FUNCTIONALISED POLYMERS

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FUNCTIONALISED POLYMERS
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Summary

Synthetic routes to polymers possessing functional groups were studied.

Direct functionalisation of poly(vinyltoluene) by lithiation and carboxylation resulted in the expected carboxylic acid but reaction was complicated by the production of a mixture of products. Reaction occurred both at the polymer backbone and at the pendant methyl group. Reaction with ethyl formate was also difficult to control and a secondary alcohol was formed even when an excess fo the carbonyl compound was employed.

Grignard formation of poly(bromostyrene) was successful but once formed, the derivative rearranged resulting in chain scission and degradation of the polymer. Therefore subsequent reactions of the Grignard reagent with carbonyl groups were unsuccessful in producing functionalised polymers.

Reactions of vinyltoluene monomer were more successful. Although complications arose when lithiation and carboxylation of the monomer were carried out using lithium diisopropylamide because the carboxylic acid product reacted with the excess lithium diisopropylamide present, metallation by potassium t-butoxide followed by reaction with 2-(3-chloropropyl)-2-methyl-1,3-dioxalane resulted in the formation of 2-methyl-2(4-(vinylphenyl)-butyl-1,3,-dioxalane. The butyllithium initiated anionic polymerisation of this protected monomer resulted in a polymer which had a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$=1.05) and subsequent hydrolysis of the polymer resulted in poly(6(vinylphenyl)-hexan-2-one) which was derivatised with 2,4 dinitrophenylhydrazine.

Functionalisation by modification of the siloxane derivative 3-(methylpropenoxycarbonyl)ltrimethoxysilane was unsuccessful. The acid catalysed exchange reactions of this monomer with alcohols such as eugenol, octan-1-ol, pentan-1-ol, and hexan-1-ol were inefficient, resulting in a mixture of products and unreacted starting materials.

KEY WORDS: FUNCTIONALISATION, GRIGNARD, LITHIATION, CARBOXYLATION, VINYLTOLUENE, DIOXALANE, ANIONIC POLYMERISATION.

To the memory of a
very dear aunt

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CHAPTER ONE

INTRODUCTION

1. Introduction

Historically polymer science has been concerned with the design and synthesis of polymers that might replace conventional materials such as metals, leather, wool, cotton etc, but of increasing importance is the production of materials with properties that have hitherto been unattainable. Of great significance in the search for new materials are functionalised polymers, which in the broadest sense may be considered to be polymers that contain some active functional group (such as a mesogen) or some chemical functionality that will allow the subsequent introduction of a group with specific activity.

Some uses of functionalised materials include:
(i) grafting with or copolymerisation with a liquid crystalline polymeric backbone.
(ii) biomedical applications such as biosensors and contact lenses
(iii) catalyst support systems.

1.1. Liquid Crystals

The liquid crystalline state is often referred to as the mesomorphic state [1] and is a transitory state between a true solid and a true liquid.

Liquid crystals exhibit certain aspects of both the solid and the liquid state but they also possess properties that are not found in either [2].

1.1.1. Structure and classification

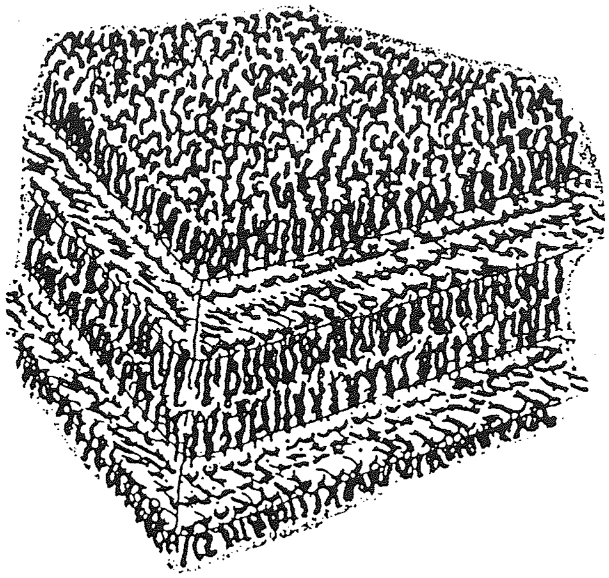
Liquid crystalline materials are classified according to the principal way in which the order of the parent solid is destroyed. In addition to forming naturally at certain temperatures liquid crystalline structures can also be formed when certain compounds are treated with controlled amounts of water.

1.1.1.1. Lyotropic liquid crystals

Lyotropic liquid crystals are formed by the action of a solvent on a solid. They are often two component systems composed of water and amphiphilic compounds, for example lipid systems containing water show lyotropic mesomorphism. [3]. Lehmann [1] was the first to recognize the mesomorphic state of ammonium oleate in aqueous solutions. Some dyes have been shown to have lyotropic mesomorphic character. Branner showed that the potassium salt of methyl orange with water gave mesomorphic phases [1].

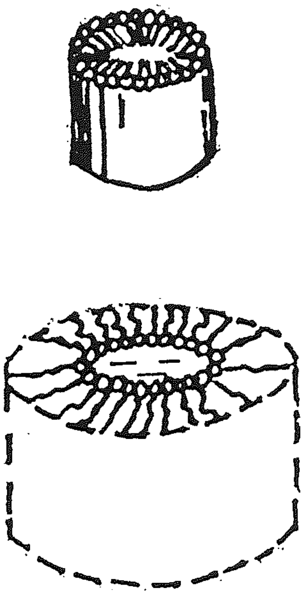
The amphiphilic compounds have polar heads (ionic) that tend to dissolve in water (hydrophilic) and organic tails that are insoluble in water (hydrophobic). Two common types of molecular geometries are found; in one type of molecule the polar head is attached to one long hydrophobic tail. A second type of molecule has its polar head attached to two hydrophobic tails [2, 3].

The structure of the lyotropically mesomorphous lattice is made up of multimolecular units called mesoaggregates. These are surrounded by an intervening liquid. [4]. Lyotropic



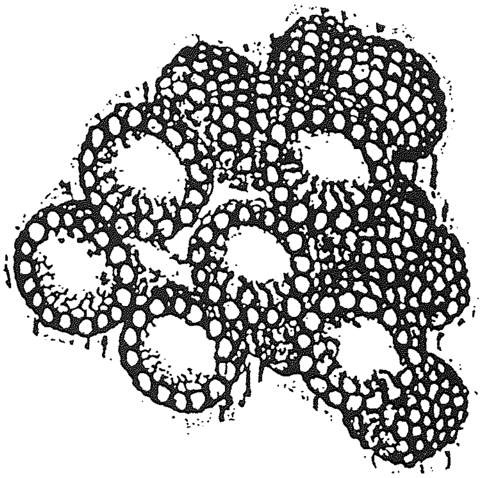
Lamellar packing

Figure 1.1



Regular or inverted

cylindrical packing



Cubic packing

mesomorphism is therefore closely related to the tendency of lipids to accumulate at interfaces. X ray investigations showed that aggregates in lyotropic mesophases are structurally very similar to micelles. [4]. Micelles are large molecular aggregates in solutions. They are thermodynamically stable because of intermolecular interactions. In contrast, however, the mesoaggregates are usually of infinite dimensions in one or two directions. They form ordered lattices which cause the characteristic anisotropy. [4].

Lyotropic liquid crystals can be divided into several categories according to structure.

(i) Lamellar structure (neat of G phase)

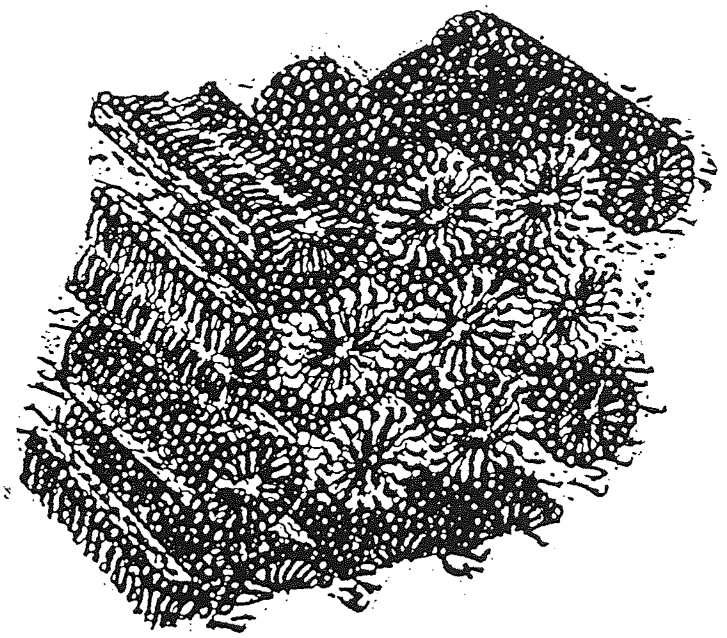
The lamellar phase consists of double layers of amphiphilic molecules with water between these layers. Molecules displaying lamellar packing may have the axis of the molecule perpendicular to the plane or tilted (see figure 1.1)

(ii) Hexagonal Structure (Middle or M_1 phase)

In this type of structure the amphiphilic molecules are grouped into rod-like clusters of indefinite length, which are arranged, in turn, side by side in a hexagonal packing (see figure 1.2). In each rod the molecules are arranged radially around the axis of the rod with the polar groups on the outside. The molecular packing can be either regular or inverted.

When both the lamellar and hexagonal structures are formed from the same compounds, the hexagonal structure is the more stable at higher concentrations of water or higher

Figure 1.2



Hexagonal packing

temperatures [2].

(iii) Cubic Structure (viscous, isotropic or V_1 phase)

The cubic structure appears in some systems at concentrations of amphiphile intermediate between those producing lamellar and hexagonal structures.

Optical observations show that this structure is isotropic and X ray diffraction studies indicate that the molecules pack in spheres but then pack in either a face centred cubic lattice or a body centred cubic lattice [2]. However, the molecules can be packed in a regular or inverted fashion (see figure 1.1).

In the lamellar structure and the regular hexagonal and cubic structures the aqueous region between the aggregates is similar to an electrolyte solution. The electrical conductivity is good because of the high mobility of the counterion. However, in the inverted forms there are no continuous water regions and the conductivity is low.

1.1.1.2 Thermotropic liquid crystals

Thermotropic liquid crystals form naturally over a specific temperature range.

Thermotropic mesomorphism is found in aromatic, aliphatic and multi-ring systems. An example of a simple aliphatic compound is 2,4-nonadienoic acid, whilst the simplest aromatic thermotropic liquid crystals are p-propoxybenzoic acid and p-butylbenzoic acid [1].

However, several general statements can be made about the structure of aromatic thermotropic liquid cystalline compounds[1]. Such factors can be summarized as follows:

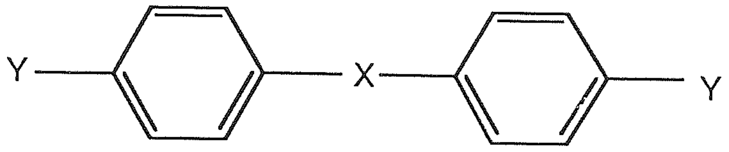
(i) the molecule is rod shaped, planar, or lath shaped - the length of the molecule is usually greater than its diameter.

(ii) the molecule must contain one group with a high dipole - a strong polar group near the centre of the molecule generally enhances liquid crystallinity. The central group usually contains either a multiple bond along the long axis of the molecule, a system of conjugated double bonds or involves dimerisation of carboxyl groups.

(iii) the molecule contains moderately active groups towards the extremities of the molecule.

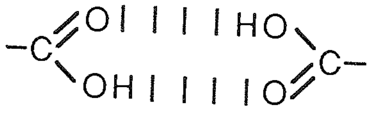
(iv) the molecule possesses intramolecular interactions e.g. dipole/dipole, ion/dipole, hydrogen bonding.

The basic structure of such aromatic compounds can be shown by use of the general formula



Examples of X groups include,

-CH=CH - , -C≡C-, -CH=N-N=CH-,



$$-C\overset{\displaystyle O\cdots\cdots HO}{\underset{\displaystyle OH\cdots\cdots O}{}}C-$$

Examples of Y groups include,

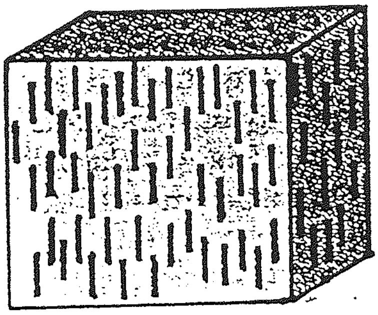
$CH_3(CH_2)_n$-, $(CH_3)_2CH(CH_2)_n$-, $CH_3(CH_2)_nO$-, $CH_3O(CH_2)_nO$-, Cl, Br, I.

When molecular structure is varied widely within a group of suitable compounds, the liquid crystalline properties change markedly. [1, 5, 6, 7]. For example the liquid crystalline transition temperatures may vary extensively, and the type and number of liquid crystalline states may be different.

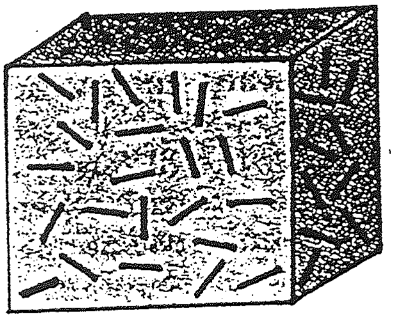
Thermotropic liquid crystalline compounds are classified into two groups.

(i) Nematic

In typical nematic mesophases the only structural restriction is that the long axes of the molecules maintain a parallel or nearly parallel arrangement over macroscopic distances [1, 2, 8]. The molecules have mobility in three directions with rotation about one axis being permitted, similar to a box of pencils (see

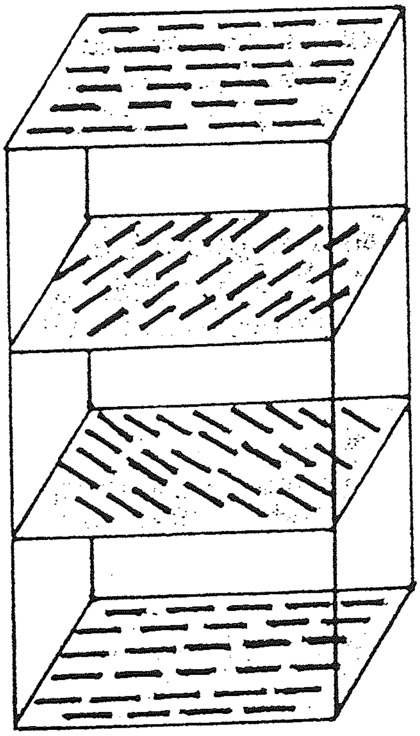


Nematic

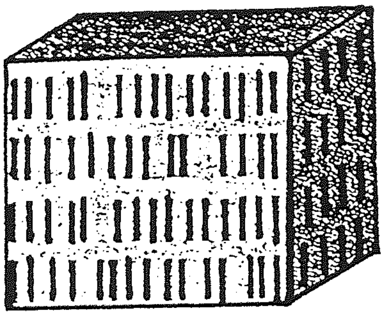


Isotropic

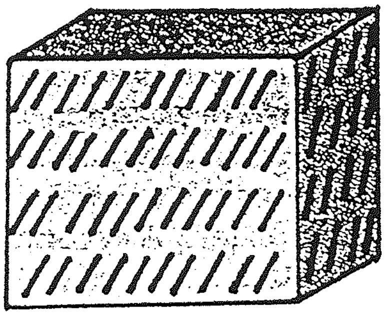
Figure 1.3



Cholesteric



Smectic A



Smectic C

figure 1.3).

Chiral nematic or cholesteric liquid crystals are formed by some optically active organic compounds. The molecules in a cholesteric mesophase are arranged in layers but have a local nematic type of packing in that within the layers the molecules have a parallel alignment [1, 2, 8] (see figure 1.3). The direction of packing is not fixed, instead it rotates spatially about an axis perpendicular to itself. Hence a helical structure results whose pitch (the distance required to rotate the axis through 360^{o}) is about the wavelength of light giving enhanced optical activity.

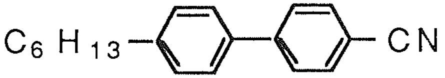
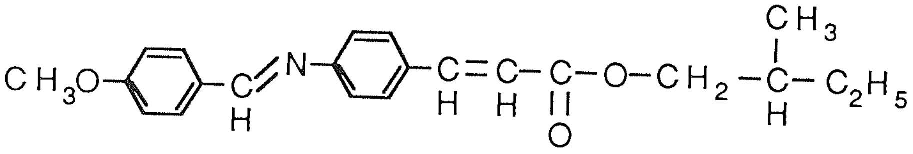
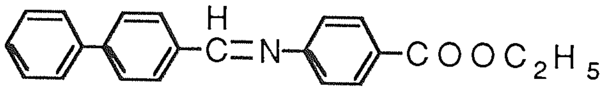
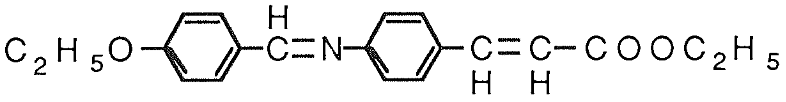
(ii) Smectic

In the smectic phase the molecules are arranged side by side in a series of layers [1, 2, 8]. There are a number of types of smectic structure and each structure possesses a characteristic type of packing within the layers. However, one structure, smectic D is optically isotropic and has cubic not layer packing [2].

