with, and indeed bring together, many principles of reactive compatibilisation derived from critical analysis of previous studies. Of particular satisfaction is the agreement of these principles with the scheme proposed earlier to show the interrelationships between influencing factors and compatibilising effects on the performance of immiscible blends (Scheme 1.8, Section 1.4.5). Thus although reactive processing offers effective compatibility enhancement of immiscible blends, according to the degree of reaction between components, this results in potential improvements in physical performance, which are only realised according to the influence of other important factors also affected by the outcome of reactive processing. The use of interlinking agent technology in this application has not provided a full solution, but has enabled a greater understanding of this problem to be developed.

5.3.4 Overall Effects and Perspective.

In this assessment of a one-step reactive blending process for the compatibilisation of otherwise immiscible PS/EPDM blends, a main objective was to target free radical reaction of both polymers with polymerisable interlinking agent for the in-situ formation of interpolymer to act as an effective compatibilising agent. "Between-phase" reaction of the dissimilar components was thus necessary to yield the required PS- + EPDM-containing products, under conditions suitable for the simultaneous modification and interlinking of both polymers, without favouring "within-phase" competitive effects. The difficulty of this was intensified due to the recognised inertness of PS, in combination with readily reactive EPDM and addition of easily polymerisable modifiers. Nevertheless, towards the end of this programme it became clear that this could be overcome by the

control of particular factors to target specific reactive processes, thus achieving optimised interpolymer formation.

From the many PS/EPDM blends processed and analysed, the learning gained from studies on component polymer modifications and the understanding developed on possible reaction mechanisms within and between components, principle factors believed to be involved in the reactive processing of immiscible blends with interlinking agents were deduced. These were :

i. - the reactivity of constituent polymers and hence blend composition ;

ii. - addition level and physico-chemical nature of the interlinking agent ;

iii. - the concentration and application route of free radical initiator.

The primary mode of action of these factors in combination was to influence the balance between different reactions routes possible within and between components, limiting the conditions under which sufficient and suitable interpolymer would result.

In line with the above factors, the important features of TRIS & DVB addition to PS/EPDM blends that were believed to have major effects on the outcome of reactive processing were :

i. - the reluctance of PS reaction and incorporation into interpolymer, unless sufficient polystyryl radicals could be initiated at an appropriate time in the process to overcome otherwise favoured competitive reactions ;

ii. - extremely facile reaction of EPDM by addition of available radicals to pendant unsaturation in the diene units ;

iii. - the ease of polymer modification by grafting of TRIS at low levels of acrylate radical generation ;

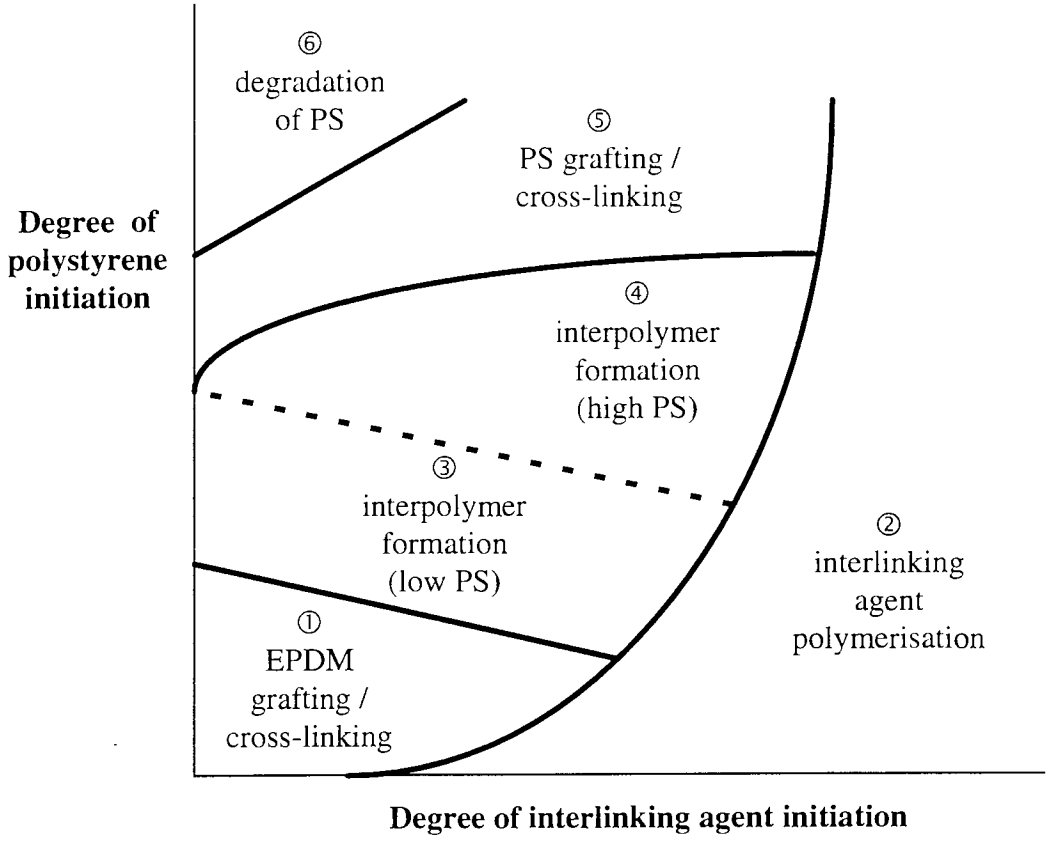
iv. - the extent of highly cross-linked gel formation by triacrylate polymerisation at high levels of initiation ;

v. - affinity of the structurally similar DVB for modification of the PS component, unless a high enough degree of initiation allowed EPDM reaction to occur before partition into the PS phase could be affected ;

vi. - the dependence of reaction rate and extent for both modifier and PS on the free radical initiator concentration and its route of application.

By mapping the predominant outcomes of these effects according to the range of conditions and different approaches attempted, it was possible to build up an overall perspective of the reactive processing of PS and EPDM blends with interlinking agents (Figure 5.24). This picture was believed to be consistent with the mechanisms thought to operate within the blends, based on a successful test of this theory by comparison of the predicted outcomes for key regions with actual results (Figure 5.24). This proved to be most satisfactory in that not only did this thesis match the results and understanding of this present study, but also fitted the outcomes of published research examined earlier (Section 5.3.1). Thus perhaps the general principles offered by this overall perspective may have universal application in the selection of appropriate polymer blends and suitable interlinking agents to harness the full potential of the chemical modification of polymer blends by reactive processing.

Figure 5.24 **Overall perspective of the predominant outcomes from the reactive processing of PS/EPDM with interlinking agent (IA).**



Test of Key Regions vs Actual Outcomes.

Region	Predicted Outcome	Actual Results
① low IA + PS initiation	EPDM grafting / cross-linking	- 4KA7 (TRIS, nil FRI) - 6KA10 (mixed RA) + Rudin & Teh[123] : PE-PE dominant at low FRI with TAIC
② very high IA initiation	IA polymerisation	- 3KA7 (TRIS, high FRI)
③ high IA + low PS initiation	Interpolymer formation (low PS content)	- 2KA7 (TRIS, low FRI) - 2KA8 (DVB, high FRI)
④ low to high IA + high PS initiation	Interpolymer formation (high PS content)	- 2KA10 (TRIS, low FRI + FRI pre-addition) - 7KA10 (mixed RA + FRI pre-addition) + Pukanszky[118] : high PS-EPDM grafting at high Lewis Acid additions
⑤ high PS initiation	PS grafting / cross-linking	- 5KA8 (DVB, low FRI) - 3KA10 (DVB, high FRI +FRI pre-addition)
⑥ very high PS initiation	PS degradation	+ Rudin & Teh[123] : at high TAIC/ROOR addition, PS MW reduced in PE/PS

CHAPTER 6.

CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK.

6.1 CONCLUSIONS.

The primary objective of this research was to examine the general concepts of the reactive processing of immiscible polymer combinations using interlinking agents for the in-situ synthesis of interpolymer, with the intention of enhancing blend compatibility and hence performance. This has been largely achieved by through the "pegs-in-the-ground" approach adopted in this work by the establishment of an experimental-scale reactive blending process and assessment of various analytical techniques for the determination of modification effectiveness. Greater understanding of the chemical and physical processes involved was developed, to the extent that advantageous effects were successfully targeted in the challenging, immiscible PS/EPDM blend system examined. Specific conclusions in support of this, from the different areas of endeavour, were thus as detailed below.

1. An experimental-scale operation was identified to provide a practical and versatile method of simultaneous melt blending and reactive processing of both polymers with interlinking agents, without the imposition of any significant interfering factors (Chapter 3). This was by manual injection of fluid reactive agent and free radical initiator mixture directly into molten polymer during mixing within a laboratory-scale HAMPDEN-RAPRA internal mixer coupled to a BRABENDER drive and torque recording unit (Scheme 2.3, Section 2.2). Accurate additions of precise reactive agent / free radical initiator (RA/FRI) mixtures to homogenised melt blends, under controlled process conditions, were possible with minimal complexity. Torque changes on RA addition were distinct and quantifiable, providing a means of monitoring the dynamics of reactive blending and allowing clear

differentiation of process effects, for which sound rationales of the underlying physical and molecular changes could be proposed (Section 3.3.2).

2. Principle concepts of PS/EPDM reactive blending using a triacrylate interlinking agent (TRIS) were determined by examination of the influence of key process variables, namely blend composition, TRIS addition level and mixing speed, on the torque behaviour during processing (Chapter 3) ;

i. - **blend composition** was the prime determinant in the magnitude of torque changes on reactive processing with 5% TRIS addition at 0.001 FRI:RA molar ratio. Significant torque rises above control levels were only apparent in EPDM or high EPDM content blends (Figure 3.10). This was believed to be due to facile reaction between initiated triacrylate units and pendant unsaturation in the EPDM, leading to substantial modification and possible cross-linking of the elastomer (Scheme 3.2, Section 3.3.3).

ii. - **TRIS addition level** ; this increased the degree of torque rise at higher additions in both 70/30 and 30/70 PS/EPDM blends (Figure 3.6), but was concurrent with a heavy loading of coarse solids at high RA levels (8%), which was considered to be the result of greater TRIS self-polymerisation under these conditions (Scheme 4.3, Section 4.3.1).

iii. - **mixing rate** altered the timing, but not the extent, of torque changes during reactive processing, indicating mass transfer of viscous components to be a main rate limiting factor, not reaction kinetics.

From these variables, suitable operating windows for the optimisation of reactive blending were defined to minimise the effects of competitive processes. These were ;

5% addition of reactive agent, to 70/30 PS/EPDM blends, at a mixing rate of 60rpm.

A principle aspect of these early reactive blends was the lack of any substantial indication of PS modification, even though blend compatibility (from morphology of 70/30 PS/EPDM - Figure 3.8, Section 3.2.3) was nevertheless improved. Unlocking PS reaction, in the presence of facile EPDM and TRIS reactions, thus appeared to be the key to enhancing blend modification by this route.

3. The effectiveness of polystyrene modification by reactive processing with interlinking agents was increased by the application of a greater understanding of possible reaction mechanisms (Section 4.3.1) for the selection of process conditions to target specific reaction routes and by the assessment of a chemically more compatible modifier, divinylbenzene. For the determination of PS modification a scheme of solvent extraction, fraction separation and FT-IR analysis was developed (Scheme 4.1). This was suitable for the measurement of TRIS binding (Section 4.2.7), but did not allow DVB to be quantified due to its structural similarity to PS (Section 4.2.8).

NMR spectroscopy of PS precipitate fractions ("P" Scheme 4.1) in deuterated chloroform solution was limited in the determination of PS modification effectiveness (Section 4.2.9). Proton NMR showed positive identification of TRIS modification only in one instance (2KA5 : Figure 4.20). ^{13}C NMR gave no positive confirmation of modifier in any PS precipitate fractions and thus neither technique was able to provide a means for the measurement of absolute modifier grafting levels. However, the presence of additional, slightly shifted, intense aromatic PS resonances in ^{13}C NMR spectra was believed to give indication of increased modifier grafting frequency at tertiary carbon sites along the PS backbone in certain compositions (Section 4.2.9).

Precise measurements of PS glass transition temperatures were obtained by DSC analysis (Section 4.2.10) ; major differences were resolvable between whole PS

compositions according to process formulations but were not significant in precipitate fractions (Table 4.20). By combination of the teaching from these analyses and process behaviour, the influence of key process conditions on the outcome of PS reactive processing with TRIS and DVB was thus realised ;

i. - **initiator concentration for triacrylate interlinking agent**, expressed as the FRI:RA molar ratio, was crucial in balancing the degree of PS modification by reactive agent and the extent of self-polymerisation of the modifier. TRIS binding to PS was raised from 50% for an addition of 5% TRIS without initiator, to 65% at a low peroxide concentration (0.001 FRI:RA molar ratio : 4KA6 vs 2KA5), which also raised TRIS polymerisation (Table 4.21, Section 4.3.2.1). At high FRI:RA (0.01 molar ratio) binding was reduced to 40%, with the remaining TRIS yielding self-polymerised solids (3KA5). Optimum initiator concentration for TRIS was thus 0.001 FRI:RA molar ratio (2KA5). It was postulated that this produced sufficient initiation of the acrylate modifier to encourage polystyryl radical generation (the critical intermediate for subsequent addition reaction to unsaturation in TRIS : Section 4.3.1.2) without causing excessive initiation of triacrylate functionalities and avoiding extensive self-reaction of the interlinking agent.

ii. - for **divinylbenzene** the highest FRI:RA (0.01 molar ratio) gave the greatest torque changes and rise in PS glass transition (1KA8 : Figure 4.33 and Table 4.20). This was without any obvious solids formation or major insoluble residue, which was taken as evidence for limited effectiveness of DVB self-polymerisation and PS cross-linking. For the addition of DVB without initiator the primary outcome was extreme plasticisation of the PS by unreacted modifier, indicated by torque behaviour (Figure 4.33) and confirmed by a reversible reduction in PS glass transition temperature (Section 4.2.10). On this basis, in the absence of a direct measurement of PS modification by divinylbenzene, 0.01 FRI:RA molar ratio appeared to be the best effort for a 5% addition of DVB to PS.

Several factors arising from the structure of DVB were proposed to account for its behaviour (Section 4.3.2.2), but because of the similarity of PS and DVB, which was believed to influence modification effectiveness, product analysis was insufficient to confirm these effects.

iii. - **pre-addition of free radical initiator** to polystyrene prior to processing and reactive agent addition was particularly beneficial in the enhancement of TRIS grafting to PS and in minimising polymerisation of the interlinking agent (Section 4.3.2.1). Binding was raised to 80% for the direct addition of TRIS alone to FRI pre-treated PS, without any evidence for self-polymerisation (3KA6 : Table 4.21), yet with distinct indication of increased modifier grafting frequency along the PS backbone from the ^{13}C NMR spectrum (Figure 4.28, Section 4.2.9). For TRIS at the optimum FRI:RA combined with FRI pre-addition, binding was also improved (75% vs 65% : 5KA6 vs 2KA5) and TRIS gel formation reduced, but not excluded. Furthermore in this case increased graft frequency was not shown by ^{13}C NMR, supporting more extensive growth of polyTRIS networks from occasional PS graft sites (Section 4.3.2). However, a side-effect of this approach was a degree of PS cross-linking, apparent by swelling on solvent extraction and the highest gain in PS Tg found (Section 4.2.10), further supporting enhanced reaction of PS. The principle of this novel concept was to target polystyryl radical formation directly, for addition to active unsaturation in the modifier. This was preferable to the reliance of PS initiation on acrylate radicals, which was in competition with much more facile triacrylate polymerisation. Initiator pre-addition did not appear to be effective for DVB ; analysis was insufficient to fully rationalise the reason why (Section 4.3.2.2).

From these investigations into modification of the relatively inert polystyrene component, effective strategies to increase PS reaction were thus achieved, particularly

with the triacrylate modifier for which an overall model of reaction outcomes could be proposed (Scheme 4.7, Section 4.3.2). This learning was then applied with greater confidence and understanding in the optimisation of PS/EPDM reactive blending with interlinking agents.