Arrangement of the molecules within the layers may be structured or unstructured. In structured smectics each layer forms a regular two dimensional lattice [1]. In unstructured smectics the molecules are positioned randomly in each layer (see figure 1.3).

Examples of some thermotropic liquid crystalline materials are shown in Table 1.1.

Table 1.1 Examples of thermotropic liquid crystalline materials

FORMULA	NAME	LIQUID CRYSTALINE RANGE (°C)
Classical nematic 	4-n-Hexyl-4'-cyanobiphenyl	14-28
Cholesteric 	(-)-2-Methylbutyl 4-methoxybenzylidene-4'-aminocinnamate	76-125
Smectic A 	Ethyl-p-(p'-phenylbenzalamino)benzoate	121-131
Smectic B 	Ethyl-p-ethoxybenzal-p'-aminocinnamate	77-116

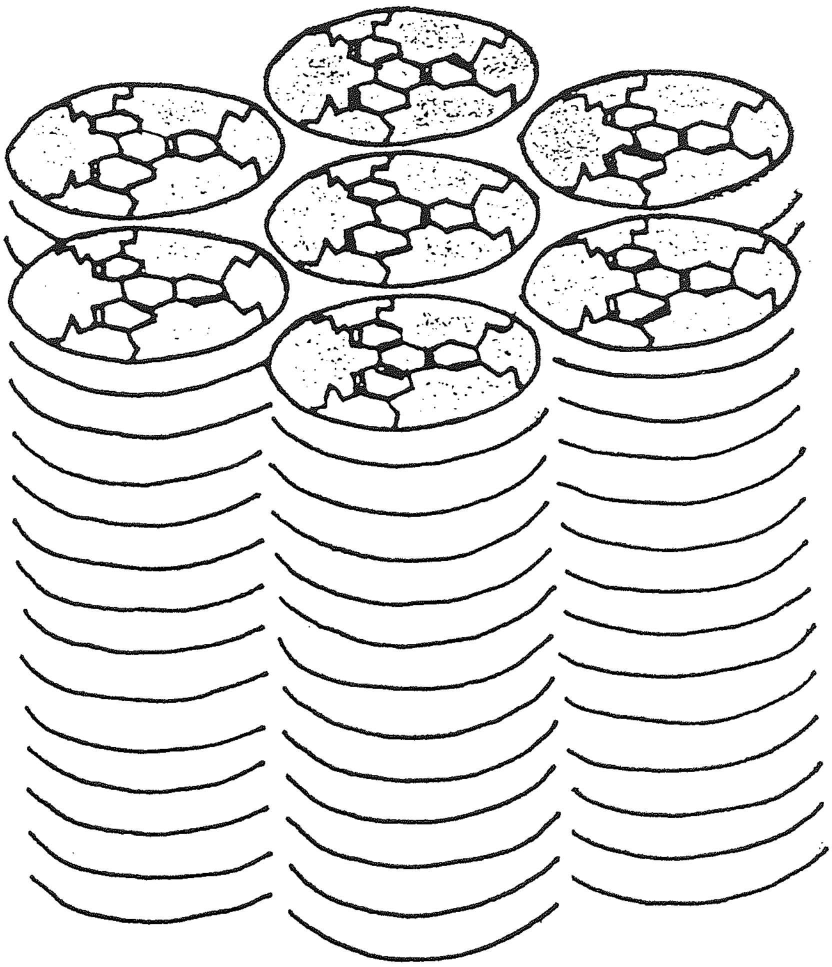


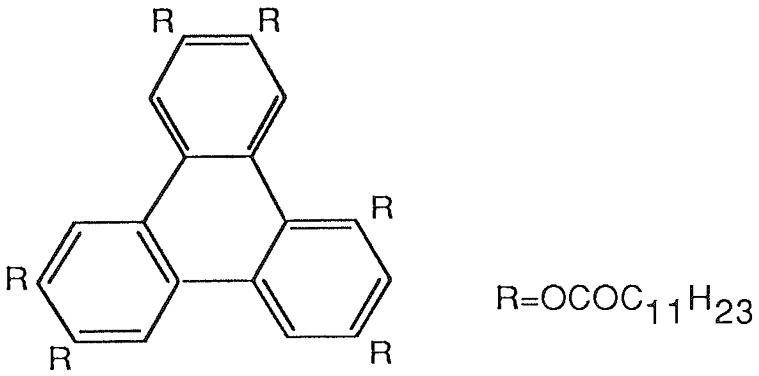
Figure 1.4

1.1.1.3. Mesophases of disc like molecules

In addition to rod-like liquid crystals a new type of discotic mesophase has been discovered. It is formed by materials which have disc shaped molecules.

The discs pack in columns although their arrangement within a column can be either ordered or random. The columns may themselves be grouped into hexagonal lattices. [2, 9]. (see figure 1.4)

Examples of discotic mesophases are formed at high temperatures during the carbonization of graphitic materials such as coal and petroleum. Triphenylene-hexa-n-dodecanoate also forms a discotic mesophase.



Triphenylene hexa-n-dodecanoate

1.1.2 Applications of liquid crystals

The basic property common to all mesophases is the presence of long range order which results in:

(i) the anisotropy of many physical properties.

(ii) the diverse and subtle changes brought about by, for example, external fields or changes in temperature; the ordering properties can be controlled by ordinary magnetic and electrical fields and some liquid crystalline materials change colour as a result of the sensitivity of their structures to temperature.

1.1.2.1. Display devices

The widest use of liquid crystals currently is as the active component in a wide variety of display devices such as wrist watches, clocks, pocket calculators, games, telephones etc.

Cholesteric liquid crystals exhibit striking colour effects due to 100% reflectivity of the wavelength of light equal to the pitch. However, the pitch, and hence the selective reflection wavelength, is sensitive to temperature, electric and magnetic fields. Hence cholesteric liquid crystals have great display potential [2, 10].

An electric field can also induce deformations in the cholesteric liquid crystal structure modifying the pitch of the material thus altering the optical properties of the material[11,12]. Displays are in use based on such textural changes of cholesterics. The cholesteric material is placed between parallel transparent conducting plates with the pitch axis parallel to the walls of the cell. Application of a perpendicular electric field then untwists the pitch and the sample becomes a transparent nematic with ordering direction perpendicular to the surface [2,13].

Nematic liquid crystals are also used in display devices. Typically a nematic liquid crystal is placed in an optical cell coated with a transparent conducting film. Application of an electric field may rotate the molecules changing the samples birefrigence.

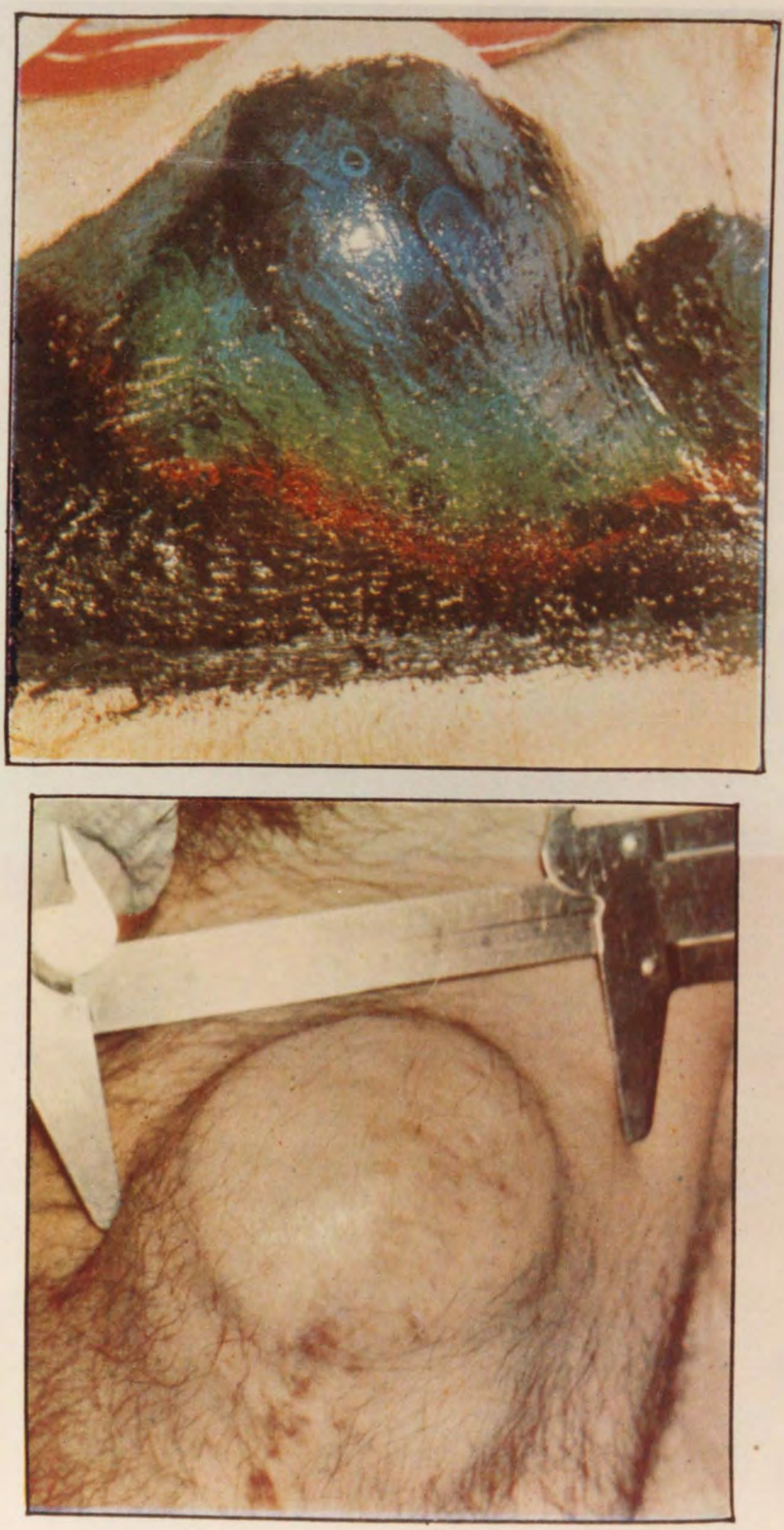
In some devices a dye such as methyl red is dissolved in the liquid crystal so that application of the field rotates the liquid crystal and hence the dye molecules into alignment with a polarised incident light beam; absorption of the light is therefore increased [2].

In some cases smectic liquid crystals are used in displays. Application of 100V to a smectic A structure and switching the frequency from 10^2Hz to 10^3Hz causes a reversible transition from a transparent structure to a light scattering structure [13].

1.1.2.2. Temperature sensors

The pitch of cholesteric liquid crystals is dependent on temperature. Use is made of this variation of the selective reflection wavelength with temperature to locate faults in printed circuit boards, welds, or bonded structures and for mapping turbulent boundary layers and other frictional effects associated with fluid flow [2].

Cholesteric materials are also used in measuring skin temperatures in man. In this way such materials can be used to detect any abnormal "hot spots"; cholesteric liquid thermography permits immediate reproducible visualization of



<u>Plate 1.1 Cholesteric thermogram of a malignant tumour</u>

surface temperature in colours which respond rapidly to temperature changes [14]. Such materials therefore are used as a diagnostic tool in detecting carcinoma of the breast and skin and in studying abnormal venous patterns. (see plate 1.1.)

1.1.2.3. Other uses

Smectic liquid crystals have use in laser addressed projection display systems. A layer of smectic A is written from one side by a laser which changes the texture of the smectic layer by heat, and is read from the other side to produce a projected image [13].

In the field of medicine liquid crystals are factors in several diseases; hardening of the arteries is as a result of deposition of liquid crystals of cholesterol esters on artery walls [15].

1.1.3. Novel liquid crystalline polymeric materials

It is possible to modify the properties of polymeric liquid crystals, thus creating novel materials, by either copolymerising the liquid crystalline backbone with, for example, a thermoplastic segment, or grafting the backbone with another polymer. In order for copolymerisation to occur the polymers concerned must possess functional end groups. In the case of grafting both polymers must contain an active functional group.

1.2. Biosensors

A biosensor is a probe, device or electrode which when contacted with a biological medium, converts the presence of a desired analyte into an electrical signal [16]. It comprises a biologically sensitive material immobilised in intimate contact with a suitable transducing system which converts the biochemical signal into a quantifiable and processable electrical signal. An example of a biologically sensitive material is a polymeric membrane which is responsible for the recognition of the analyte and thus the specificity and sensitivity of the final device.

The major impetus for the development of biosensors has undoubtedly come from the rapid advances in health care technology. For example it is now generally appreciated that the frequent measurement of biochemical parameters such as blood cations, gases and metabolites, is an essential pre-requisite for the delivery of effective patient care. Thus cheap and reliable "in vitro" sensors are required for monitoring key metabolites in the ward, surgery, home and laboratory on samples derived from tissue fluids such as blood, sweat, saliva and urine.

The continuous signal provided by some categories of biosensor may be exploited in an alternative mode, that of "in vivo" monitoring of the metabolically unstable patient in which rapid and potentially injurious biochemical changes can be missed by discrete measurement. Such "in vivo" sensors could monitor metabolites intravascularly (in the blood system) or transcutaneously (across the skin surface). Work is currently being carried out on a long range project and there are plans to develop an array of on-line sensors for selected coagulation proteins in blood, based on detection using total internal reflection fluorescence [17]. This would give valuable information of blood damage and activation of coagulation. The industrial equivalent of "in vivo" sensors would be devices incorporated into reactors such as plants to monitor dissolved gases, ions etc. Such on-line sensors would provide essential information on the progress of reactions.

In many cases biosensors are in contact with biological fluids such as blood. Hence, it is essential, particularly in "in vivo" sensors that the biosensor is biocompatible. Biocompatibility is the term used to describe the state of affairs when a material exists within a physiological environment without either the material adversely and significantly affecting the body or the environment of the body adversely or significantly affecting the material [18].

Two major factors have to be considered when selecting a biocompatible material:

(i) Wettability - one of the main constituents of tissue fluid is water and the polymer must be wettable in order to be biocompatible.

(ii) Blood clotting - within a few seconds of exposure to blood all non-physiological materials acquire a rapidly thickening coat of essentially pure protein which significantly modifies the surface of these materials. The surface of the polymer must be modified to avoid this happening [19].

1.2.1. Different forms of biosensors

There are two main types of biosensor

(i) Potentiometric

In the potentiometric type a membrane or sensing surface acts as a battery generating a potential proportional to the logarithm of the analyte concentration [16, 20]. The best known potentiometric device is the ion sensitive electrode - the concentrations of ions in solution are measured by observing changes in the electrode potential brought about by binding selective ions to a sensing membrane.

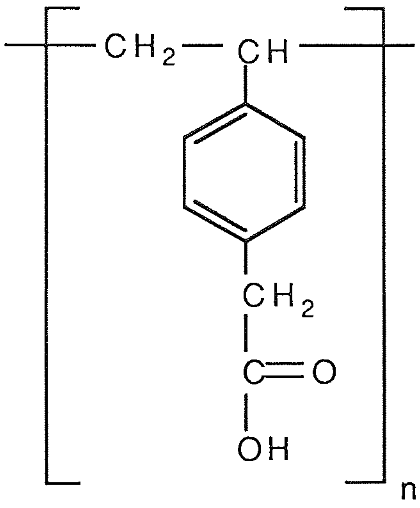
(ii) Amperometric

In the case of an amperometric sensor a voltage is applied causing a current flow that is proportional to the concentration of the analyte [16, 20].

There have been recent advances in the field of optical biosensors. For example, simple fibre optic technology can be used to devise reflective, transmission or fluorescence based biosensors by immobilisation of reactive chemicals at the termination of small fibre optic probes. Thus the determination of pH has been made possible with miniaturised probes in which pH sensitive dyes have been immobilised at fibre termini [16].

1.2.2. Novel Biosensors

One of the major uses of biosensors is to detect and measure the concentration of ions in a solution. Thus the sensing surface must possess the ability to combine with a specific ion. A polymer which has functionality in terms of containing a reactive chemical group could act in this way. An example of such a polymeric substance is:



poly(p-vinylphenylacetic acid)

For example, sodium ions in an alkaline environment may react with the functional carboxylic acid group. Therefore the carboxylic acid group provides the polymer with binding properties whilst the polystyrene backbone gives the polymer characteristic thermoplastic properties. However, greater flexibility could be achieved by copolymerisation of the polystyrene backbone with a flexible elastomer such as butadiene.

Nevertheless, if the polymer is to be used in contact with a biological fluid other factors such as wettability must be considered. Wettability is measured in terms of contact angles; polystyrene has a contact angle of 90^{o} with water at $25^{o}C$ [21] showing that it has poor wettability.

Hence all the properties of a polymer must be taken into account when considering its suitability as a biosensor.

1.3 Catalyst support systems

Catalysts for many reactions can often be polymer bound systems. Such systems rely on functionalisation of a monomer or a polymer to provide the reactive species used in the formation of an active catalyst.