4. In the optimisation phase of PS/EPDM reactive blending, strategies to enhance PS reaction in the presence of EPDM and reactive agent, and hence improve in-situ formation of suitable interpolymer for compatibilisation, were successfully examined (Chapter 5). A scheme of analysis to determine the amount and probable composition of interpolymer gel was devised, using sequential extraction of soluble fractions (Scheme 2.4 and Section 5.2.4), from which the degree of reaction of each component was inferred (Section 5.3.1). This was supported by DSC and FT-IR analysis of whole blend and insoluble gel fractions for important cells (Sections 5.2.6 & 5.2.5). Compatibility modification was assessed by measurement of blend tensile properties (of pressed films - Section 5.2.2) and from examination of blend morphology by SEM (Section 5.2.3). The major outcomes of the strategies evaluated were ;

i. - **for TRIS addition, initiator concentration** had the maximum positive effect at 0.001 FRI:RA molar ratio ; torque rise was higher than the others of this series and the 16% gel content was believed to be an intimate mixture of TRIS-modified PS and EPDM. Only a minor PS contribution was incorporated however (2KA7: Figure 5.21, Section 5.3.1) ; 18% by extraction analysis, qualitatively substantiated by FT-IR of the gel fraction, an analysis which also confirmed the significant presence of triacrylate interlinking agent in this residue (Figure 5.17, Section 5.2.5). Component Tgs in the insoluble gel were raised in line with homopolymer modifications, thus "within-phase" grafting of TRIS to each blend component was believed to be predominant (Section 5.3.1). Compatibility

between PS and EPDM was nevertheless improved over the physical blend (1KA7), TRIS addition without FRI (4KA7) and for higher FRI:RA (2KA7 : Table 5.8, Section 5.3.3).

Dependence of the overall outcome of PS/EPDM blend reactive processing on free radical initiator concentration was believed to arise from the effect of this factor on the degree of reaction of each component (Figure 5.22, Section 5.3.1), due to their principle reaction mechanisms ;

- PS was considered to react principally through polystyryl radicals, generated via acrylate radicals or directly by peroxide initiator (Scheme 4.4, Section 4.3.1), such that the degree of PS reaction was predominantly low, but raised at higher initiator concentration.

- EPDM reacted by facile addition of radicals to unsaturation in the minor diene content of the terpolymer (Scheme 3.2, Section 3.3.3), and was thus readily modified or incorporated into interpolymer, independent of initiator concentration.

- acrylate functionalities in TRIS were readily reactive via peroxide initiation and subsequent addition to active unsaturation in other units (Scheme 4.3, Section 4.3.1). Due to its trifunctionality, TRIS reaction was especially prevalent at high initiator concentration, resulting in predominant self-polymerisation and extensively cross-linked, insoluble polyTRIS gels.

An important concept in the reactive processing of polymer blends was thus recognised, in that for the optimisation of desired interpolymer formation conditions should be selected for the equalisation of differing component reactivities and avoidance of excessive competitive reaction processes (particularly interlinking agent self-polymerisation).

ii. - **initiator pre-addition** combined with TRIS at optimum FRI:RA produced a considerable interpolymer gel fraction (15%) of which the most substantial portion was PS (83% ; 2KA10, Figure 5.21), shown to be partially cross-linked from swelling behaviour during dichloromethane extraction (Section 5.2.4). Of major importance were the shifts in

component glass transitions for the 2KA10 gel fraction ; EPDM was significantly raised and PS was absent (Section 5.2.6). This was taken as a good indication of effective "between-phase" reaction of PS and EPDM to the extent that the substantial PS content must have been grafted throughout the resulting interpolymer at a scale below which an independent glass transition could be discernible by DSC (Section 5.3.1). This major transformation in the composition of interpolymer was believed to have been achieved through targetting the direct formation of polystyryl radicals and effectively increasing the degree of PS reaction (as modeled in Figure 5.23, Section 5.3.1).

iii. - **DVB** specificity for PS was clearly demonstrated in reactively processed blends with zero or low initiator contents, by the exclusion of EPDM from interpolymer (9KA8 & 5KA8 : Figure 5.21). Yet, at high FRI:RA ratio, EPDM reaction became dominant and the highest interpolymer yield was obtained (2KA8). Physical and chemical features of the DVB modifier were thought to be important in producing these effects (Section 5.3.2). Initiator pre-addition was disadvantageous in blends with DVB ; substantial PS cross-linking was shown indicating promotion of PS reaction to be excessive rather than balanced with other components, as required for effective interpolymer formation.

iv. - **combined TRIS+DVB addition** was ineffective as a simple direct application at optimum initiator concentrations, causing almost complete suppression of PS reaction, with the resulting interpolymer gel composed almost totally of EPDM (6KA10 : Figure 5.21). For <u>initiator pre-addition with combined TRIS+DVB reactive agents</u>, the large gel fraction produced (21%) was composed of near equal proportions of PS and EPDM as true interpolymer, and <u>was considered to be the optimum formulation</u> (7KA10 : Figure 5.21). The presence of PS, EPDM and TRIS was qualitatively confirmed (by FT-IR, Figure 5.18, Section 5.2.5) and from the substantial modifications of component glass transitions in the interpolymer gel (EPDM significantly raised, PS absent - Section 5.2.6) effective

"between-phase" grafting was believed to have been achieved from targetting balanced reaction of blend components (Section 5.3.1).

An overall perspective of the understanding developed throughout the optimisation of PS/EPDM reactive blending using interlinking agents was possible for consistent integration of the range of reaction outcomes experienced (Section 5.3.4). A model relating the predominant reaction outcome to the major system variables (degree of initiation for interlinking agent and PS) was proposed (Figure 5.24, Section 5.3.4), which satisfied the results of the present work and could also be applied to other reactively processed blends in published research (Section 5.3.4). General principles offered by this overall perspective may thus have potential for universal application in the reactive processing of other polymer blends with interlinking agents.

5. Blend compatibilisation effectiveness was assessed by measurement of the tensile properties of pressed film samples and examination of blend morphology, supported by blend thermal analysis, and correlated with predominant reaction outcome (Table 5.11, Section 5.3.3). For all compositions which resulted in significant interpolymer reaction, blend morphology was indicative of increased compatibility between PS/EPDM phases ;

2KA7	5% TRIS, 0.001 FRI:RA molar ratio
2KA10	5% TRIS, 0.001 FRI:RA molar ratio, FRI pre-addition
2KA8	5% DVB, 0.01 FRI:RA molar ratio
3KA10	5% DVB, 0.01 FRI:RA molar ratio, FRI pre-addition
7KA10	2.5% TRIS (0.001 FRI:RA) + 2.5% DVB (0.01 FRI:RA), FRI pre-addition

Tensile properties were not enhanced in all cases in accordance with these improvements in compatibility ; other important factors were also realised, particularly blend morphology and the influence of competitive reaction processes on component properties within either

phase or acting throughout the blend (Section 5.3.3). The effects of these influencing factors were consistent with the scheme developed early-on in this programme, based on a study of the relevant literature, linking the interrelationships between compatibilising effects and immiscible polymer blend performance, which indicated the positive and negative potential of attempted blend reactive compatibilisation (Scheme 1.8, Section 1.4.5).

Gains in physical performance due to PS/EPDM blend compatibilisation on reactive processing with interlinking agents were nevertheless achieved in specific instances where "between-phase" interpolymer formation was successful ;

2KA10 5% TRIS, 0.001 FRI:RA molar ratio, FRI pre-addition

- elongation and stress to break improved over control blend

7KA10 2.5% TRIS (0.001 FRI:RA) + 2.5% DVB (0.01 FRI:RA), FRI pre-addition

- highest elongation to break of all cells (almost x2 control blend).

In the final case optimum interpolymer was obtained (21% yield, near equal PS + EPDM content ; Figure 5.21, Section 5.3.1) and increased interfacial interaction in the blend was indicated by the largest gain in elongation to break of all cells ; realising the potential of effective compatibilisation by the chemical modification of polymer blends by reactive processing.

6.2 RECOMMENDATIONS FOR FURTHER WORK.

Recommendations for further work fall into three areas, namely, additional analysis of current compositions, suggestions for further process investigations and application studies of compatibilised PS/EPDM blends from reactive processing.

1. Further analysis of compositions from the present study can be proposed to aid understanding of reactive processing using interlinking agents in several different areas ;

i. - determination of molecular structures proposed for the different reaction outcomes of TRIS modification of PS alone according to process routes (Scheme 4.7, Section 4.3.2) is required and could perhaps be carried out using gel permeation chromatography (gpc) to separate different molecular weight fractions in which modifier may be concentrated and then further analysed to identify chemical structure by FT-IR and NMR spectroscopy (for which the use of 2-dimensional NMR and computer modelling for spectra analysis may be beneficial).

ii. - an analytical method for the measurement of PS modification effectiveness by DVB was required ; molecular weight distribution analysis by gpc was thought to be one route, solution viscometry from which chain branching estimations may be derived was another possibility and melt rheology of whole and extracted fractions was a further, particularly low shear rate oscillatory measurements from which adjustments in polymer viscoelastic behaviour may indicate the molecular effects of DVB modification.

iii. - EPDM modification characterisation by spectroscopic methods (FT-IR and NMR) was required to confirm the proposed reaction with modifier (Scheme 3.2, Section 3.3.3) and identify any influence of ethylene/propylene units in EPDM modification.

iv. - use of the analytical tools developed in this work, and those proposed above, could be extended for mechanistic investigation of the reactive modifications, particularly identification of the molecular basis for transient torque peaks experienced during reactive processing for certain formulations, by sampling materials for analysis at different times throughout the processing cycle.

v. - by coupling homopolymer modification analyses to component fractions from extraction of reactively processed blends it was thought that better quantification of "within-" and "between-phase" interlinking agent effects could be achieved.

vi. - compositional data was not directly possible from blend and interpolymer gel FT-IR analysis carried out , due to a) opacity of samples and b) overlap of key PS and EPDM absorptions. This is an area for improvement, perhaps by application of an acoustic or reflectance FT-IR technique which would overcome deficiencies of the transmission method used. Manipulation of data through operating software from better resolved spectra could then enable correction for PS/EPDM overlap to be carried out and compositional quantification to be attained.

vii. - a technique assessed in the later part of this programme for the determination of component glass transitions in PS/EPDM blends was dynamic mechanical analysis (on samples of pressed film using a PERKIN-ELMER DMA7 in tensile mode). This was replaced by DSC as the preferred method for precise Tg determination (Section 5.2.6), nevertheless the DMA method does have its part to play in resolving the mechanical components of an immiscible or partially miscible blend from modulus changes through a temperature/frequency sweep from which compatibilising interactions may be inferred. With such large differences in the mechanical and thermal responses of the PS and EPDM blend components development of a suitable DMA method was not straightforward ; further work is recommended for the definition of suitable test geometries (perhaps three-

point bending or dual cantilever) and temperature range. The nature of the materials are such that two different analyses may be required at low and high temperatures to fully characterise transitions of both components and compatibilisation effects achieved in reactively processed blends.

2. Further processing studies may also be suggested to assess opportunities presented from the learning developed in the present study ;

i. - an omission in terms of potential to target desired interpolymer formation in the PS/EPDM blends and test of the model proposed for increasing PS reactivity was the reactive processing of a 70/30 PS/EPDM blend with FRI pre-addition to the PS followed by direct addition of TRIS without FRI during melt blending. This formulation was successful in TRIS modification of PS alone ; 80% TRIS binding to PS was obtained without any TRIS self-polymerisation (3KA6 : Table 4.21, Section 4.3.2). In a blend perhaps a better balance between PS, EPDM and TRIS reactions could be achieved from this route, which would be shown by increased PS incorporation in interpolymer (over 4KA7 at least : Figure 5.21, Section 5.3.1) in line with the proposed model for raising PS reactivity by FRI pre-addition (Figure 5.23, Section 5.3.1).

ii. - an alternative means of adjusting the degree of initiation for PS and interlinking agent may be by the selection of different free radical initiators ; it may be possible to chose an appropriate FRI with a suitable half-life and different radical centre for selective initiation of PS.

iii. - from studying the polymerisation mechanism for acrylates and possible reactions with PS (Section 4.3.1.2) another route to improved PS modification was suggested from the influence of oxygen, which was believed to inhibit acrylate polymerisation and

enhance PS degradation. Such conditions would be found by processing in an open mixer. Thus comparison with closed mixer processing (as in this present study) may be a possible line of further enquiry.

iv. - in this study only one particular grade of EPDM was employed (Section 2.1) ; there are many more commercially available grades with different ethylene/propylene contents and, perhaps of greater interest, different diene types. Comparison of the effectiveness of reactive processing by the routes detailed in the present work across a range of these EPDM compounds may further indicate the importance of component reactivity in blend compatibilisation using interlinking agents.

v. - two contrasting interlinking agents were examined in this research ; a trifunctional aliphatic acrylate (TRIS) and a difunctional aromatic vinyl modifier (DVB). The acrylate chemistry was shown to have potential in PS modification, though self-polymerisation was often excessive, and DVB suggested the benefits of being a "compatible" modifier, though absolute determination of modifier effectiveness was not possible by the analyses used. Combined TRIS + DVB addition in the blends, coupled with FRI pre-addition to PS was realised as the "star" performer (7KA10 : Section 5.3.2). Therefore another line of further enquiry into the use of interlinking agents could be in the selection of a more appropriate modifier for the PS/EPDM blend. Aromatic, or partially aromatic, multifunctional acrylates are the most obvious choice for the assessment of a series of compounds in which the aromatic/aliphatic centres and number of acrylate functionalities may be varied according to available or even synthesised compounds.

vi. - focus was maintained in this programme on a single stage reaction blending process which was believed to be the simplest (and hence cost-effective) route to reactively compatibilised blends. However recognising that component reactivities in the

challenging PS/EPDM blend were very different, homopolymer modification prior to reactive blending may have potential that should be evaluated, particularly by preparation of modified PS using the most effective routes found in this study and subsequently melt blending with unmodified EPDM and suitable addition of interlinking agent.

vii. - during the initial stages of research, operation at the small experimental scale was beneficial for examination of the many possible variables and to develop confidence and understanding of the reactive blending process using interlinking agents. Transfer of this understanding to a laboratory-scale extrusion process would be an important next step. A suitable unit would be the BETOL 30mm TWIN-SCREW EXTRUDER ; material consumption would be dramatically increased (over 10 kg/hour), though process versatility would be a significant advantage with the opportunity to configure multiple solids feeders, liquid injection points and specific mixing characteristics along the extruder screws for a "real-world" engineered, continuous process. At this scale of operation suitable quantities of blend could be produced for assessment of material characteristics by further downstream processing, such as injection molding of standard test pieces for physical evaluation.

3. Application studies of PS/EPDM blends reactively compatibilised by interlinking agents should be carried out to determine any longer-term, in-service advantages of this technology by comparison with similar materials, such as PS copolymers and copolymer compatibilised blends. Three areas could be considered ;

i. - impact resistance modification of PS by reactively compatibilised EPDM ; increased compatibility between PS and a dispersed phase elastomer may improve stress transfer, though it is recognised that rubber toughening mechanisms rely critically upon

morphological factors also. Compatibilised multiphase polymer blends have been thoroughly examined in this area, which may be better satisfied by existing HIPS copolymer technology. Nevertheless a further comparative study of impact resistance to position PS/EPDM blends compatibilised with interlinking agents would be valid.

ii. - the potential for PS/EPDM blends compatibilised with interlinking agents as thermoplastic elastomers should also be examined ; a range of elastomeric properties may be possible according to blend composition and degree of interpolymer formation, with the maintenance of beneficial PS processing characteristics.

iii. - a further application for PS/EPDM blends containing optimised interpolymer may be as compatibilising aids in other styrenic/olefinic polymer blends ; comparison with traditional copolymer compatibilisers may show advantages of reactively modified interpolymer.

This research programme was an initial venture into the evaluation of interlinking agent technology for application in polymer blend compatibilisation and thus it is appropriate that many additional lines of enquiry can be proposed for the PS/EPDM blend examined. However it is also believed that many of the general principles and much of the understanding developed may be further applied to other reactively processed polymer blend systems. It is thus this learning that is strongly recommended for use in further work to at least assist in the realisation of this technology for effective compatibilisation by the chemical modification of polymer blends by reactive processing.

LIST OF REFERENCES

1 Brown S.B., Orlando C.M., "Reactive Extrusion" in The Encyclopedia of Polymer Science and Technology, 2nd Ed., Vol. 14, 169-189, John Wiley & Sons Inc., New York, (1989).

2 Frund Z.N., "Reactive Extrusion", Plast. Compounding, **9** (5), 24-38, (1986).

3 Peron P.J., "Unique materials produced by reactive compounding", Plast. Eng., Dec., 47-79, (1988).

4 Wielgolinksi L., Nangeroni J., "The twin-screw extruder - a versatile tool for reactions and polymerisations", Adv. Polym. Technol., **3** (2), 99-105, (1983).