An example is a polystyrene bearing cyclopentadienyl metal catalyst. Bromostyrene is first functionalised by making its Grignard derivative. This is reacted with norborn-2-en-7-one to give anti-7-(p-styryl)norborn-2-ene-7-ol which is then converted to anti-7-chloro-7-(p-styryl)norborn-2-ene. The latter product is then copolymerised with styrene and divinylbenzene. The resulting copolymer is treated with butyl lithium to give polymer bound cyclopentadienyl anions which can be converted to polymer bound 2-cyclopentadienyldicarbonyl rhodium catalyst (see figure 1.5). Such catalysts are used in the hydroformylation of 1-hexene[22].

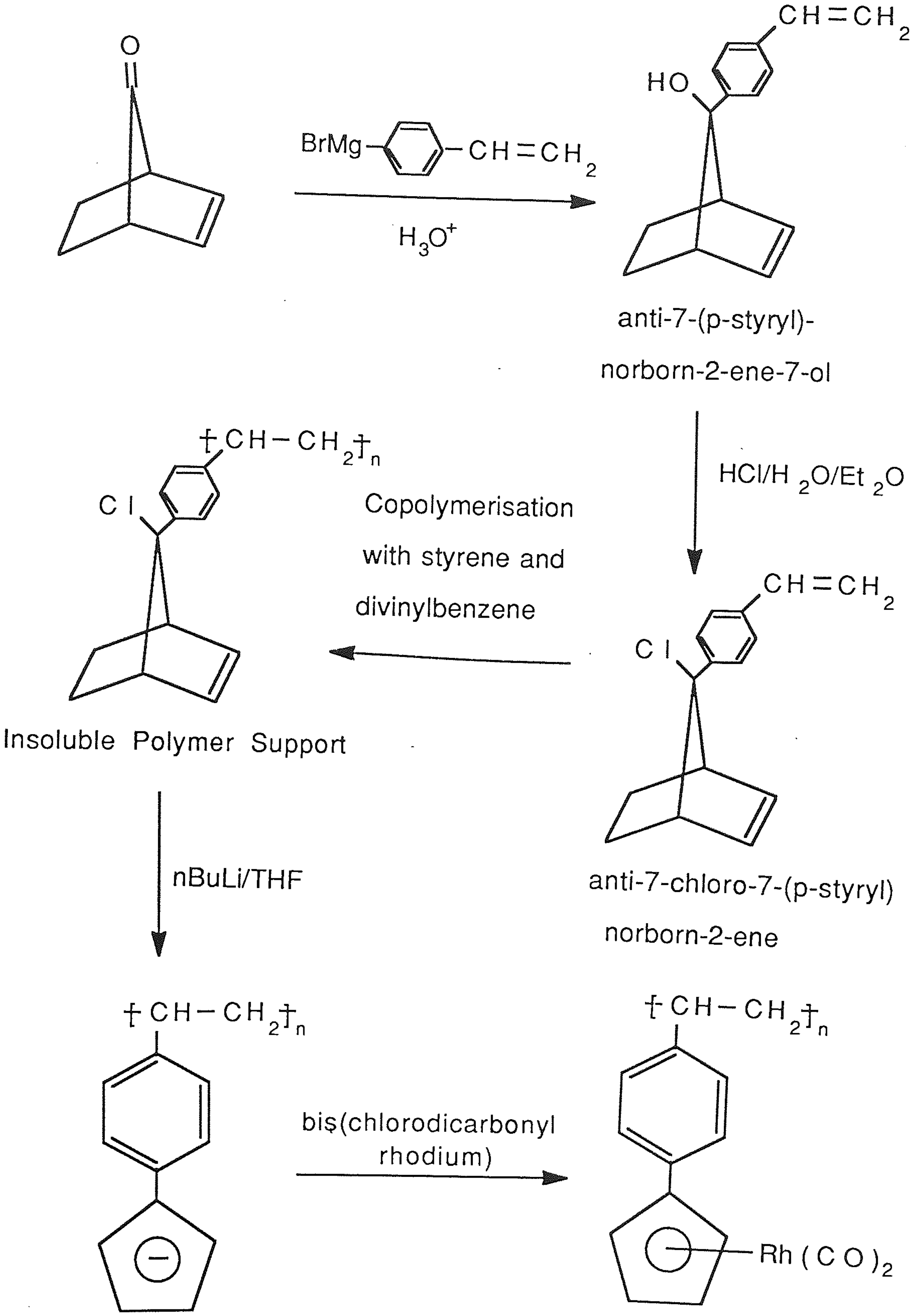
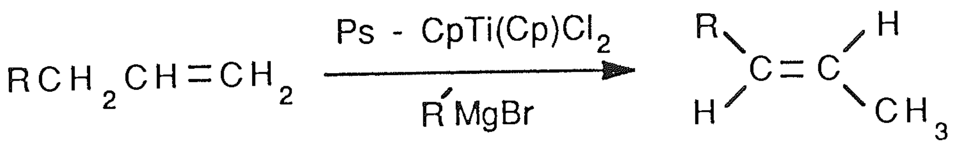

O
BrMg
CH=CH2
H3O+
HO
CH=CH2
anti-7-(p-styryl)-
norborn-2-ene-7-ol
HCl/H 2O/Et 2O
CH=CH2
Cl
anti-7-chloro-7-(p-styryl)
norborn-2-ene
Copolymerisation
with styrene and
divinylbenzene
CH-CH2 n
Cl
Insoluble Polymer Support
nBuLi/THF
CH-CH2 n
bis(chlorodicarbonyl
rhodium)
CH-CH2 n
Rh (CO)2

Figure 1.5

Other examples include the immobilisation of bis(cyclopentadienyl)titanium dichloride on a polystyrene matrix. In order for attachment to occur the polymer must first be functionalised; cyclopentadiene is first bound to a styrene - divinylbenzene copolymer and converted to the cyclopentadienyl anion. The resin bound anion is treated with cyclopentadienyltitanium trichloride and polymer - attached $(C_5H_5)_2Ti\ Cl_2$ is formed. Grubbs and Brubaker [23, 24] used this type of immobilised system and reduced it by using butyllithium to produce an alkene hydrogenation catalyst. This type of catalyst is used in the reduction of olefins such as cyclohexene. The reduced polymer bound catalyst shows considerably greater acitivity - hydrogenation is enhanced by a factor of 25-120- compared to the corresponding reduced non-supported catalyst.

Other interesting chemistry has been carried out using polymer bound bis(cyclopentadienyl)titanium dichloride. It has been shown to react with Grignard reagents to form a reactive alkene isomerisation catalyst which converts 1-alkenes primarily to E-2-alkenes at room temperature [25]. This reaction can be summarised as follows:



This reaction is successful with 1-butene, 1-pentene, and 1-octene.

In contrast the equivalent non-supported titanocene catalyst produced very different results. When 1-octene was allowed to react with unbound bis(cyclopentadienyl)titanium dichloride and isopropylmagnesuim bromide 70% octane was produced by protonation of the intermediate n-octylmagnesium halide.

In addition to forming catalysts functionalised polymeric materials may in certain cases act as initiators to further polymerisation reactions. One such example is the use of lithiated polystyrene as a polymeric anionic initiator. It has been shown that the polymerisation of styrene in a polar medium using a lithiated polystyrene/n-butyllithium mixture proceeds at a faster rate than in the presence of pure butyllithium [26].

Another example of a use of a polymeric anionic initiator is the formation of metallated ethylene-propylene terpolymers and then grafting with monomers such as styrene and butadiene [27].

One further use of a functionalised polymeric material is to act as a support or point of attachment for organic reactants. In this way the polymeric material may act as a blocking device in that the attached reactant has only one remaining reactive site. An example of this is the use of a divinylbenzene/styrene copolymer, containing vicinal functional diol groups, to produce the monoacetals of symmetrical diketones such as 1,3-cyclohexanedione. After attachment to the polymer the remaining free ketone groups react with phenylmagnesium bromide. Subsequent acid hydrolysis from the polymer results in the production of 3-phenyl-2-cyclohexen-1-one in high yield[28].

CHAPTER TWO

EXPERIMENTAL WORK

2. Experimental

2.1. Vacuum techniques

Many of the reactions and polymerisations carried out were extremely sensitive to air and moisture. There are two general techniques which eliminate these two factors, blanket and vacuum techniques. Blanket techniques usually necessitate manipulations in a nitrogen or argon glove box which are unfortunately unreliable and subject to leakages. For this reason vacuum techniques are preferred to blanket techniques.

2.1.1. The vacuum line

The vacuum line shown in figure 2.1 consisted of a main manifold (A), four taps (W), (X), (Y) and (Z) with joints (W'), (X'), (Y') and (Z'), and the adjoining bulb (B). The bulb increased the internal volume of the system so aiding the degassing of materials. The manifold was evacuated by an Edwards rotary vacuum pump (C) in conjunction with a mercury diffusion pump (D). Pressure as low as 10^{-5} mmHg ($10^{-5}\mathcal{T}$) could be maintained for long periods in this equipment; the pressure in the system was estimated by use of a vacustat gauge (E). Liquid nitrogen cold traps (F) were used to condense any organic or mercury vapours from the manifold and diffusion pump respectively.

Flasks or specially constructed apparatus could be attached to the manifold at one of the greased joints (W'), (X'), (Y') or (Z').

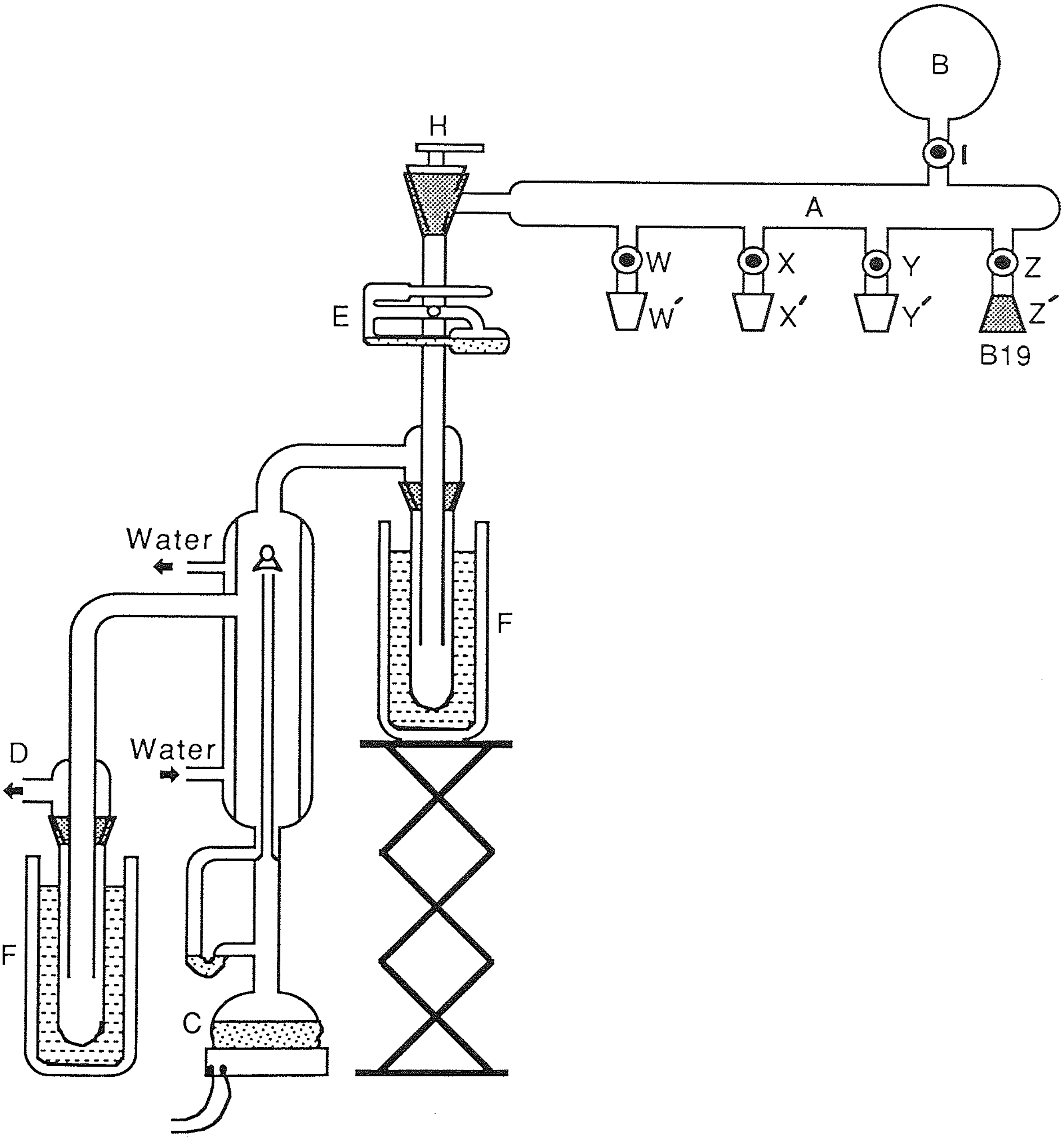


Figure 2.1 The vacuum line

2.1.2. Degassing Solvents

In order for a solvent to be distilled under vacuum the solvent first had to be degassed. A high vacuum was produced with bulb (B) open to the manifold. A flask similar to that shown in figure 2.2 containing the solvent and with tap (P) closed was attached to the manifold via one of the greased joints (W'), (X') or (Y'). The joint was evacuated by opening the corresponding tap (W), (X) or (Y). The solvent was then cooled by immersion of the flask into a Dewar filled with liquid nitrogen. Once the solvent had frozen the tap on the flask (P) was opened, thus evacuating the vessel. When a high vacuum had been formed once more tap (H) was closed and the solvent was allowed to thaw by gentle heating with a hair dryer; gas trapped in the frozen solvent was then released and equilibrated in the atmosphere above the solvent. Once the solvent had completely thawed tap (P) was closed and tap (H) opened. The solvent was refrozen before tap (P) was opened again and a high vacuum re-established. This process of freezing and thawing was repeated until a high vacuum was observed between the two processes. When the solvent was finally thawed it was ready for distillation.

2.1.3. Trap to trap distillation

The flask containing the degassed solvent or monomer was attached to the main manifold via a greased joint. A second empty flask was also connected to the vacuum line via an adjacent greased joint. The empty flask was then evacuated. Once a high vacuum had been obtained in the system both the empty receiver flask and the main manifold were heated very strongly with a hair dryer to remove the last traces of

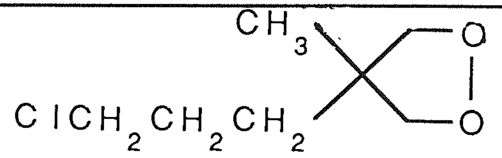
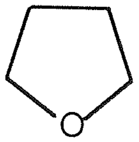
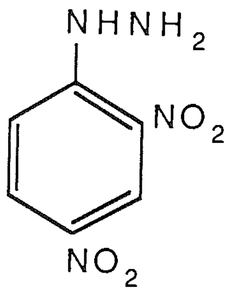
Table 2.1 List of Chemicals

CHEMICAL	FORMULA	SOURCE	MOLECULAR WEIGHT g/mol	MELTING POINT^{o}C	BOILING POINT^{o}C	SPECIFIC GRAVITY
METHYL METHACRYLATE (MMA)	$H_2C{=}C(CH_3)CO_2CH_3$	ALDRICH	100.12	-48	100	0.936
4-BROMOSTYRENE (BS)	$H_2C{=}CHC_6H_4Br$	ALDRICH	183.05	-	102-104	1.4
VINYLTOLUENE (VT)	$CH_3C_6H_4CH{=}CH_2$	FLUKA	118.18		169-172	0.896
BENZOYL PEROXIDE	$(C_6H_5CO)_2O_2$	ALDRICH	242.23	95	-	-
1-AZOISO-BUTYRONITRILE (AZBN)	$(CH_3)_2C(CN)N{:}NC(CH_3)_2CN$	FLUKA	164.21	102-104	-	-
ETHYLENE GLYCOL DIMETHACRYLATE (EGDMA)	$[H_2C{=}C(CH_3)CO_2CH_2]_2$	ALDRICH	198.22	-	66-68	1.051
TETRAMETHYL - ETHYLENE DIAMINE (TMEDA)	$[(CH_3)_2NCH_2CH_2N(CH_3)_2]_2$	ALDRICH	116.21	-55	120-122	0.770
OCTAN - I -OL	$CH_3(CH_2)_7OH$	ALDRICH	130.23	-15	196	0.827
EUGENOL	$4\text{-}(H_2C{=}CHCH_2)C_6H_3\text{-}2\text{-}(OCH_3)OH$	ALDRICH	164.20	-12- (-10^{o}C)	2.54	1.066

Table 2.1 cont.

CHEMICAL	FORMULA	SOURCE	MOLECULAR WEIGHT	MELTING POINT°C	BOILING POINT°C	SPECIFIC GRAVITY
HEXAN - 1- OL	$CH_3(CH_2)_5OH$	ALDRICH	102.18	-52	156.5	0.814
PENTAN - 1 -OL	$CH_3(CH_2)_4OH$	ALDRICH	88.15	-78	136-138	0.811
CYCLOHEXANE	C_6H_{12}	BDH	84.16	6.5	80-81	0.777-0.779
TOLUENE	$C_6H_5CH_3$	ALDRICH	92.14	-93	111	0.864-0.867
3-(METHLYPROPENOXY CARBONYL) PROPYLTRIMETHOXYSILANE (A174)	$CH_2=C(CH_3)COO(CH_2)_3SiO(CH_3)_3$	SIGMA	248	-	-	1.04
44'-BIS(DIMETHYLAMINO) BENZOPHENONE (MICHLERS KETONE)	$[(CH3)2NC6H4]2CO$	ALDRICH	268.36	174.176	-	-
ETHYL FORMATE	$HCO_2C_2H_5$	ALDRICH	74.08	-80	52-54	0.917
n-BUTYL LITHIUM (1.6M IN HEXANE)	$CH_3(CH_2)_2\overset{-}{C}H_2\overset{+}{Li}$	ALDRICH	-	-	-	-
POTASSIUM t - BUTOXIDE (K Bu^t O)	$(CH_3)_3COK$	ALDRICH	112.22	256-258	-	-
DIISOPROPYLAMINE	$[(CH_3)_2CH]_2NH$	ALDRICH	101.19	-61	84	0.722

Table 2.1 cont.

CHEMICAL	FORMULA	SOURCE	MOLECULAR WEIGHT	MELTING POINT°C	BOILING POINT°C	SPECIFIC GRAVITY
2-(3-CHLOROPROPYL)-2-METHYL- 1,3, - DIOXALANE (CPMD)		ALDRICH	164.23		198-200	1.094
TETRAHYDROFURAN (THF)		BDH	72.11	-108	67	0.886-0.887
1, 2, DIBROMOETHANE	$BrCH_2CH_2Br$	ALDRICH	187.87	9-10	131-132	2.180
2, 4, DINITROPHENYL HYDRAZINE		ALDRICH	198.14			

moisture from the equipment. After allowing the empty flask to cool to room temperature the flask was placed in a Dewar flask containing liquid nitrogen. The manifold was isolated from the pumping system and bulb (B) by closing taps (H) and (I). Tap (P) on the flask containing the degassed monomer or solvent was opened and liquid was allowed to gently distil into the receiving flask. The rate of distillation was controlled by adjusting the taps attached to the greased joints but, occasionally, warming the flask containing the solvent to be distilled was found to be necessary in order to facilitate the process.

2.2. Treatment of glassware

Most of the glass apparatus, apart from the vacuum line, was cleaned very effectively by first washing with repeated amounts of water, acetone, and toluene and then soaking overnight in concentrated sulphuric acid. The apparatus was then washed again with copious amounts of water and dried in an air oven at $240^{o}C$. In some cases this treatment was not sufficient to remove the last traces of contaminating material. Consequently, the apparatus was washed with HF, repeatedly with water and then dried in an oven at $240^{o}C$.

After having been dried in an oven, syringes were allowed to cool in a dessicator containing powdered calcium chloride.

2.3. Purification and drying of materials

The materials used during the course of this project are shown in Table 2.1.

2.3.1. Monomers

2.3.1.1. 3-(methylpropenoxycarbonyl)propyl-trimethoxysilane-(A174)

Attempts were made to remove the inhibitor from A174 by the following processes:

(a) Distillation under reduced pressure
(b) Extraction with sodium hydroxide solution
(c) Extraction with ferrous sulphate solution

2.3.1.2. Methyl methacrylate

The inhibitor (10ppm hydroquinone) was removed by shaking three times with an equal volume of 10% w/v sodium hydroxide solution and then washing several times with water. The monomer was dried over magnesium sulphate, filtered and then distilled at 55^{o}C, under reduced pressure, in a conventional distillation apparatus.

2.3.1.3. 4-Bromostyrene

This was often found to have polymerised by 30-40%; 50ml of ether was added to 50g of 4-bromostyrene to precipitate the polymer. The latter was then removed by filtering and the inhibitor (10% hydroquinone) was removed from the monomer solution using 10% w/v sodium hydroxide solution and washing with water as described previously. The ether was removed from the monomer solution by distillation under vacuum; gas liquid chromatography (GLC) confirmed the removal of ether from the monomer solution. The 4-bromostyrene monomer was then dried over activated alumina and stored in a flask similar to the one shown in figure 2.2 which was kept under vacuum and at low temperature.

2.3.1.4. Vinyltoluene (mixture of meta and para isomers)

Method A

The inhibitor (0.001% of 4-tert-butylcatechol) was removed using a 10% w/v sodium hydroxide solution as described in section 2.3.1.2.

Method B

The monomer was maintained over calcium hydride powder in a stoppered flask for at least three days and then stored in a standard storage flask (shown in figure 2.2) which was kept under vacuum.

2.3.2. Polymerisation initiators

2.3.2.1. Benzoyl peroxide

This was recrystallised from chloroform and stored in a storage flask (shown in figure 2.2.) which was kept under vacuum and at low temperature.

2.3.3. Complexing agents

2.3.3.1. Tetramethylethylenediamine (TMEDA)

This was fractionally distilled and the middle fraction collected. This fraction was then dried over activated alumina and stored in a flask, (shown in figure 2.2.) kept under vacuum.

2.3.4. Functionalisation agents

2.3.4.1. Diisopropylamine

This was transferred to an evacuated storage vessel (shown in figure 2.3) in an atmosphere of argon inside a glove box. The storage vessel containing the transferred liquid was then degassed.

2.3.4.2. Ethyl formate

This was stored under vacuum in a storage flask similar to the one shown in figure 2.2.

2.3.4.3. 2-(3-chloropropyl)-2-methyl-1,3-dioxalane (CPMD)

This was transferred to an evacuated storage vessel (shown in figure 2.3) in an atmosphere of argon inside a glove box. The storage vessel containing the transferred liquid was then degassed.

2.3.4.4. Potassium t-butoxide (K Bu^{t}O)

This reagent was stored under vacuum in a standard storage flask (shown in figure 2.2)

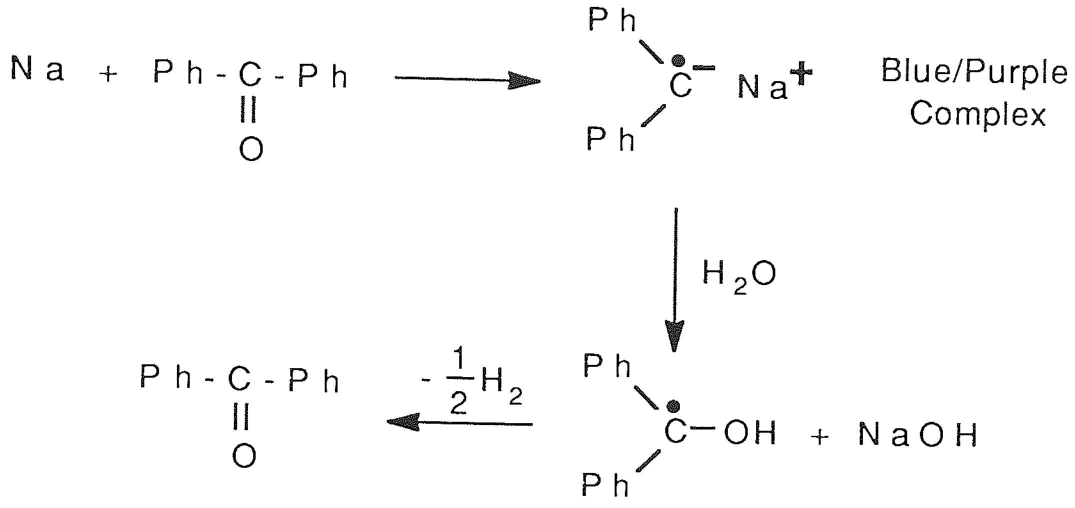
2.3.4.5. Carbon dioxide

Carbon dioxide gas was dried by bubbling through concentrated H_2SO_4.

2.3.5. Solvents

2.3.5.1. Cyclohexane, THF

Such solvents were first maintained over calcium hydride in a stoppered flask for at least three days. Calcium hydride powder was removed by filtration and the filtrate distilled under vacuum into another flask containing small slices of freshly cut sodium and 5-10g of benzophenone. The distillate was degassed to remove the hydrogen evolved and when completely dry a blue solution was produced in the case of cyclohexane and a purple solution was produced in the case of THF. These colours resulted from the production of a sodium/benzophenone complex which will only develop in a completely dry environment and hence acts as an indication of the solvents' dryness.



2.3.5.2. Toluene

Toluene was degassed with nitrogen for approximately 30 minutes.

2.3.6. Drying agents

2.3.6.1. Alumina

About 200ml of chromatographic grade alumina was heated in a furnace to 550^{o}C for at least 16 hours. After allowing the alumina to cool in the furnace it was then stored in an oven at 160^{o}C until required.

2.4 Dispension of chemicals from storage flasks

All chemicals stored under vacuum were either distilled under vacuum directly into reaction vessels, or dispensed under nitrogen. Two types of storage flask were used type A (figure 2.3) and type B (figure 2.2), and the methods employed for dispensation are described below.

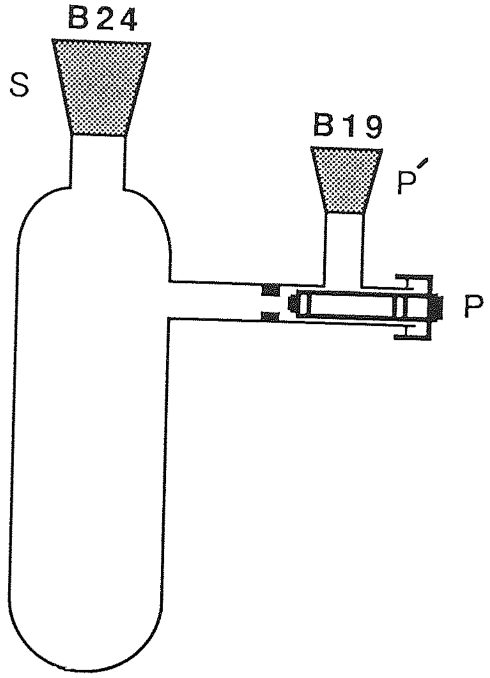


Figure 2.2 Flask B

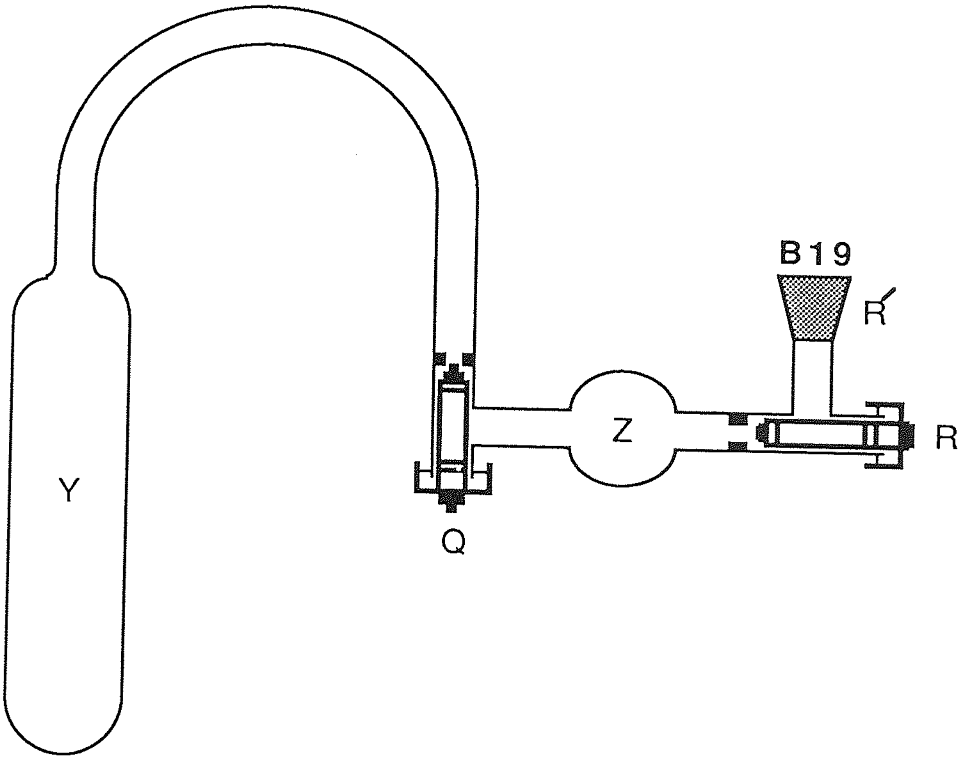


Figure 2.3 Flask A

2.4.1. Flask A

Section Z was evacuated via tap (R), tap (Q) remaining closed. Tap (R) was then closed and the flask removed from the vacuum line. Tap (Q) was opened and liquid was poured into section (Z). When section (Z) contained approximately the correct volume of liquid, tap (Q) was closed. A nitrogen bleed was attached to joint (R') and tap (R) removed. The required volume of liquid was then transferred from the flask by a syringe inserted at point (R). The nitrogen bleed was removed and any excess liquid discarded. Tap (R) was then replaced and closed. In this way liquid in section (Y) was kept under constant vacuum.

2.4.2. Flask B

A nitrogen bleed was attached to joint (P'). Tap (P) was then opened and the stopper (S) removed from the flask. The solid or liquid sample was removed from the flask, the stopper replaced, tap (P) closed and the nitrogen bleed removed. The flask was then degassed as described in section 2.1.2.

2.5. Preparation of solutions

2.5.1. Preparation of a solution of BuLi/TMEDA in cylclohexane

The required volume of dry cyclohexane was distilled into section (E) of a flask similar to that shown in figure 2.4., tap (D) remaining closed. Tap (D) was then opened and a known volume of BuLi solution was injected via the "subaseal" (B) fitted at joint (C). A pre-determined amount of TMEDA was removed from the storage flask by the method described in

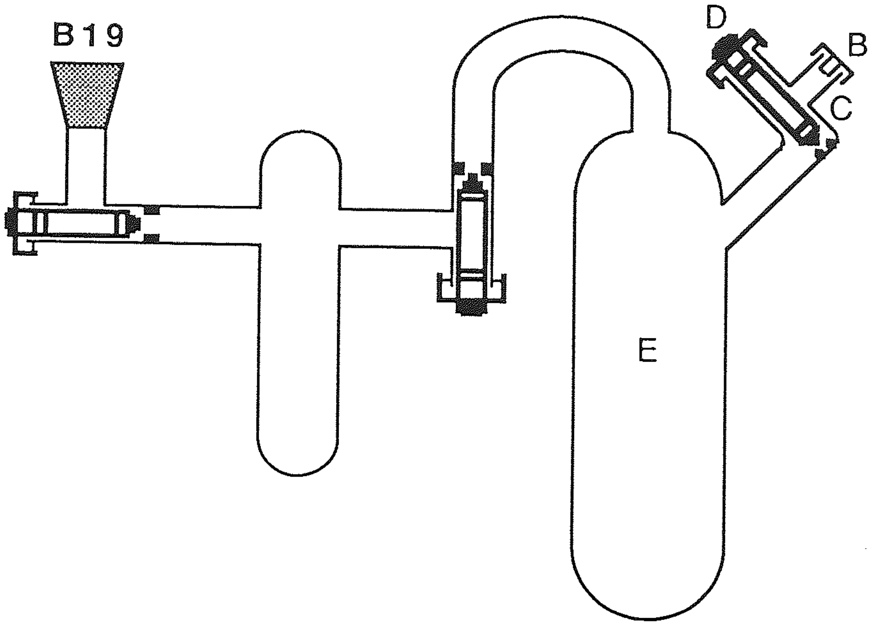


Figure 2.4 Flask for the preparation of BuLi/TMEDA solution in THF

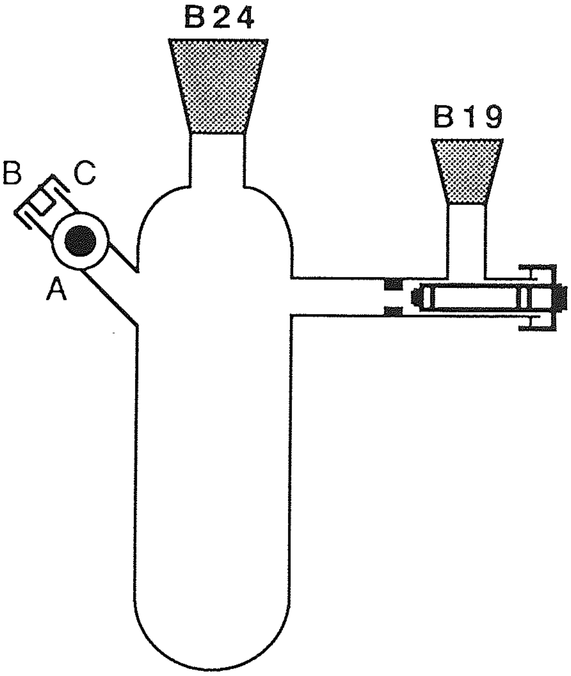


Figure 2.5 Flask for the preparation of KBu^tO suspension in THF

section 2.4.2. and injected through "subaseal" (B). Tap (D) was then closed.

2.5.2. Preparation of a suspension of K Bu^{t}O in LiBu/THF

A weighed amount of K Bu^{t}O was removed by the method described in section 2.4.2., placed in a flask (shown in figure 2.5) containing a few dry glass beads and further dried by attaching the flask to the vacuum system for two hours. A known volume of dry THF was distilled under vacuum into the flask and the flask placed on a shaker for two days. Tap (A) was opened and butyllithium was injected via the subaseal (B) fitted at joint (C).