5 Tucker C., Nichols R.J., "Twin-screw geometry a key to reactive processing", Plast. Eng., **43**, 27-30, (1987).

6 Eise K., "Recent developments in extrusion and processing machinery", Adv. Polym. Technol., **3** (2), 113-30, (1983).

7 Hohlfeld R.W., "Splicing technique creates 'never-before' polymers", Plast. World, **43** (8), 85-87, (1985).

8 Baker W.E., Saleem M., "Coupling of reactive polystyrene and polyethylene in melts", Polymer, **28**, 2057-62, (1987).

9 Baker W.E., Saleem M., "Polystyrene-polyethylene melt blends obtained through reactive mixing process", Polym. Eng. Sci., **27** (20), 1634-41, (1987).

10 Al-Malaika S., "Reactive modifiers for polymers", 409-425 in Chemical Reactions on Polymers, ACS Symposium Series 364, Washington, (1988).

11 Gaylord N.G., Mehta M., "Role of homopolymerisation in the peroxide-catalysed reaction of maleic anhydride and polyethylene in theabsence of solvent", J. Polym. Sci.: Polym. Lett. Ed., **20**, 481-486, (1982).

12 Callais P.A., Kazmierczak R.T., "The use of organic peroxides in the graft modifications of polyolefins with maleic anhydride", 1368-1369 in ANTEC '89 Conference Proceedings, Society of Plastics Engineers 47th Annual Technical Conference, New York, May 1-4, (1989).

13 Hobbs S.Y., Bopp R.C., Watkins V.H., "Toughened Nylon Resins", Polym. Eng. Sci., **23** (7), 380-389, (1983).

14 Avella M., Greco R., Lanzetta N., Maglio G., Malinconico M., Martuscelli M., Palumbo R., Ragosta G., "Synthesis of interfacial agents and their use in nylon 6 / rubber alloys", from Polymer Blends: Processing, Morphology and Properties : 1st Joint Italian - Polish Seminar on Multicomponent Polymeric Systems, Capri, 16-21 October 1979, Martuscelli E., Palumbo R., Kryszewski M. (eds.), Plenum Press, New York, (1980).

LIST OF REFERENCES

15 Borggreve R.J.M., Gaymans R.J., Luttmer A.R., "Influence of structure on the impact behaviour of nylon-rubber blends", Makromol. Chem., Macromol. Symp., **16**, 195-207, (1988).

16 Cimmino S., D'Orazio L., Greco R., Maglio G., Malinconico M., Mancarella C., Martuscelli E., Palumbo R., Ragosta G., "Morphology-property relationships in binary polyamide 6/rubber blends : influence of the addition of a functionalized rubber", Polym. Eng. Sci., **24** (1), 48-56, (1984).

17 Ide F., Hasegawa A., "Studies on polymer blend of nylon 6 and polypropylene or nylon 6 and polystyrene using reaction of polymer", J. App. Polym. Sci., **18**, 963-74, (1974).

18 Al-Malaika S., Quinn N., Aston University, (1988), in preparation for publication.

19 Paul D.R., Barlow J.W., Keskkula H., "Polymer Blends" in The Encyclopedia of Polymer Science and Technology, 2nd Ed., Vol. 12, 399-461, John Wiley & Sons Inc., New York, (1989).

20 Pilati F., Marianucci E., Berti C., "Study of the reactions occurring during melt mixing of poly(ethylene terephthalate) & polycarbonate", J. App. Polym. Sci., **30**, 1267-1275, (1985).

21 Huang Z.H., Li Hui Wang, "Infra-red studies of transesterification in poly(ethylene terephthalate)/polycarbonate blends", Makromol. Chem. Rapid Commun., **7** (5), 255-259, (1986).

22 Devaux J., Goddard P., Mercier J.P., "The transesterification of bisphenol-A polycarbonate (PC) and polybutylene terephthalate (PBTP): a new route to block polycondensates", Polym. Eng. Sci., **22**, 229-233, (1982).

23 Devaux J., Goddard P., Mercier JP, "Bisphenol-A polycarbonate-poly(butylene terephthalate) transesterification", Parts I-IV, J. Polym. Sci.: Polym. Phys., **20**, 1875-1907, (1982).

24 Porter R.S., Casale A., "Mechanochemical Reactions" in TheEncyclopedia of Polymer Science and Technology, 2nd Ed, Vol. 9, 467-485, John Wiley & Sons Inc., New York, (1989).

25 Hajian M., Sadromoahaghegh C., Scott G., "Solid phase dispersants synthesised by a mechanochemical procedure", Eur. Poly. J., **20** (2), 135-138, (1981).

26 Al-Malaika S., Amir E.J., "Thermoplastic rubbers I. Effect of processing variables on tensile properties of natural rubber/polypropylene blends", J. Natural Rubber Research, **1** (2), 104-121, (1986).

27 Aharoni S.M., "Polymer Reactions During Melt Processing", 390-393 in Integration of Fundamental Polymer Science and Technology, Kleintjens L.A., Lemstra P.J. (eds.), Elsevier Applied Science Publishers, London, (1986).

LIST OF REFERENCES

28 Coran A.Y., "Thermoplastic elastomers based on elastomer- thermoplastic blends dynamically vulcanized", Chapter 7 in Thermoplastic Elastomers - A Comprehensive Review, Legge N.R., Holden G., Schroerer E. (eds.), Carl Hanser Verlag Publishers, (1987).

29 Holden G., "Elastomers, Thermoplastic" in The Encyclopedia of Polymer Science and Technology, 2nd Ed., Vol. 5, 416-430, John Wiley & Sons Inc., New York, (1989).

30 Kresge E.N., "Rubbery Thermoplastic Blends", Chapter 20 in Polymer Blends, Vol. 2, Paul D.R., Newman S. (eds.), Academic Press, London, (1978).

31 Coran A.Y., Patel R., "Rubber thermoplastic compositions. Part VII. Chlorinated polyethylene rubber-nylon compositions", Rubb. Chem. Technol., **56**, 210-225, (1983).

32 Coran A.Y., Patel R., "Rubber thermoplastic compositions. Part VIII. Nitrile rubber polyolefin blends with technological compatibilization", Rubb. Chem. Technol., **56**, 1045-60, (1983).

33 Coran A.Y., Patel R., Williams-Headd D., "Rubber-thermoplastic compositions. Part IX. Blends of dissimilar rubbers and plastics with technological compatibilization", Rubb. Chem. Technol., **58**, 1014-23, (1985).

34 "TPEs Special Survey", Plast. Rub. Weekly, October 15, 16-35, No. 1257, (1988).

35 Al-Malaika S., "Modifications of polyolefins in-situ: reactive processing in mixers and extruders", Polymer Preprints, **29** (1), 555-556, (1988).

36 Adur A., "Enhancement of properties of reinforced polypropylene by grafted polyolefin coupling agents", at Reactive Processing - Practise and Possibilities, A Two-Day Seminar at RAPRA Technology Ltd., Shawbury, UK, 11-12 September 1989.

37 Adur A., "Industrial applications of grafted polyolefins produced by reactive extrusion processing", at Reactive Processing - Practise and Possibilities, A Two-Day Seminar at RAPRA Technology Ltd., Shawbury, UK, 11-12 September 1989.

38 Gaylord N.G., Mehta M., Kumar V., Org. Coat. Appl. Polym. Sci. Proc., **46**, 87- , (1982).

39 Gaylord N.G., Mishra M.K., "Nondegradative reaction of maleic anhydride and molten polypropylene in the presence of peroxides", J. Polym. Sci.: Polym. Lett. Ed., **21**, 23-30, (1983).

40 Shiah C.M., Chen I.M., "Grafting of maleic anhydride onto thermoplastic elastomers by melt blending", ANTEC '89.

LIST OF REFERENCES

41 Willoughby B., "Polymer modification and grafting in the cavity transfer mixer", at Reactive Processing - Practise and Possibilities, A Two-Day Seminar at RAPRA Technology Ltd., Shawbury, UK, 11-12 September 1989.

42 Cartasegna S., "Silane-Grafted/Moisture-Curable Ethylene-Propylene Elastomers for the Cable Industry", Rubb. Chem. Technol., **59** (5), 722-739, (1986).

43 Gallucci R., Going R., "Preparation and reactions of epoxy-modified polyethylene", J. App. Polym. Sci., **27**, 425-437, (1982).

44 Al-Malaika S., Aston University, unpublished work, (1988-89).

45 Fox D.W., Allen R.B., "Compatibility" in The Encyclopedia of Polymer Science and Technology, 2nd Ed., Vol. 3, 758-775, John Wiley & Sons Inc., New York, (1989).