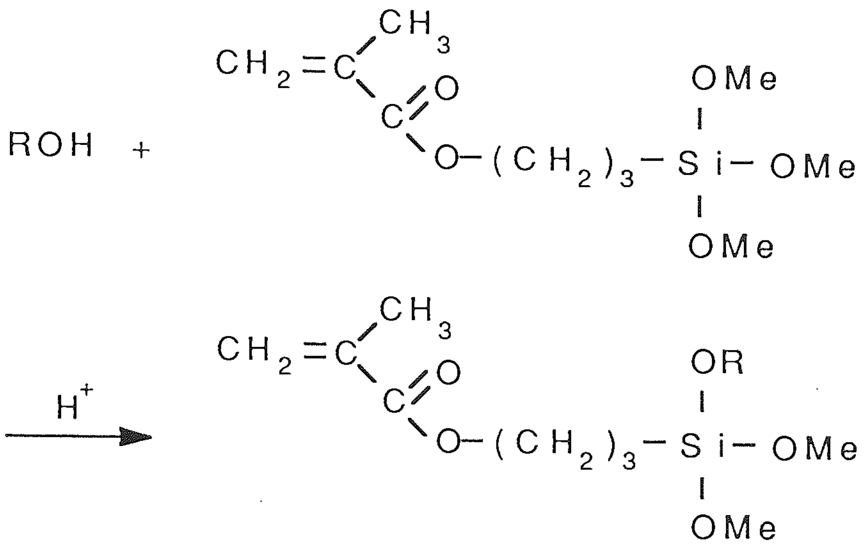
2.5.3. Preparation of a suspension of K Bu^{t}O in THF

A weighed amount of K Bu^{t}O was removed by the method described in section 2.4.2. and placed in a flask similar to that shown in figure 2.2 which contained a few dry glass beads. The contents of the vessel were further dried by attaching the flask to the vacuum for two hours. A known volume of dry THF was distilled under vacuum into the flask and the flask placed on a shaker for two days.

2.6. Monomer synthesis

2.6.1. Acid catalysed alcohol exchange reactions of A174

A number of monomers were prepared by the reaction between A174 and a series of alcohols under acidic conditions as described in section 3.3.2. The reactions are summarised by:



The required amount of alcohol and A174 (molar ratio alcohol: A174 = 3:1) were added to a three necked round bottomed flask fitted with a dropping funnel, nitrogen bleed and gas outlet. The flask was placed in an ice bath and the contents were stirred with a magnetic stirrer. The acid catalyst was added dropwise from the dropping funnel to the stirred reaction mixture. After addition of the catalyst was complete the mixture was stirred at room temperature for two days. The mixture was then washed twice with distilled water, twice with 10% w/v sodium bicarbonate solution and once again with distilled water. A solution of the monomer in cyclohexane was generated by adding the solvent to the extracted product. The solution was shaken with anhydrous magnesium sulphate, which was subsequently removed by filtration. Purification of the comonomer was then attempted using a Dean and Stark apparatus attached to a simple reflux system. The pressure in the system was controlled by including a 3-way tap between the vacuum pump and the system.

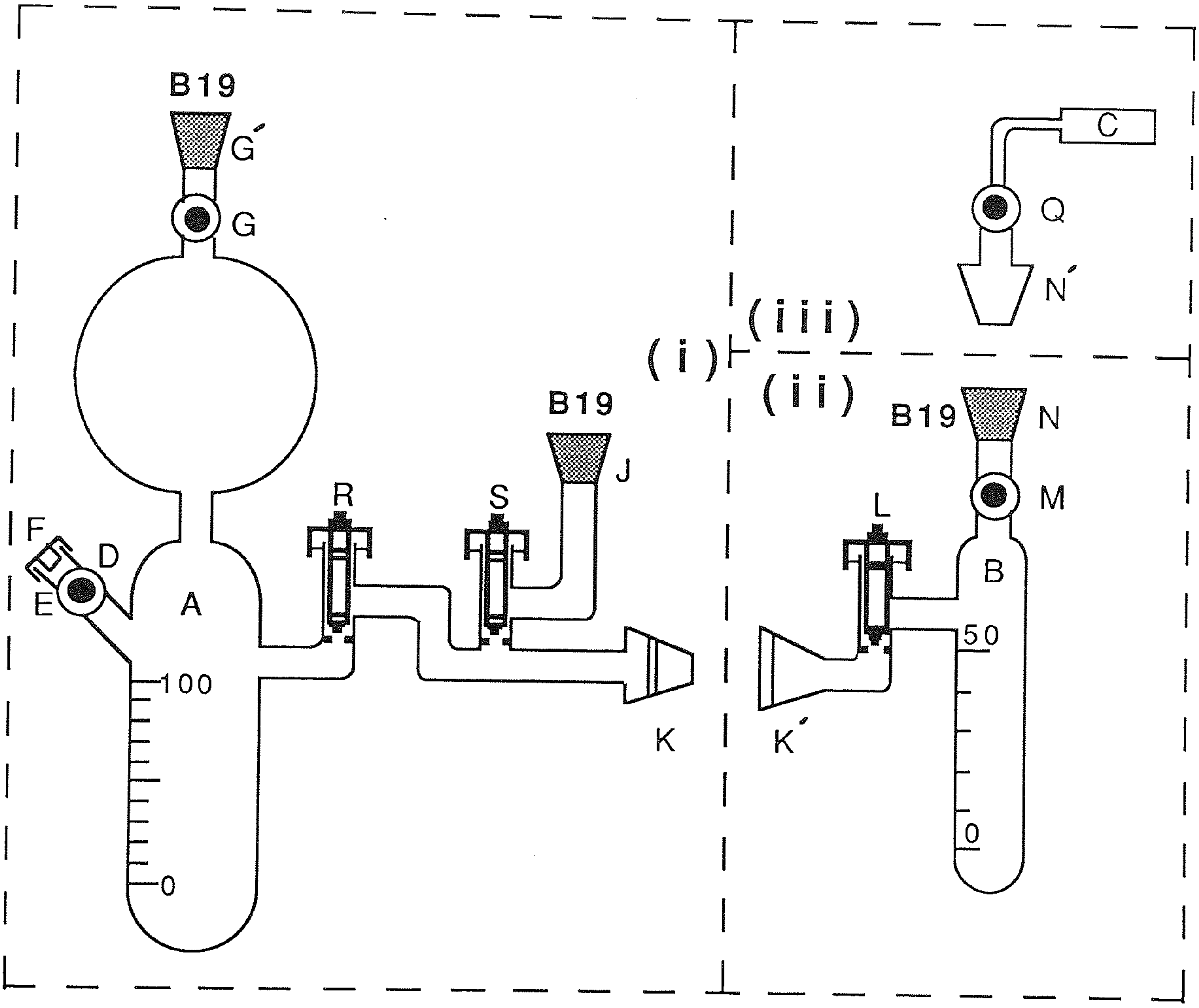


Figure 2.6 Apparatus used for metallation and polymerisation reactions

2.6.2. Functionalisation of vinyltoluene

2.6.2.1. Metallation

The required amount of dry THF was distilled under vacuum into the calibrated vessel (A) shown in figure 2.6 (i) Tap (D) was then opened. A pre-determined amount of diisopropylamine was removed from the storage flask by the method described in section 2.4.1. and injected through a subaseal (F) fitted at joint (E). The equivalent quantity of butyllithium to maintain a 2:1 molar ratio of diisopropylamine : BuLi was then injected. Tap (D) was closed. After five minutes a known volume of vinyltoluene, which had been purified by method (B), and distilled under vacuum into the calibrated vessel (B) shown in figure 2.6 (ii), was added to vessel (A) by the following procedure. Vessels (A) and (B) were joined at K/K' and the joint evacuated via tap (S), taps (R) and (L) remaining closed. Tap (S) was closed and the apparatus was removed from the vacuum line. Taps (R) and (L) were opened and the contents of (B) were poured into (A) and thoroughly mixed. Tap (R) was then closed and vessel (B) removed from the apparatus. The colour of the reaction mixture was seen to turn yellow immediately after the addition of the monomer. The reaction vessel (A) was placed in a constant temperature water bath for five hours; the colour of the reaction mixture was more intense on removal from the water bath indicative of the high degree of metallation.

2.6.2.2. Carboxylation

The apparatus containing the metallated monomer was attached to the vacuum line at joint G'/Y' and the region was evacuated.

Taps (G) and (Y) were then closed. The manifold and expansion bulb (B) were filled with carbon dioxide by closing the main tap (H), attaching a gas bleed at joint (Z') and opening tap (Z). When sufficient gas had been added tap (Z) was closed. Taps (Y) and (G) were then opened and carbon dioxide diffused slowly into the reaction vessel. The contents of the flask became warm and pale yellow. When the colour change was complete the contents were degassed, IM hydrochloric acid was added, the organic layer was separated and a sample was removed from this layer for IR analysis. Any residual solvent was removed by vacuum distillation from the organic layer to leave the monomer ready for polymerisation.

2.6.2.3. Synthesis of 2-methyl-2(4-(vinylphenyl)-butyl)-1,3-dioxalane

2.6.2.3.1. Method one

Vinyltoluene was lithiated as described in section 2.6.2.1. Five hours after the addition of the monomer to the reaction flask the required amount 2-(3-chloropropyl)-2-methyl-1,3,-dioxalane (CPMD) was removed from the storage flask by the method described in section 2.4.1. and injected via the subaseal fitted joint (E). A white precipitate formed in the reaction vessel. The precipitate was removed by filtration and dried. A sample of the filtrate was removed for analysis by IR.

2.6.2.3.2. Method two

2.6.2.3.2.1. Metallation of the monomer

A known volume of dry THF was distilled under vacuum into vessel (A) of the apparatus shown in figure 2.6 (i) and a known volume of vinyltoluene into vessel (B) shown in figure 2.6 (ii). The monomer was transferred from vessel (B) to vessel (A) by the procedure described in section 2.6.2.1. The required volume of K Bu^tO /THF suspension was prepared as described in section 2.5.3. removed by the procedure described in section 2.4.2. and injected through the subaseal (F) fitted at joint (E). Tap (D) was closed and the contents of the reaction vessel (A) were then stirred magnetically at room temperature for four hours..

2.6.2.3.2.2. Sampling of the reaction mixture

Vessel (B) was cleaned, dried and returned to vessel (A) at K/K' together with a spectrophotometer cell (C) attached at N/N'. The apparatus was returned to the vacuum line at joint (J) and taps (S), (L), (M) and (Q) were opened to evacuate this part of the apparatus. Tap (S) was closed. Tap (R) was opened and a sample of the reaction mixture was poured under vacuum into vessel (B). Taps (R) and (L) were closed and the apparatus separated at K/K'. A sample of the reaction solution was then poured into the spectrophotometer cell (C) and taps (Q) and (M) were closed. The joint N/N' was then separated and the UV/visible spectrum of the sample in (C) was recorded. When appropriate the remaining solution could be used for IR analysis. UV analysis was carried out on either neat samples or dilute solutions made by distilling dry THF into the reaction vessel (A).

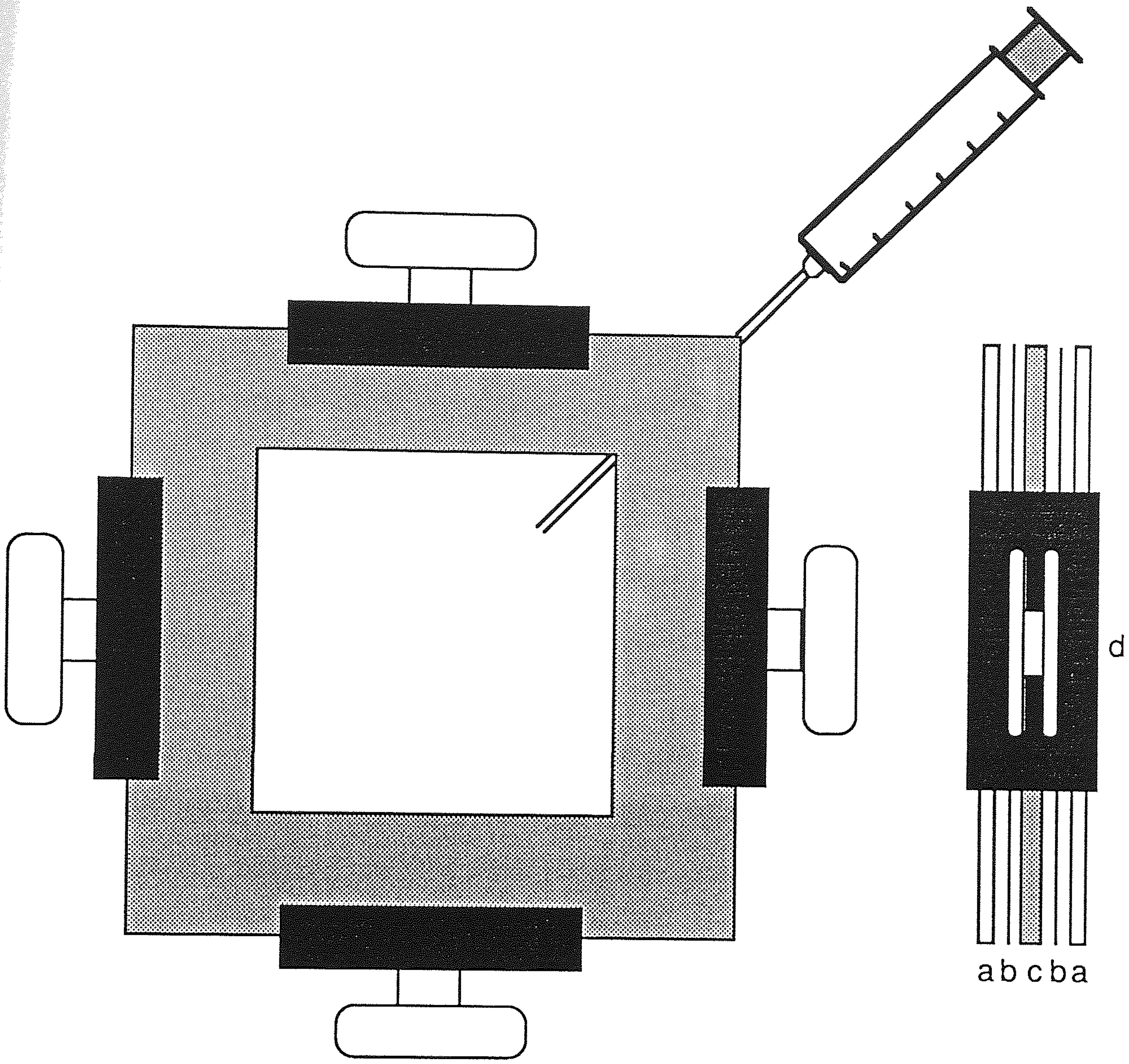
2.6.2.3.2.3. Reactions of the metallated monomer

(i) Michlers ketone

An amount of Michlers ketone in dry THF equivalent to the number of moles of monomer was removed from the storage flask as described in section 2.4.2 and injected into the reaction mixture through the subaseal (F) fitted at joint (E). Tap (D) was closed and a sample was removed immediately by the method described in section 2.6.2.3.2.2.

(ii) 2-(3-chloropropyl)-2-methyl-1,3-dioxalane (CPMD)

The required amount of CPMD was removed from the storage flask by the procedure described in section 2.4.1. and added to the reaction mixture contained in vessel (A) via the subaseal at joint (E). A sample was then removed immediately by the method described in section 2.6.2.3.2.2. The contents of vessel (A) were allowed to react for four hours and a further sample removed by the method described in section 2.6.2.3.2.2. The remaining product was used without further purification for polymerisation.



KEY: a=glass plate, b=melinex film, c=polyethylene film, d=Bulldog clip

Figure 2.7 Apparatus for the Preparation of Copolymer Sheets

2.7. Polymer synthesis

2.7.1. Free radical polymerisation

2.7.1.1. Copolymerisation of siloxane monomers and methyl methacrylate

2.7.1.1.1. Solution polymerisation

The polymerisation apparatus consisted of a sealed round bottomed flask fitted with a nitrogen bleed and gas outlet. The required amounts of the comonomers were mixed in the polymerisation flask and degassed for an hour. AZBN initiator in toluene was then injected by syringe into the comonomer mixture and the reaction vessel placed in a constant temperature water bath for 18 hours. The contents of the reaction mixture were then poured into methanol when any polymer product was purified by dissolving in chloroform and reprecipitating into methanol.

2.7.1.1.2. Copolymer sheet preparation

The apparatus for copolymer sheet preparation was set up as shown in figure 2.7. It consisted of two glass plates separated by two polyethylene spacer gaskets. The plates and sheets were clamped together by spring clips. The space between the melinex sheets, approximately 0.5mm apart, was filled with copolymerisation solution. A typical copolymerisation solution was prepared by mixing weighed amounts of each comonomer, ethylene glycol dimethacrylate crosslinking agent, and AZBN initiator. The solution contained in a sample bottle was degassed with nitrogen for approximately ten minutes and then

5ml were introduced by a syringe into the space between the plates. The plates were then placed in an oven kept at constant temperature for three days and post cured for two hours.

The polymer was obtained as a sheet. On removal of the polymer samples from the plates a small piece of the sheet was taken, weighed, and placed in toluene overnight. The sample was then removed, dried in a vacuum oven and reweighed. Any difference in weight was recorded.

2.7.1.2. Polymerisation of 4-Bromostyrene

The apparatus was set up as described in section 2.7.1.1.1. 4-Bromostyrene was removed from the storage flask as described in section 2.4.2 and then placed in the polymerisation flask. Polymerisation was carried out as described in section 2.7.1.1.1. but benzoyl peroxide was employed as initiator. On completion of polymerisation the polymer was precipitated in methanol and purified by dissolution in THF and reprecipitation into methanol.

2.7.1.3. Polymerisation of vinyltoluene

The polymerisation of vinyltoluene which had been purified by method (A) was carried out as described in section 2.7.1.2.

2.7.1.4. Polymerisation of (4-vinylphenyl)acetic acid

The monomer was produced as described in section 2.6.2.2. A weighed amount of benzoyl peroxide dissolved in a known volume of toluene was injected into the reaction flask (A) via the "subaseal" at joint (E). Tap (D) was then closed and the

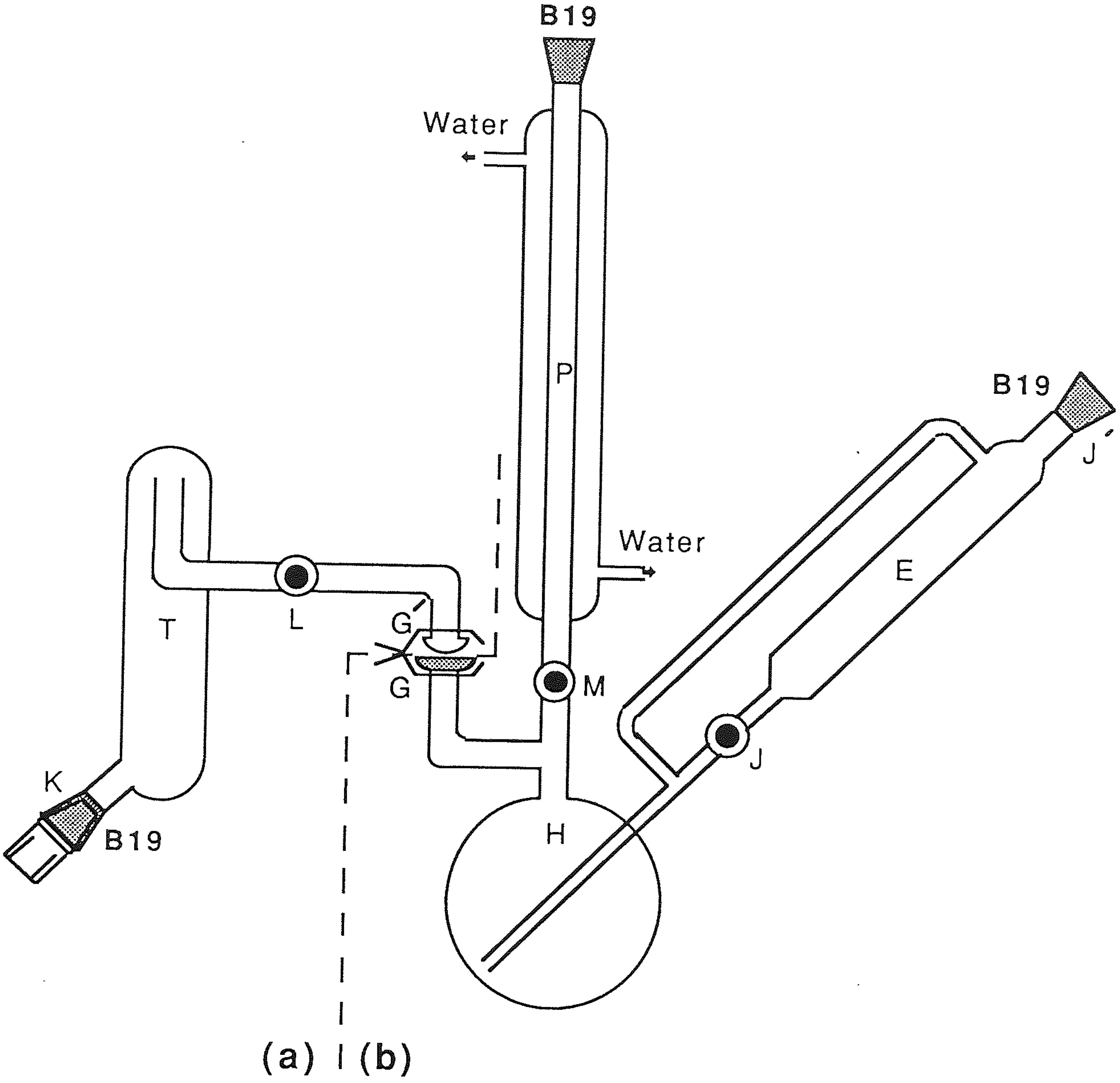


Fig. 2.8 Apparatus for the preparation of Grignard reagents

flask placed in a constant temperature water bath for 18 hours. The polymer was precipitated by adding the reaction mixture to an excess of methanol. Once precipitated the polymer product was then not completely soluble in common organic solvents such as THF and chloroform. Hence purification was difficult.

2.7.2. Anionic polymerisation

2.7.2.1. Polymerisation of 2-methyl-2(4-(vinylphenyl)-butyl)-1,3-dioxalane

The monomer was prepared as described in section 2.6.2.3.2. The required amount of butyllithium was injected into the reaction vessel (A) through the "subaseal" at joint (E). Tap (D) was then closed and the vessel placed in an ice bath for eight hours. The polymer was precipitated by adding the reaction mixture to an excess of methanol. The polymer was purified by dissolution in THF and reprecipitation into methanol.

2.8. Functionalisation of polymers

2.8.1. Grignard reagents

2.8.1.1. Formation of polymeric Grignards

The apparatus was set up as shown in figure 2.8(b) with a cap stopper, held in place by a metal clip, attached at joint (G). The apparatus was flushed with nitrogen for approximately 15 minutes, taps (J) and (M) were closed and a stopper attached to joint J'. The required amount of poly(bromostyrene) was placed in a sealed glass vessel which had also been flushed with nitrogen. A known volume of dry THF was removed from the storage flask by the method described in section 2.4.2. and injected into the glass vessel. When the polymer had dissolved 1,2,dibromoethane was injected. This mixture was then transferredby syringe to the dropping funnel (E) with removal of the stopper fitted at joint (J'). A nitrogen bleed was then attached to the apparatus at joint (J'). A known volume of dry THF was removed by the method described in section 2.4.2, and injected into the reaction flask (H), which contained a weighed amount of magnesium turnings, by the temporary removal of the cap stopper at joint (G). Tap (M) was opened to connect the reaction flask to the reflux apparatus (P). The contents of the dropping funnel were then added dropwise to the reaction flask by opening tap (J). The reaction mixture was stirred continually and heated gently in order to initiate reaction. Once addition of the polymer solution was complete tap (J) was closed and the reaction was left for five hours.

2.8.1.2. Carboxylation

On completion of Grignard formation the contents of the reaction vessel were poured into a slurry of solid CO_2 in dry THF. Once effervescence had ceased IM HCl was added to remove the excess magnesium. The reaction was then poured into an excess of methanol to precipitate the polymer product. The polymer was then dried, dissolved in THF and reprecipitated into methanol.

2.8.1.3. Reaction with esters

The polymeric Grignard was formed as described in section 2.8.1.1. but using a crystal of iodine in the reaction flask (H) in place of 1,2 dibromoethane.

On completion of reaction vessel (T) shown in figure 2.8(a) was flushed with nitrogen, a stopper attached to joint (K) and tap (L) closed. A known volume of ethyl formate was removed by the method described in section 2.4.2. and injected into vessel (T) by removal of the stopper at joint (K). The cap stopper at joint G was then replaced by vessel (T) as shown in figure 2.8.; the vessels (T) and (H) were attached by means of a ball and socket joint, held in place by a metal clip, at G/G'. Tap (L) was opened, the contents of the reaction flask (H) were poured into vessel (T) via G/G' and thoroughly mixed. Tap (L) was closed and the reaction was left for a further hour. The reaction mixture was then decanted from excess magnesium and poured into methanol to precipitate the polymer product. The polymer was dried and purified by reprecipitation into methanol from a solution in THF.

2.8.2 Lithiated polymer synthesis

2.8.2.1. Lithiation and reaction with esters

The apparatus was set up as shown in figure 2.6(i). A predetermined weight of poly(vinyltoluene) was placed in the flask (A) and dried by attaching the flask to the vacuum system for two hours. A known volume of dry cyclohexane was then distilled under vacuum into the flask and the polymer allowed to dissolve. The required amount of BuLi/TMEDA in dry cyclohexane was prepared as described in section 2.5.1. removed by the method described in section 2.4.1. and injected into the flask through the subaseal (F) fitted at joint (E). The flask (A) was placed in a constant temperature water bath when the contents were seen to go orange and then deep red. The reaction was left for six hours. The contents of the flask were now viscous and small amounts of jelly-like substance could be seen on the walls of the vessel. The reaction flask containing the lithiated polymer was attached to the vacuum line at G' via a greased joint. The storage flask containing ethyl formate was attached to the vacuum line via an adjacent greased joint. Ethyl formate was slowly distilled into the reaction flask and the reaction mixture was seen to become yellow and eventually form a brown gel. 1M hydrochloric acid was then added to destroy the gel. The thick viscous organic layer was poured into methanol to precipitate the polymer. Purification of the precipitated polymer was difficult since it only showed partial solubility in most of the common organic solvents.

2.8.2.2. Lithiation and carboxylation

The apparatus was set up as shown in figure 2.6(i). A weighed amount of poly(vinyltoluene) was placed in the reaction flask (A) and dried for two hours by attaching the flask to the vacuum system. A known volume of dry THF was then distilled under vacuum into the reaction flask. A predetermined volume of K Bu^{t}O suspension in BuLi/THF was prepared as described in section 2.5.2, removed by the method described in section 2.4.2 and injected into the flask (A) via the "subaseal" at joint (E). The reaction vessel (A) was placed in a constant temperature water bath when the contents were seen to become orange and then deep red. The reaction was left for seven hours. The reaction mixture was now viscous and some gel like material had accumulated on the interior of the vessel. Samples were, however, also removed in a similar manner to that described in section 2.6.2.3.2.2 after one hour and four hours' reaction time.

Each of the samples was carboxylated separately. Carboxylation was carried out as described in section 2.6.2.2. During carboxylation the reaction mixture slowly changed colour from deep red to clear and then gelled. IM hydrochloric acid was added to the reaction flask to destroy the gel. The contents of the flask were then added to an excess of water to precipitate the polymer. The polymer was dried under vacuum and purified by reprecipitation into water from a solution in THF.

2.8.3 Synthesis of poly(6-(vinylphenyl)hexan-2-one)

A weighed amount of the polymer which was prepared as described in section 2.7.1.4 was dissolved in a known volume of THF. The required amount of acid was then added to the polymer solution and the mixture refluxed for ten hours. The mixture was poured into an excess of water to precipitate the polymer which was then purified by drying, dissolving in THF and reprecipitating into an excess of water.

2.8.3.1. Reaction of poly(6-(vinylphenyl)hexan-2-one) with 2,4-dinitrophenylhydrazine

A weighed amount of poly 6-(vinylphenyl)hexan-2-one) was placed in a sample bottle and a known quantity of THF was added to it. Once the polymer had dissolved a solution of 2,4 dinitrophenylhydrazine in THF was added dropwise. The resulting solution was then analysed by IR.

2.9. Analytical techniques

2.9.1. Nuclear magnetic resonance (NMR)

NMR is a spectroscopic technique associated with the magnetic properties of certain atomic nuclei. Analysis of a molecule by NMR spectroscopy enables one to study the differences in the environments of a particular type of nucleus present in the molecule and to deduce the structure of the molecule. The environment of the nucleus in the molecule can be dependent upon not only the type of group but also the nature of adjacent groups.

The only nuclei that exhibit the NMR phenomenon are those for which the spin quantum number (I) is greater than O; the spin quantum number (I), the mass number (M) and atomic number (Z) of the nuclei are associated as follows:

Mass number	Atomic number	Spin quantum number
odd	odd or even	$^1/_2$, $^3/_2$, $^5/_2$....
even	even	0
even	odd	1, 2, 3

The nuclei of ^1H and ^{13}C exhibit $I = {}^1/_2$ whereas ^{12}C and ^{16}O have $I = O$.

Under the influence of an external magnetic field the magnetic nucleus can take up (2I +1) different orientations with respect to the field so that for a nucleus with spin $^1/_2$ only two orientations are allowed. A nucleus such as this precesses around the axis of an applied external field in two principal orientations, either aligned with the field (low energy) or opposed to the field (high energy). The precessional frequency is directly proportional to the strength of the external field. If the nucleus is precessing in the opposed orientation, subsequently it can lose this extra energy and relax back into the aligned position. If the precessing nuclei are irradiating with a beam of radiofrequency energy of the correct frequency the low energy nuclei may absorb this energy and move to the higher energy state. The NMR signal observed is due to the net absorption of radiofrequency radiation. The nuclei then lose the energy (relaxation) by either transfer to a neighbouring nucleus - (spin - spin relaxation) - or transfer to other surrounding molecules such as solvent molecules - (spin - lattice relaxation).

The precessional frequencies of all nuclei of the same type in the same external field are not, however, identical. Several signals may be observed for one compound; the shift in frequency is called the chemical shift. Usually the chemical shift is measured in units of δ with respect to a reference group of nuclei. For ^1H and ^{13}C the universally accepted reference is tetramethylsilane (TMS). This is chosen because it gives a sharp signal even at low concentrations and the signal arises on the NMR spectrum well clear of most common organic protons and ^{13}C nuclei. The relationship between δ values in ppm and frequency in H_z is expressed as follows

$$\delta_X = \frac{\nu_X - \nu_{TMS}}{\nu_o}$$

Where δ_X = the chemical shift, ν_X and ν_{TMS} are the frequencies of the signals for X and TMS respectively and ν_o is the operating frequency of the instrument.

The chemical shift of a specific nucleus depends on a number of factors such as:

(a) Electronegativity - shielding and deshielding

When a nucleus is attached to a group of greater electronegativity than itself resonance occurs at high δ values. Electronegative groups withdraw electron density from the nucleus and this deshielding effect means that a lower value of the applied magnetic field is needed to bring the nucleus to resonance. However, for an electropositive group the opposite effect operates; electrons are pushed into the nucleus and this shielding effect means that the nucleus comes to resonance at higher fields (lower δ).

(b) Van der Waals deshielding

If a nucleus occupies a sterically hindered position the electron cloud of the hindering group will tend to repel, by electrostatic repulsion, the electron cloud of the magnetic nucleus. Thus the nucleus will be deshielded and appear at higher δ values.

(c) π bonding effects

The chemical shift for nuclei attached to, for example C=C in alkenes, is higher than can be accounted for by electronegativity alone. The explanation is collated with the manner in which electrons, in this case π electrons, circulate under the influence of the applied field. The effect is complex and can lead to downfield shifts (paramagnetic shifts) or upfield shifts (diamagnetic shifts). In addition the effects are paramagnetic in certain directions and diamagnetic in others.

The two most common nuclei used in NMR are ^{13}C and ^{1}H. However, ^{13}C has a lower receptivity than ^{1}H as it is less abundant and its nuclear magnetic properties are less favourable.

^{1}H spectra are often complicated by coupling occurring between ^{1}H nuclei in adjacent groups. However, in ^{13}C spectra to eliminate the complicating effects of coupling with protons the ^{1}H nuclei are decoupled by application of a second radio-frequency which includes all proton resonance frequencies. In this way the protons undergo rapid transitions between spin states so that adjacent carbon nuclei sense an average orientation.

^{13}C NMR unlike ^{1}H NMR is not quantitative since in normal ^{13}C NMR the pulses are applied with only short delays between each successive pair; carbon nuclei with long relaxation times will not have relaxed fully after one pulse before the next pulse is applied. As a result these signals are of lower intensity.

Samples can be analysed by NMR either in solution or in the solid state.

A common solvent used in solution NMR is $CDCl_3$. Sharp signals are produced in solution NMR since molecular orientations in a liquid are random and transfer of energy by spin lattice relaxation is inefficient. In consequence T_1 (the spin - lattice relaxation time) is large.

Solid samples are analysed by a technique called magic angle spinning; the sample is spun at an angle of 54.7^{o} in a Delrin rotor (which has a chemical shift of 89δ). This particular angle is chosen since it reduces chemical shift anisotropy and dipolar decoupling. The spinning speed is also important in that it must be greater than T_2 (the spin - spin relaxation time). Thus solid samples can only be analysed by ^{13}C since the machine could not cope with a spin speed in the order of T_2 for a proton.

As T_1 is relatively large for ^{13}C solid state spectra a technique called cross-polarisation is used; this is achieved by magnetisation transfer from ^{13}C to abundant ^{1}H nuclei by application of a radiofrequency pulse. Hence it enhances the sensitivity of the ^{13}C nuclei and relaxation occurs at the proton rate which is much faster.

Samples were analysed on a Bruker AC 300 Fourier Transform spectrometer. In Fourier Transform (FT) NMR the sample is irradiated (at fixed field) with a strong pulse of radiofrequency energy containing all the frequencies for the particular nucleus e.g ^{13}C being studied. The nuclei in each environment then absorb their appropriate frequencies. However, in Continuous Wave (CW) NMR each transition is induced in succession by continuous scan from low field to high field, the radiofrequency signal remaining constant. The main advantage of FT NMR over CW NMR is that an entire spectrum can be recorded, computerised and transformed in a few seconds; with a repetition every two seconds, for example, 400 spectra can be accumulated in 13 minutes, giving twenty times the signal enhancement thus enabling work to be carried out on samples at very low concentrations and on nuclei with low natural abundance.