46 Barlow J.M., Paul D.R., "The importance of enthalpic interactions in polymeric systems", Polym. Eng. Sci., **27**, 1482-1493, (1987).

47 Cowie J.M.G., "Miscibility" in The Encyclopedia of Polymer Science and Technology, 2nd Ed., Supplement Volume, 455-480, John Wiley & Sons Inc., New York, (1989).

48 Krause S., "Polymer-Polymer Compatibility", Chapter 2 in Polymer Blends, Vol. 1, Paul D.R., Newman S. (eds.), Academic Press, London, (1978).

49 Smith P., Hara M., Eisenberg A., "A review of miscibility enhancement via ion-ion and ion-dipole interactions", Part 6.3 in Current Topics in Polymer Science Vol. II - Rheology and Polymer Processing /Multiphase Systems, Ottenbrite R.M., Utracki L.A., Inoue S. (eds.), Carl Hanser Verlag, Munich, (1987).

50 Olabisi O., Robeson L.M., Shaw M.T., Polymer-Polymer Miscibility, Academic Press, London, (1979).

51 Paul D.R., Newman S. (eds.), Polymer Blends, Vol. 1, Academic Press, London, (1978).

52 Paul D.R., Newman S. (eds.), Polymer Blends, Vol. 2, Academic Press, London, (1978).

53 Sheldon R.P., "Polymer blends and block copolymers", Chapter 6 in Composite Polymeric Materials, Applied Science Publishers Ltd., London, (1982).

54 Rabek J.F., Experimental Methods in Polymer Chemistry, John Wiley and Sons Ltd., Chichester, (1983).

55 "Making More of the Cavity Transfer Mixer", A One-Day Seminar at RAPRA Technology Ltd., Shawbury, UK, 15 November 1988.

LIST OF REFERENCES

56 Gale G.M., Hindmarch R.S., "Developments in polymer blending with the cavity transfer mixer", at Engineering with Blends and Alloys, A One-Day Seminar at RAPRA Technology Ltd, Shawbury, UK, 29 November 1989.

57 White J.L., Min K., "Processing and phase morphology of incompatible polymer blends" in Polymer Blends and Mixtures, 413-428, Walsh D.J., Higgins J.S., Maconnachie A. (eds.), Mintinus Nijoff Publishers, (1985).

58 Meijer H.E.H., Lemstra P.J., Elemans P.H.M., "Structured polymerblends", Macromol. Chem., Macromol. Symp., **16**, 113-135, (1988).

59 White J.L., Min K., "Development of polymer blend phase morphology during processing", Macromol. Chem., Macromol. Symp., **16**, 19-39, (1988).

60 Artus K.J., Birch R.D., ICI Fibres, Gloucester, unpublished work, (1987-1993).

61 European Patent Application 87303484.7, Fibres and Hollow Fibrous Tubes, to ICI Chemicals and Polymers Ltd., Pub.No.246752 A2 25/11/87.

62 Gergen W.P., Lutz R.G., Davison S., "Hydrogenated block copolymers in thermoplastic elastomer IPNs", Chapter 14 in Thermoplastic Elastomers - A Comprehensive Review, Legge N.R., Holden G., Schroerer E. (eds.), Carl Hanser Verlag Publishers, (1987).

63 Olabisi O., Robeson L.M., Shaw M.T., "Methods of enhancing miscibility", Chapter 4 in Polymer - Polymer Miscibility, Academic Press, London, (1979).

64 Cowie J.M.G., "Specific interactions in polymer blends", at Engineering with Blends and Alloys, A One-Day Seminar at RAPRA Technology Ltd, Shawbury, UK, 29 November 1989.

65 Ranalli R., "Ethylene-propylene rubber-polypropylene blends", Chapter 2 in Developments in Rubber Technol., Vol. 3, Wheelan A., Le K.S. (eds.), Elsevier Applied Science Publishers, London, (1982).

66 Brydson J.A., "Thermoplastic rubbers - an introductory review", Chapter 1 in Developments in Rubber Technol., Vol. 3, Wheelan A., Le K.S. (eds.), Elsvier Applied Science Publishers, London, (1982).

67 Paul D.R., "Interfacial agents", Chapter 12 in Polymer Blends, Vol. 2, Paul D.R., Newman S. (eds.), Academic Press, London, (1978).

68 Rudin A, "Copolymers in polymer blends", J. Macromol. Sci. Rev. Macromol. Chem., **C19** (2), 267-292, (1980).

LIST OF REFERENCES

69 Maglio G., Palumbo R., "The role of interfacial agents in polymer blends", in Polymer Blends: Processing, Morphology and Properties, Proceedings 2nd Polish-Italian Joint Seminar on Multi-component Polymeric Systems, Lodtz, Poland , 7-12 September 1982, Kryszewski M., Galeski A., Martuscelli E. (eds.), Plenum Press, New York, (1984).

70 Gaylord N.G., "Compatibizing agents: structure and function in polyblends", J. Macromol. Sci. - Chem., **A26** (8), 1211-29, (1989).

71 Ghaffar A., Sadrmohaghegh C., Scott G., "The use of solid phase dispersants to improve the properties of binary mixtures of incompatible polymers", Eur. Polym. J., **17**, 941-946, (1981).

72 Sadrmohaghegh C., Scott G., "Recycling of mixed plastics", Polym. Plast. Technol. Eng., **24** (2 & 3), 149-185, (1985).

73 Al-Malaika S., Amir E.J., "Thermoplastic elastomers: part 2 - effect of natural rubber/polypropylene as solid phase dispersant in polypropylene/polyethylene blends", Polym. Degrad. Stab., **16**, 347-359, (1986).

74 Nolley E., Barlow J.W., Paul D.R., "Mechanical properties of polypropylene-low density polyethylene blends", Polym. Eng. Sci., **20** (5), 364-369, (1986).

75 D'Orazio L., Greco R., Mancarella C., Martuscelli E., Ragosta G., Silvestre C., "Linear polyethylene/polypropylene/ethylene-propylene copolymer ternary blends : I. Relationship between impact properties and morphology", in Polymer Blends; Processing, Morphology and Properties, Proceedings 2nd Polish-Italian Joint Seminar on Multi-Component Polymeric Systems, Lodtz, Poland , 7-12 September 1982, Kryszewski M., Galeski A., Martuscelli E. (eds.), Plenum Press, New York, (1984).

76 D'Orazio L., Greco R., Martuscelli E., Ragosta G., "Linear polyethylene/ polypropylene/ ethylene-propylene copolymer ternary blends : II. Relationship between mechanical properties and morphology", in Polymer Blends; Processing, Morphology and Properties, Proceedings 2nd Polish-Italian Joint Seminar on Multi-Component Polymeric Systems, Lodtz, Poland , 7-12 September 1982, Kryszewski M., Galeski A., Martuscelli E. (eds.), Plenum Press, New York, (1984).

77 Xanthos M., "Interfacial agents for multiphase polymer sytems: recent advances", Polym. Eng. Sci., **28** (21), 1392-1400, (1988).

78 Ghaffar A., Sadrmohaghegh C., Scott G., "Polymer blends: part III -the interaction between polyethylene and polyvinyl chloride during melt blending and photo-oxidation", Poly. Degrad. Stab., **3**, 341-347, (1980-81).

79 Macknight W.J., Lenz R.W., Musto P.V., Somani R.J., "Binary alloys of nylon 6 and ethylene-methacrylic acid copolymers: morphological, thermal and mechanical analysis", Polym. Eng. Sci., **25** (18), 1124-1134, (1985).

LIST OF REFERENCES

80 Dagli S.S., Xanthos M., Biesenberger J.A., "Process requirements of the reactive compatibilization of nylon 6 / polypropylene blends", ACS Polymer Preprints, **32** (2), 150-151, (1991).

81 Young M.W., Xanthos M., Biesenberger J.A., "Polyblends of PP with PET: effects of chemical modification", 1835-1837 in ANTEC '89 Conference Proceedings, Society of Plastics Engineers 47th Annual Technical Conference, New York, May 1-4, (1989).

82 Moore E.R. (ed.), "Styrene Polymers", in The Encyclopedia of Polymer Science and Technology, 2nd Ed., Vol. 13, 1-246, John Wliey & Sons Inc., New York, (1989).