Furthermore, the application of a modern NMR sequence to ^{13}C solution spectroscopy was also undertaken. The J modulation spin echo technique provides a method of distinguishing between different protonated (CH_3, CH_2, CH) and non-protonated (quarternary) carbons. The method exploits the fact that relaxation times differ depending on the degree of protonation. The spectra are edited by varying a time delay in the pulse sequence resulting in refocussing of the contributions by carbons of different degrees of protonation giving spectra with either enhanced or reduced signal intensities.

2.9.2. Gas liquid chromatography (GLC)

In GLC the mobile phase is an inert gas such as N_2 and the stationary phase, a non-volatile liquid coated on a solid support, contained within a column which is heated. The sample is introduced as a vapour at the head of the column; those components that have a finite solubility in the stationary liquid phase distribute themselves between this phase and the gas phase according to the equilibrium law. Elution is then accomplished by passing a gas such as nitrogen or helium through the column. The rate at which the various components migrate down the column depends on their tendency to dissolve in the stationary liquid phase. A favourable partition coefficient results in a slow rate. On the other hand, components with low solubility in the liquid phase migrate rapidly. On elution the material is detected by means of a suitable detector - flame ionisation, catherometer, and electron capture detectors are commonly used depending on the nature of the substrates eluted. When using flame ionisation detection the column eluate is mixed with H_2 and air and burned in a flame inside the detector. Carbon atoms of organic compounds can produce CH radicals which go on to produce CHO^+ ions in the hydrogen oxygen flame. The CHO^+ produced in the flame carries current to the cathodic collector above the flame. The current flowing between the anode at the base of the flame and the cathodic collector is measured and translated to a signal on the recorder. Qualitative identification of a component is based upon time required for its peak to appear at the end of the column whilst quantitative data is obtained from evaluation of peak areas. The most common method of measuring the area of a peak (A) is to multiply the height of the peak by its width at half height. This product is then equal to 0.84A.

In general the column temperature need not be above the boiling point of all solutes, it must only be hot enough for each solute to have sufficient vapour pressure to be eluted in a reasonable time. However, when separating a mixture of compounds with a wide range of boiling points or polarities it is very useful to be able to change the column temperature during the separation. For example, at a constant temperature of 150^oC the more volatile compounds of a mixture may emerge very close together and the less volatile compounds may not even be eluted from the column. If the temperature is increased from $50^{o}C$ to $250^{o}C$ at a rate of 8^{o}/minute all the compounds are eluted and the separation between the peaks is fairly uniform.

Samples were analysed on a Pye Unicam Flame Ionisation GCD Chromatograph using a 25% silicone grease column.

2.9.3. Ultraviolet spectroscopy (UV)

The absorption of ultraviolet/visible radiation by a molecule leads to transitions among the electronic levels of the molecule and for this reason the alternative title of electronic spectroscopy is often preferred.

The strength of electronic spectroscopy lies in its ability to measure the extent of multiple bond or aromatic conjugation within molecules.

Compounds that absorb light of wavelength 400 - 800 nm (visible light) appear coloured to the human eye, the precise colour being a complicated function of which wavelengths the compound subtracts from white light. Very many compounds have strong UV absorption bands, the shoulders of which may tail into the visible region - absorbing the violet end of the white light spectrum. Subtraction of violet from white light leaves the complementary colours which appear yellow/orange to the human eye and for this reason the most common colour for organic compounds is orange/yellow. Progressive absorption from 400nm upwards leads to progressive darkening through yellow, orange, red, green, blue, violet and ultimately black.

A chromophore is the term used to describe any functional group that absorbs electromagnetic radiation, for example, the carbonyl group or a carbon-carbon double bond are chromophores of ultraviolet light.

When a molecule absorbs UV/visible light of a particular energy an electron is promoted to a higher energy level. In simple alkenes several transitions are available but the lowest energy transition is the most important : this is the $\pi \longrightarrow \pi^*$ transition which is responsible for an absorption band around 170-190nm in unconjugated dienes. In conjugated dienes such as butadiene the π orbitals of the separate alkene groups combine to form new orbitals - two bonding orbitals π_1 and π_2 and two antibonding orbitals $\pi_3{}^*$ and $\pi_4{}^*$. A new $\pi \rightarrow \pi^*$ transition of very low enegy ($\pi_2 \rightarrow \pi_3{}^*$) is now possible as a result of conjugation. Conjugated dienes therefore show absorption at much longer wavelength than isolated alkene groups.

The modern UV/visible spectrometer consists of a light source, double beams (reference and sample beams), a monochromator, a detector and amplification, and recording devices. The recorder trace is invariably absorbance (A) against wavelength (λ).

For most organic work cells of path length 1cm are used, made up of either synthetic silica or natural silica as Pyrex glass absorbs below 300nm.

Electronic spectra are usually measured on very dilute solutions and the solvent must be transparent within the

Figure 2.9 The gel permeation chromatograph

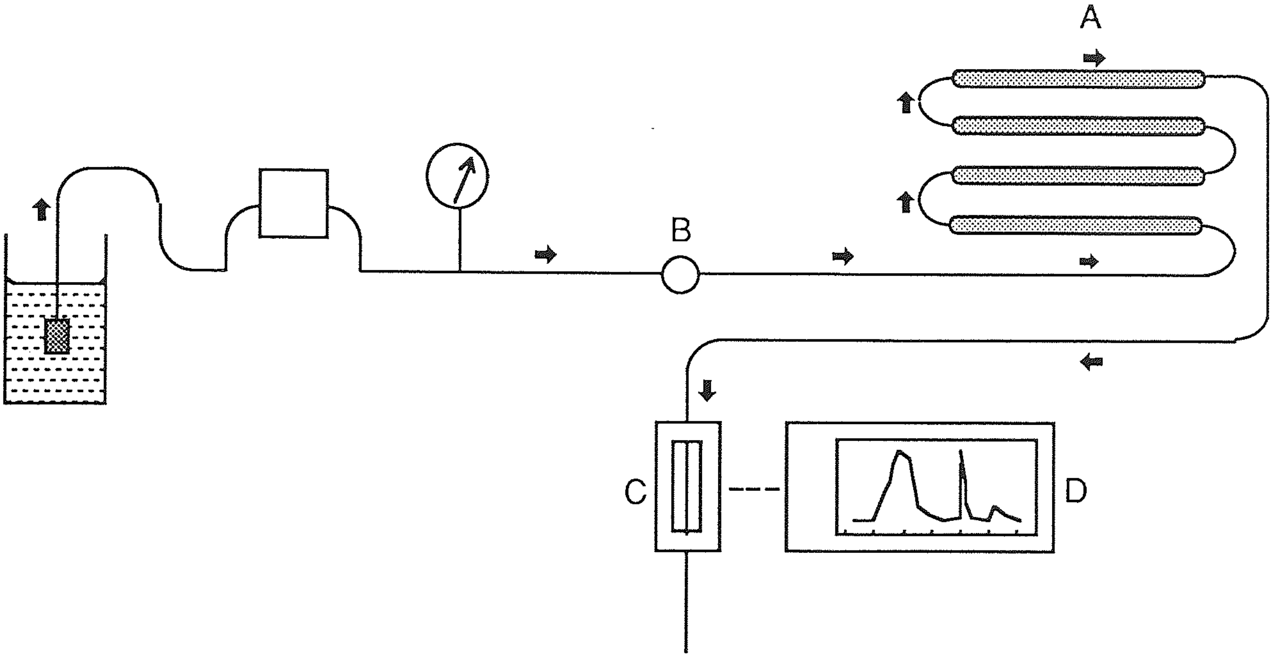
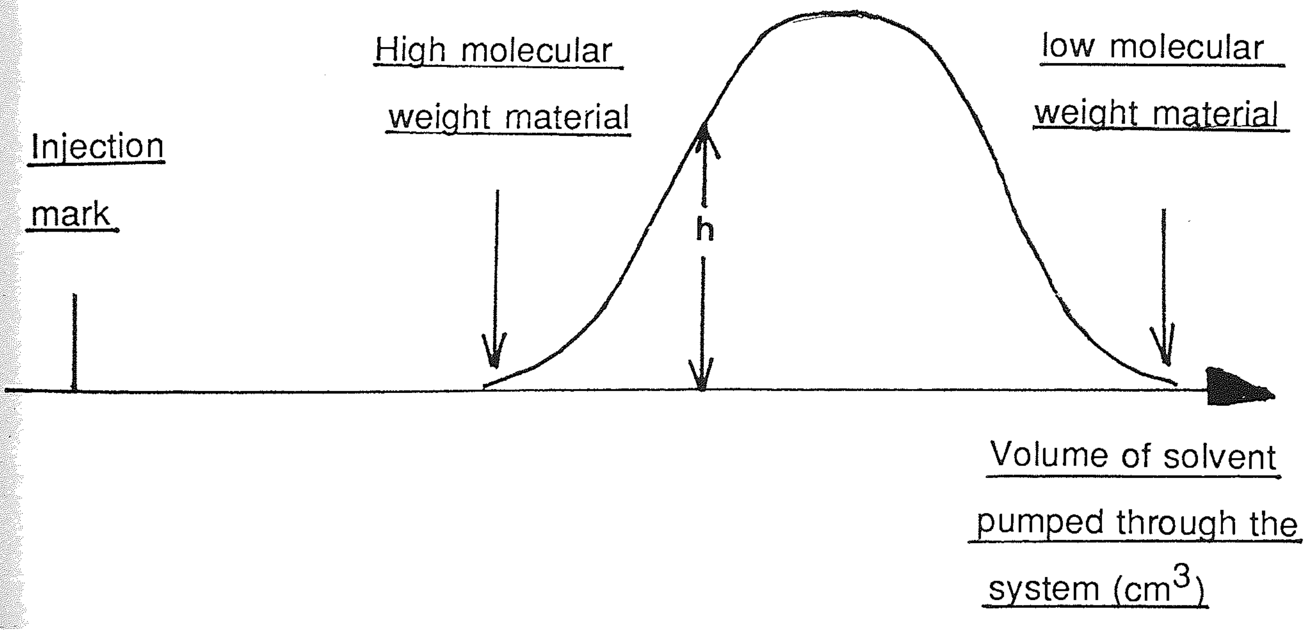


Figure 2.10 A "typical" GPC



wavelength range being examined. For example, the lower wavelength limit of THF is 220nm; below this limit the solvent shows excessive absorbance and sample absorbance will not be recorded linearly. In addition, the solvent can have an effect on some of the electronic transitions e.g. in $\alpha \beta$ unsaturated carbonyl compounds.

Samples were analysed on a Beckman DU7 UV/Visible spectrometer.

2.9.4. Gel permeation chromatography (GPC)

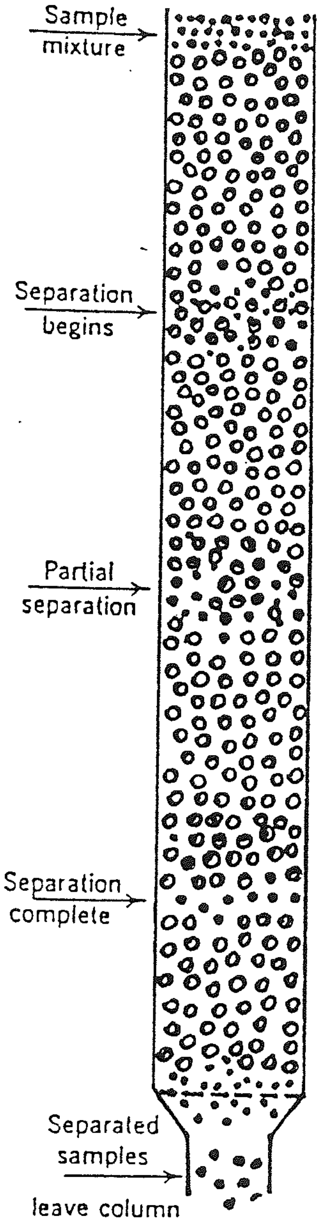
GPC is an extremely valuable technique for the determination of molecular weight averages and molecular weight distributions in polymer samples.

A schematic diagram of the gel permeation chromatogram is shown in figure 2.9. The principal components of GPC are:

(a) a stationary phase (a cross-linked porous gel)
(b) a mobile phase (solvent for the polymer and swellant for the gel)
(c) an injector system (valve and loop)
(d) a detector (differential refractometer)

The object of GPC is to separate a polymer into its component fractions according to their size. A stationary phase is packed in a series of columns (A) and solvent is pumped at a constant rate (1cm^3/minute) through the columns. The stationary phase is a crosslinked gel which swells when solvent is introduced. The gel is constructed so that there are pores between the particles. There is a range of pore sizes and the gel particles

Figure 2.11 Principle of separation of polymer molecules down a GPC column



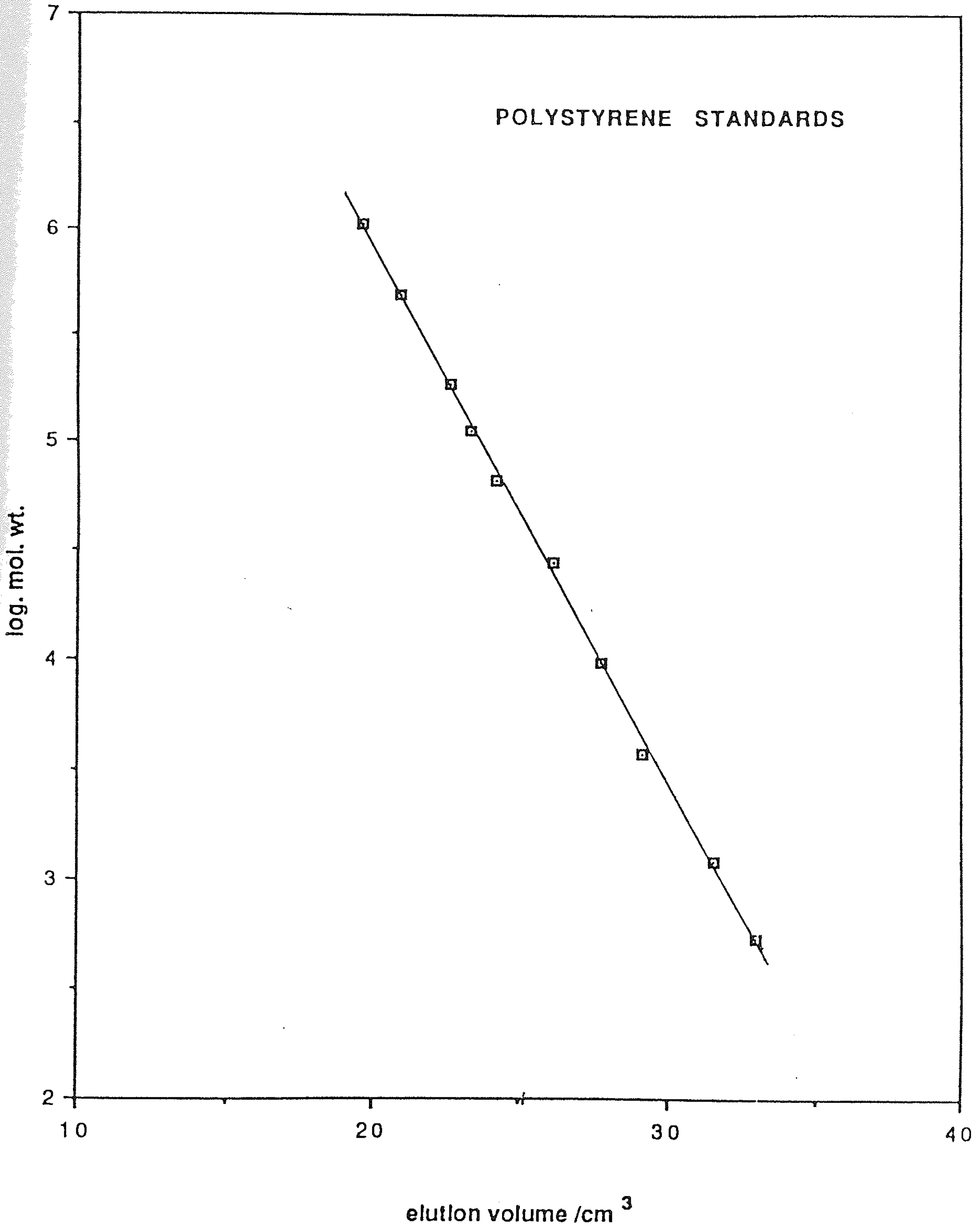
are 10μm in diameter.

A sample of the polymer may be introduced at the inlet of the column using the valve and loop (B) injector system. Because solvent is being continuously pumped through the column the polymer will be transported by the solvent. The polymer molecules will permeate the pores of the gel; the extent of diffusion is governed by the size of the polymer molecule and the pore size distribution in the gel. Larger molecules can enter only a small fraction of the pores of the gel, or are completely excluded, whereas smaller molecules penetrate a larger fraction of the pores. Larger molecules therefore spend less time inside the gel and so are eluted quickly from the column. Smaller molecules spend more time in the pore structure of the gel and so are eluted more slowly from the column. Figure 2.11 shows the principle of separation of molecules by GPC according to their size.