83 Brydson J.A., "Plastics based on styrene", Chapter 16 in Plastics Materials, 5th Ed., Butterworths, London, (1989).

84 Dunn J.R., "Blends of elastomers and thermoplastics - a review", Rubber Chem. Technol., **49** (4), 978-991, (1976).

85 Fayt R., Jerome R., Teyssie P., "Poly(hydrogenated butadiene-b-styrene) copolymers in LDPE/PS blends", J. Polym. Sci.: Polym. Lett. Ed., **19**, 79-84, (1981).

86 Heikens D., Hoen N., Barentsen W., Piet P., Ladan H., "Mechanical properties and morphology of copolymer modified polymer blends", J. Polym. Sci.: Polym. Symp., **62**, 309-341, (1978).

87 Fayt R., Jerome R., Teyssie P., "Molecular design of multicomponent polymer systems. XIV. Control of the mechanical properties of polyethylene-polystyrene blends by block copolymers", J. Polym. Sci.: Part B: Polym. Phys., **27**, 775-793, (1989).

88 Locke C.E., Paul D.R., "Graft copolymer modification of polyethylene-polystyrene blends. II. Properties of modified blends", J. Appl. Polym. Sci., **17**, 2791-2800, (1973).

89 Barentsen W.M., Heikens D., "Mechanical properties of polystyrene/low-density polyethylene blends", Polym., **14**, 579-583, (1973).

90 Barentsen W.M., Heikens D., Piet P., "Effect of addition of graft copolymer on the microstructure and impact strength of PS/LDPE blends", Polym., **15**, 119-122, (1974).

91 Heikens D., Barentsen W.M., "Particle dimensions in polystyrene/polyethylene blends as a function of their melt viscosity and of the concentration of added graft copolymer", Polym., **18**, 69-72, (1977).

LIST OF REFERENCES

92 Sjoerdsma S.D., Bleijenberg A.C.A.M., Heikens D., "Tensile properties and morphology of copolymer modified blends of polystyrene and polyethylene", in Polymer Blends; Processing, Morphology and Properties, Proceedings 1st Polish-Italian Joint Seminar on Multi-Component Polymeric Systems, Capri, 16-21 October 1979, Martuscelli E., Palumbo R., Kryszewski M. (eds.), Plenum Press, New York, (1980).

93 Barentsen W.M., Heijdenrijk P.J., Heikens D., Piet P., "Mechanical properties of polystyrene/ethylene-propylene copolymer blends", Brit. Polym. J., **10**, 17-22, (1978).

94 Sjeordsma S.D., Dalmolen J., Bleijenberg A.C.A.M., Heikens D., "Dynamic mechanical properties of polystyrene/low density polyethylene blends", Polym., **21**, 1469-1474, (1980).

95 Jan Coumans W., Heikens D., Sjoerdsma S.D., "Dilatometric investigation of deformation mechanisms in polystyrene-polyethylene block copolymer blends: correlation between Poisson ratio and adhesion", Polym., **21**, 103-108, (1980).

96 Lindsey C.R., Paul D.R., Barlow J.W., "Mechanical properties of HDPE-PS-SEBS blends", J. Appl. Polym. Sci., **26**, 1-8, (1981).

97 Lambla M., Yu R.X., Lorek S., "Coreactive polymer alloys", Chapter 3 in Multiphase Polymers: Blends and Ionomers, Utracki L.A., Weiss R.A.(eds.), ACS Symposium Series 395, (1989).

98 Scott G., Setoudeh E., "Effects of reprocessing on polymers - IV. Photo-oxidation of polyethylene-polystyrene blends containing a styrene-butadiene block copolymer as solid phase dispersant", Eur. Polym. J., **18**, 901-902, (1982).

99 Fayt R., Jerome R., Teyssie Ph., "Molecular design of multicomponent polymer systems. II. Emulsifying effect of a poly(hydrogenated butadiene-b-styrene) copolymer in high-density polyethylene/ polystyrene blends", J. Polym. Sci.: Polym. Phys. Ed., **19**, 1269-1272, (1981).

100 Fayt R., Jerome R., Teyssie Ph., "Molecular design of multicomponent polymer systems. III. Comparitive behaviour of pure and tapered block copolymers in emulsification of blends of low-density polyethylene and polystyrene", J. Polym. Sci,: Polym. Phys. Ed., **20**, 2209-2217, (1982).

101 Fayt R., Hadjiandreou P., Teyssie Ph., "Molecular design of multicomponent polymer systems. VII. Emulsifying effects ofpoly(ethylene-b-styrene) copolymers in high-density polyethylene/polystyrene blends", J. Polym. Sci.: Polym. Chem. Ed., **23**, 337-342, (1985).

102 Fayt R., Jerome R., Teyssie Ph., "Molecular design of multicomponent polymer systems. XII. Direct observation of the location of a block copolymer in low-density polyethylene-polystyrene blends", J. Polym. Sci.: Polym. Lett. Ed., **24**, 25-28, (1986).

LIST OF REFERENCES

103 Fayt R., Jerome R., Teyssie Ph., "Molecular design of multicomponent polymer systems, 13. Control of the morphology of polyethylene/polystyrene blends by block copolymers", Makromol. Chem., **187**, 837-852, (1986).

104 Natta G., Pegoraro M., Severini F., Dabhade S., "Improvement of impact strength of polystyrene by compounding with styrene-graftedethylene propylene elastomeric copolymers", Rubber Chem. Technol., **39**, 1667-1675, (1966).

105 Shaw S., Singh R.P., "Studies on impact modification of polystyrene (PS) by ethylene-propylene-diene (EPDM) rubber and its graft copolymers. I. PS/EPDM and PS/EPDM-g-styrene blends", J. Appl. Polym. Sci., **40**, 685-692, (1990).

106 Shaw S., Singh R.P., "Studies on impact modification of polystyrene (PS) by ethylene-propylene-diene (EPDM) rubber and its graft copolymers. II. PS/EPDM-g-(styrene-co-methylmethacrylate) blends", J. Appl. Polym. Sci., **40**, 693-699, (1990).

107 Shaw S., Singh R.P., "Studies on impact modification of polystyrene (PS) by ethylene-propylene-diene (EPDM) rubber and its graft copolymers. III. PS/EPDM-g-(styrene-co-maleic anhydride) blends and its relative performance", J. Appl. Polym. Sci., **40**, 701-707, (1990).

108 Slusarski L., Kuczynski J., "The influence of interfacial grafting on the properties of elastomer-plastomer mixtures", in Polymer Blends; Processing, Morphology and Properties, Proceedings 2nd Polish-Italian Joint Seminar on Multi-Component Polymeric Systems, Lodtz, Poland , 7-12 September 1982, Kryszewski M., Galeski A., Martuscelli E. (eds.), Plenum Press, New York, (1984).

109 Peiffer D.G., Duvdevani I., Agarwal P.K., Lundberg R.D., "Transition metal coordination for complexing polymer blends", J. Polym. Sci.: Polym. Lett. Ed., **24**, 581-586, (1986).

110 Agarwal P.K., Duvdevani I., Peiffer D.G., Lundberg R.D., "Polymer blend complexes based on coordination chemistry", J. Polym. Sci.: Part B: Polym. Phys., **25**, 839-854, (1987).

111 Saleem M., Baker W.E., "In situ reactive compatibilization in polymer blends: effects of functional group concentrations", J. Appl. Polym. Sci., **39**, 655-678, (1990).

112 Fowler M.W., Baker W.E., "Rubber toughening of polystyrene through reactive blending", Polym. Eng. Sci., **28** (21), 1427-1433, (1988).

113 Simmons A., Baker W.E., "Compatibility enhancement in polyethylene/styrene-maleic anhydride blends via polar interactions", Polym. Communications, **31**, 20-22, (1990).

LIST OF REFERENCES

114 Song Z., Baker W.E., "In situ compatibilization of polystyrene/polyethylene blends using amino-methacrylate-grafted polyethylene", J. Appl. Polym. Sci., **44**, 2167-2177, (1992).

115 Molnar A., Eisenberg A., "Compatibilization of nylon 6 and polystyrene through the functionalisation of polystyrene", Polym. Communications, **32**, 370-373, (1991).

116 Sullivan M.J., Weiss R.A., "Characterisation of blends of an amorphous polyamide with lightly sulfonated polystyrene ionomers", Polym. Eng. Sci., **32** (8), 517-523, (1992).

117 Pukanszky B., Kennedy J.P., Kelen T., Tudos F., "Cationic reactions in the melt. 3. grafting polystyrene onto ethylene-propylene co- and or-terpolymers", Polym. Bull., **6**, 335-341, (1982).

118 Mori E., Pukanszky B., Kelen T., Tudos F., "Lewis acid initiated melt reactions of polystyrene and EPDM rubber", Polym. Bull., **12**, 157-163, (1984).

119 Pukanszky B., Kennedy J.P., Kelen T., Tudos F., "Cationic reactions in the melt. 1. The effect of Lewis acids on polystyrene", Polym. Bull., **5**, 469-476, (1981).

120 Pukanszky B., Kennedy J.P., Kelen T., Tudos F., "Cationic reactions in the melt. 2. The effect of Lewis acids on the ethylene-propylene co- and terpolymers", Polym. Bull., **6**, 327-333, (1982).

121 van Ballegooie P., Rudin A., "Reactive extrusion of polystyrene/ polyethylene blends", Polym. Eng. Sci., **28** (21), 1434-1442, (1988).

122 van Ballegooie P., Rudin A., "Reactive extrusion of polystyrene/ polyethylene blends", Polym. Mat. Sci. Eng., **58**, 835-839, (1988).

123 Teh J.W., Rudin A., "Properties and morphology of polystyrene and linear low density polyethylene polyblend and polyalloy", Polym. Eng. Sci., **31** (14), 1033-1042, (1991).

124 Willis J.M., Favis B.D., Lunt J., "Reactive processing of polystyrene-co-maleic anhydride/elastomer blends: processing-morphology-property relationships", Polym. Eng. Sci., **30** (17), 1073-1084, (1990).

125 Fayt R., Teyssie Ph., "Molecular design of multicomponent polymer systems. XVI. Emulsification of polystyrene and nylon-6 by a reactive block copolymer", J. Polym. Sci.: Part C: Polym. Lett. Ed., **27**, 481-488, (1989).

126 Chen C.C., Fontan E., Min K., White J.L., "An investigation of instability of phase morphology of blends of nylons with polyethylenes and polystyrenes and effects of compatibilizing agents", Polym. Eng. Sci., **28** (2), 69-80, (1988).

LIST OF REFERENCES

127 Chang F.-C., Hwu Y.-C., "Styrene maleic anhydride and styrene glycidyl methacrylate copolymers as in situ reactive compatibilizers of polystyrene/nylon 6,6 blends", Polym. Sci. Eng., **31** (21), 1509-1519, (1991).

128 Park I., Barlow J.W., Paul D.R., "The in situ reactive compatibilization of nylon-6/polystyrene blends using anhydride functionalized polystyrenes", J. Polym. Sci.: Part B: Polym. Phys., **30**, 1021-1033, (1992).

129 Al-Malaika S., Scott G., "Modified Polymers", International Patent Application, No. PCT/GB89/00909

130 Brydson J.A., "Aliphatic polyolefins other than polyethylene, and diene rubbers", Chapter 11 in Plastics Materials, 5th Ed.,Butterworths, London, (1989).

131 Ver Strate G., "Ethylene-propylene elastomers", in The Encyclopedia of Polymer Science and Technology, 2nd Ed., Vol 6, 522-564, John Wiley & Sons Inc., New York, (1989).

132 Shaw S., Singh R.P., "Study of compatibility of polystyrene with ethylene-propylene-diene rubber", Eur. Polym. J., **23** (7), 547-550, (1987).

133 ASTM D 882-83 Standard Test Methods for Tensile Properties of Thin Plastic Sheeting.

134 Brydson J.A., "Additives for plastics", Chapter 7 in PlasticsMaterials, 5th Ed., Butterworths, London, (1989).

135 Cogswell F.N., "Rheology and structure", Chapter 4 in Polymer Melt Rheology, George Goodwin Ltd., London, (1981).

136 Dealy J.M., "Effects of molecular structure", Chapter 10 in Melt Rheology and its Role in Plastics Processing: Theory and Applications, Van Nostrand Reinhold, New York, (1990).

137 Dealy J.M., "Rheology of multiphase systems", Chapter 11 in Melt Rheology and its Role in Plastics Processing: Theory and Applications, Van Nostrand Reinhold, New York, (1990).

138 Al-Malaika S., Scott G., Wirjosentono B., "Mechanisms of antioxidant action : polymer-bound hindered amines by reactive processing, Part III Effect of reactive antioxidant structure", Polym. Deg. Stab., **40**, 233-238, (1993).

139 Van Oene H., "Rheology of polymer blends and dispersions", Chapter 7 in Polymer Blends, Vol. 1, Paul D.R., Newman S. (eds.), Academic Press, London, (1978).

140 Grassie N., Scott G., "Oxidation of Polymers", Chapter 4 in Polymer Degradation and Stabilisation, Cambridge University Press, (1985).

LIST OF REFERENCES

141 Henman T.J., "Melt Stabilisation of Polypropylene", Chapter 2 in Developments in Polymer Stabilisation - 1, Scott G., (ed.), Applied Science Publishers, London (1979).

142 Maecker N.L., Armentrout D.N., "Degradation (Styrene Polymers)", in The Encyclopedia of Polymer Science and Technology, 2nd Ed., Vol 16, 180-193, John Wiley & Sons Inc., New York, (1989).

143 Dickens B., Marchal J., "Oxidation of polystyrene in solution", Polym. Degrad. Stab., **6**, 211-241, (1984).

144 Lawrence J.B., Weir N.A., "The kinetics of oxidation of atactic polystyrene in solution", J. Appl. Polym. Sci., **18**, 1821-1835, (1974).

145 Crouzet C., Marchal J., "Dégradation oxydante du polystyrène à 25°C. Origine du benzaldéhyde et de l'acétophénone", Makromol. Chem., **177**, 2819-2832, (1976).

146 Crouzet C., Marchal J., "Oxidative degradation of polystyrene", J. Appl. Polym. Sci.: Appl. Polym. Symp., **35**, 151-160, (1979).

147 Le-Khac-Bi, Kamiya Y., "Autooxidation of polystyrene catalysed by cobalt salt and sodium bromide in chlorobenzene-acetic acid", J. Polym. Sci.: Part A-1, **7** (4), 1131-1143, (1969).

148 Vu Duc T., Huynh C.K., "Détermination par GC-MS des produits de thermo-oxydation des revêtements en polystyrène d'emballages alimentaires fabriqués par thermoformage", Trav. chim. aliment. hyg., **76**, 48-59, (1986).

149 Kine B.B., Novak R.W., "Acrylic and methacrylic ester polymers", in The Encyclopedia of Polymer Science and Technology, 2nd Ed., Vol 1, 234-299, John Wiley & Sons Inc., New York, (1989).

150 Brydson J.A., "Relation of structure to chemical properties (polymer solubility)", Chapter 5 in Plastics Materials, 5th Ed., Butterworths, London, (1989).

151 Silverstein R.M., Bassler G.C., Morrill T.C., Chapter 4 "Proton Magnetic Resonance Spectroscopy" and Chapter 5 "^{13}C NMR Spectroscopy" in Spectrometric Identification of Organic Compounds, Fourth Edition, John Wiley & Sons, 1981.

152 Cheng H.M., "NMR Characterisation of Polymers" Chapter 11 in Modern Methods of Polymer Characterisation, Chemical Analysis Vol. 113, Barth H.G. and Mays J.W. (eds.), John Wiley and Sons, 1991.

153 Ebdon J.R., "Copolymer Characterisation by ^{13}C NMR" Chapter 1 in Developments of Polymer Characterisation 2, Dawkins J.V. (ed.), Applied Science Publishers, 1980.

LIST OF REFERENCES

154 Wunderlich B., "The Basis of Thermal Analysis" Chapter 2 in Thermal Characterization of Polymeric Materials, Turi E.A., Academic Press, 1981.

155 Shalaby S.W., "Thermoplastic Polymers" Chapter 3 in Thermal Characterization of Polymeric Materials, Turi E.A., Academic Press, 1981.

156 ASTM D 3900-86 Standard Test Method for Rubber, Raw - Determination of Ethylene Units in EPM (Ethylene-Propylene Copolymers) and EPDM (Ethylene-Propylene- Diene Terpolymers.

157 Fried J.R., "Applications of Thermal Analysis to the Study of Polymer Blends" Chapter 2 in Developments of Polymer Characterisation 4, Dawkins J.V. (ed.), Applied Science Publishers, 1983.

158 Homer J. and Perry M.C., "New Method for NMR Signal Enhancement by Polarization Transfer, and Attached Nucleus Testing", J. Chem. Soc., Chem. Commun., 373-374, 1994