It is essential to detect the polymer in solution as it elutes from the base of the column. A differential refractometer (C) is usually used for this purpose. It continuously monitors the refractive index (RI) of the eluting solution and compares it with the RI of pure solvent. Any difference causes a deflection on the chart recorder (D) which is proportional to the concentration of eluting polymer at that time i.e. weight of polymer per unit volume. A typical chromatogram is shown in figure 2.10.

In order to estimate the average molecular weights it must first be determined how the molecular weight of eluted polymer varies over the range of elution volumes. For this purpose samples of polystyrene of very narrow molecular

Figure 2.12 GPC Calibration Graph



weight distribution and known molecular weights are injected in turn into the column. The volume of solvent pumped through the column which is required to elute a polymer of a specific molecular weight can thus be measured and a calibration curve plotted for the columns used, as shown in figure 2.12.

By comparing retention volumes of different polymers it is possible to obtain polystyrene equivalent molecular weights for polymer samples in solution.

Average molecular weights can be calculated by the equation

$$\bar{M}_n = \frac{\sum N_iM_i}{\sum N_i} \quad \text{and} \quad \bar{M}_w = \frac{\sum N_iM_i^2}{\sum N_iM_i}$$

$\bar{M}_n$ = number average molecular weight

$\bar{M}_w$ = weight average molecualr weight

M_i = molecular weight of a certain molecule

N_i = number of moles of a certain molecule in a sample

If W_i is the weight of polymer of molecular weight M_i in a given fraction.

$$N_i = \frac{W_i}{M_i}$$

therefore $$\bar{M}_n = \frac{\sum W_i}{\sum W_i | M_i} \quad \text{and} \quad \bar{M}_w = \frac{\sum W_iM_i}{\sum M_i}$$

Since the RI response (h_i) is a measure of the concentration of polymer of molecular weight M_i W_i may be substituted by h_i. Therefore

$$\overline{M}_n = \frac{\sum h_i}{\sum h_i/M_i} \quad \text{and} \quad \overline{M}_w = \frac{\sum h_i M_i}{\sum M_i}$$

Thus values of h_i at given elution volumes V_i are taken at regular intervals from the initial elution volume of the sample (as shown in figure 2.10) These values are then fed into the programme shown in appendix (2) to calculate the values of $\overline{M}_n$ and $\overline{M}_w$. The programme first takes the value of V_i and determines the molecular weight M_i of polymer eluted at that time. The values fo h_i, h_i/M_i and h_iM_i are then fed into the summations. Finally by manipulation of the three summations $\sum h_i$, $\sum h_i/M_i$ and $\sum h_iM_i$ the value of $\overline{M}_n$ and $\overline{M}_w$ can be determined.

The polystyrene molecular weight standard values can also be converted to a chart relating elution volumes, from 18cm^3 upwards, to approximate molecular weights. In this way values of $\overline{M}_n$ may be obtained by placing the GPC trace over this chart but the computer programme is used for more accurate estimation of $\overline{M}_n$ and $\overline{M}_w$.

The instrument used was a Perkin Elmer series 10 liquid chromatograph fitted with a Knauer Differential Refractometer detector. Four 10 μl PL gel columns were used of exclusion limits 10^5, 10^4, 10^3 and 10^2 A^o.

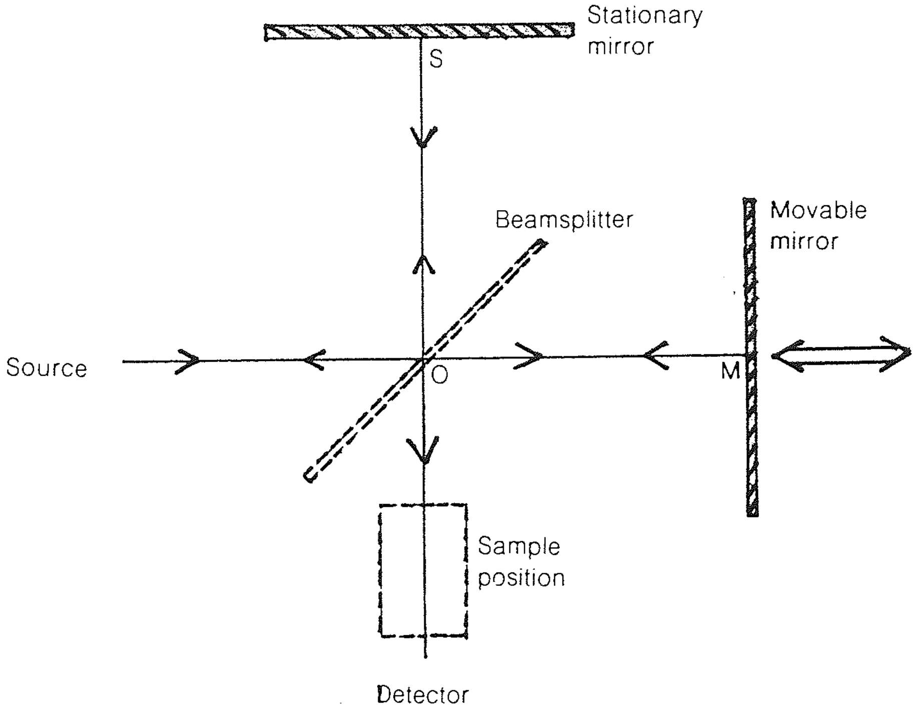


Figure 2.13 Schematic diagram of Michelson interferometer

2.9.5. Infrared spectroscopy (IR)

When infrared light is passed through a sample of an organic compound some of the frequencies are absorbed while other frequencies are transmitted through the sample without being absorbed. If the % absorbance or % transmittance is plotted against frequency the result is an IR spectrum.

The essential features of an infrared spectrometer are a source of infrared light, a monochromator, and a detector. Light from the source is passed through an organic sample, split into its individual frequencies in the monochromator and the relative intensities of the individual frequencies measured by the detector.

However, conventional infrared spectrometers suffer from several disadvantages in sensitivity, speed and wavelength accuracy. Most of the light from the souce does not in fact pass through the sample to the detector but is lost in the narrowness of focussing slits; only poor sensitivity results. Since the spectrum takes minutes to record, this method cannot be applied to fast processes such as recording the IR spectra of peaks being eluted from a chromatography column. For these reasons Fourier Transform IR (FT IR) is used in preference to conventional methods.

The heart of the FT IR spectrometer is the interferometer designed by Albert Michelson. In this device light is shone on a beam splitter that transmits some light and reflects the remainder (see figure 2.13). When light strikes the beamsplitter at point O, some is reflected to a stationary mirror at distance OS and some is transmitted to a movable mirror at distance OM. The rays reflected by the mirrors travel back to the beamsplitter, where half of each ray is transmitted and half is reflected. One recombined ray travels in the direction of the detector and one heads back to the source. If paths OM and OS are not equal the two waves reaching the detector are not in phase. However, if the two waves are in phase they interfere contructively and give a wave with twice the amplitude. For any intermediate phase difference there is partial cancellation. If one mirror moves away from the beamsplitter at a constant speed the light emerging toward the detector goes through a steady sequence of maxima and minima as the interference alternates between constructive and destructive phases. The result is an interferogram. Fourier analysis of the interferogram then shows which frequencies went into the interferogram. When a sample compound is placed in the beam (either before or after the interferometer) it absorbs particular frequencies so that their intensities are reduced in the interferogram. In a FT Spectrometer the interferogram of the source is first measured without a sample present. The sample is then placed in the beam and a second interferogram recorded. The transforms of the interferograms tell what frequencies of light reach the detector with or without the sample present. The quotient of the two transforms is then the transmission spectrum.

Samples were analysed by Perkin Elmer 1710 Fourier Transform IR Spectrometer.

Some of the samples were analysed as KBr discs. In making a disc of this type small amounts of the substance were mixed with KBr until an homogenous mixture was produced. Discs of this mixture were then prepared by means of a hydraulic press

CHAPTER THREE

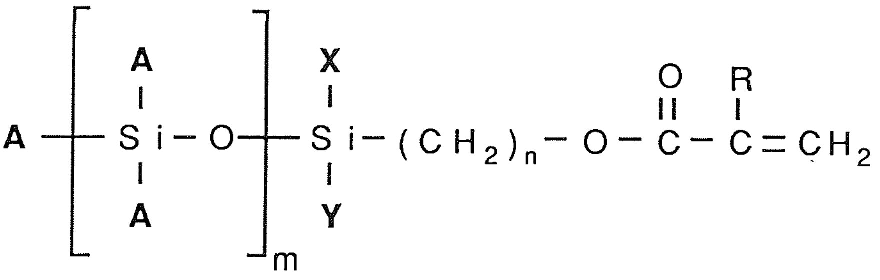
MODIFICATION OF FUNCTIONALISED MONOMERS AND THE SUBSEQUENT SYNTHESIS OF NOVEL POLYMERS

3. Modification of functionalised monomers and the subsequent synthesis of novel polymers

3.1. Introduction

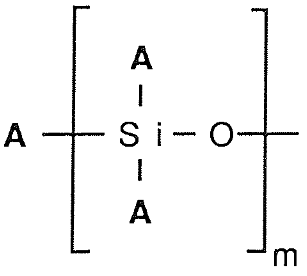
A group of novel polymers of recent interest are the copolymers of poly(methylmethacrylate) (PMMA) and silicone containing vinyl monomers. Earliest examples by Gaylord [29] consisted of copolymers of polysiloxanylalkyl esters of acrylic or methacrylic acid and an alkanol ester of acrylic or methacrylic acid.

The polysiloxanylalkyl ester monomer may be represented by the formula:



$$A-\left[\mathrm{Si}(A)_2-O\right]_m-\mathrm{Si}(X)(Y)-(CH_2)_n-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{R}{|}}{C}=CH_2$$

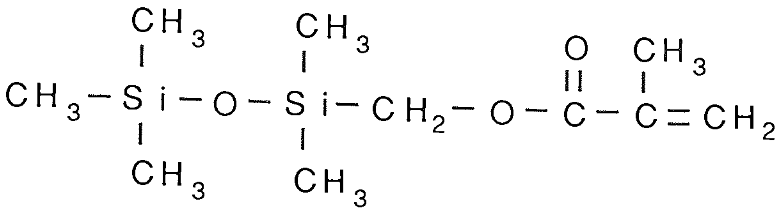
X and Y are either C_1 - C_5 alkyl groups, phenyl groups or Z groups where Z is a group of the structure:



$$A-\left[\mathrm{Si}(A)_2-O\right]_m-$$

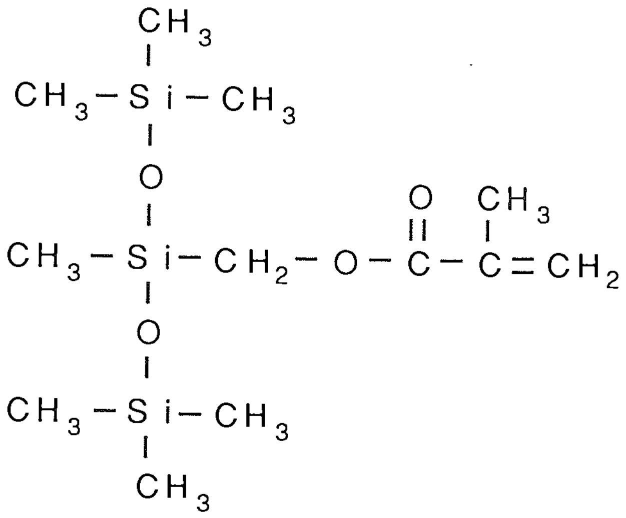
A may be either a C_1 - C_5 alkyl group or a phenyl group, M is an integer from one to five, and N is an integer from one to three. R is either a methyl group or a hydrogen atom.

Examples are:



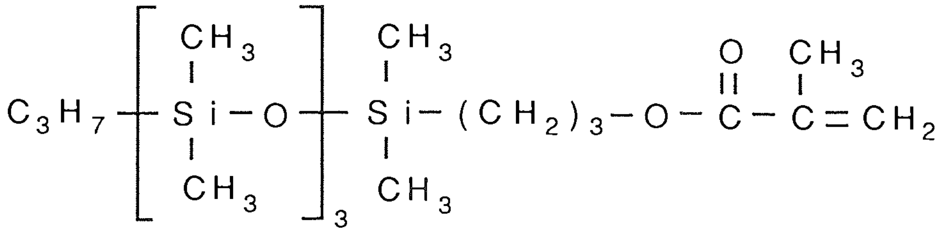
$$CH_3-Si(CH_3)_2-O-Si(CH_3)_2-CH_2-O-C(=O)-C(CH_3)=CH_2$$

pentamethyldisiloxanylmethyl methacrylate



$$CH_3-Si[O-Si(CH_3)_3]_2-CH_2-O-C(=O)-C(CH_3)=CH_2$$

methyldi(trimethylsiloxy)-methacryloxymethylsilane



$$C_3H_7-\left[Si(CH_3)_2-O\right]_3-Si(CH_3)_2-(CH_2)_3-O-C(=O)-C(CH_3)=CH_2$$

n-propyloctamethyltetrasiloxanylpropyl methacrylate

Examples of the alkanol ester monomers are: methyl acrylate, methyl methacrylate, butyl acrylate and butyl methacrylate.

Such copolymers were found to have vastly increased oxygen permeability compared to thermoplastic materials and hydrogels; the oxygen permeability was at least four times and as much as a hundred times greater than that of PMMA and the hydrogel poly(hydroxyethylmethacrylate).

The rigidity of these materials could be altered by varying the ratio of comonomers or their chemical composition. Thus polymers prepared from acrylate monomers were more flexible than those prepared from methacrylate monomers. A copolymer of poly(siloxanylalkyl methacrylate) and alkyl methacrylate could be fabricated into a material that is more rigid than a material prepared from the copolymer of the corresponding acrylates; the lower the alkyl methacrylate content of the copolymer the more flexible was the material. The rigidity of these materials could be further increased by the incorporation into the copolymer composition of 0.01% of a crosslinking monomer such as ethylene glycol dimethacrylate. Rigidity is often an advantageous property since soft materials such as hydrogels are subject to mechanical damage.

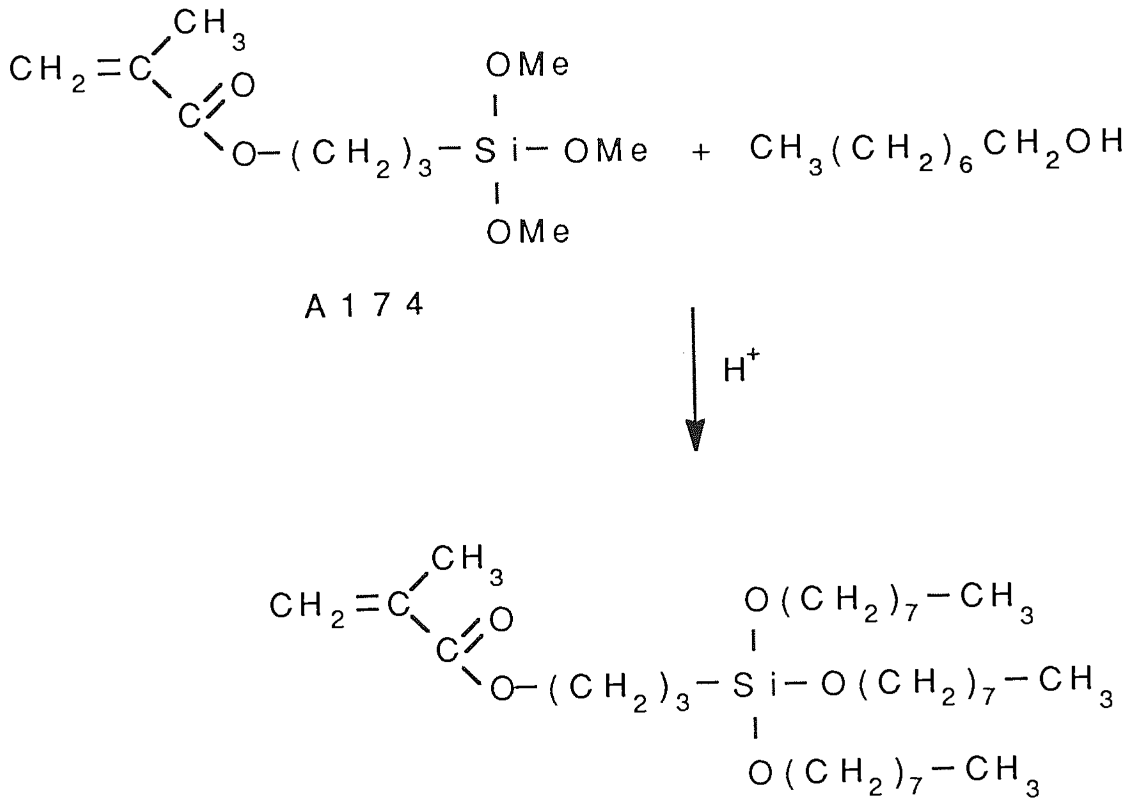
The refractive indices of these materials were also good; they could be varied between 1.35 and 1.50 by varying the ratio and the nature of the monomers. This is comparable to the refractive index of PMMA which is 1.49

The disadvantage of these materials was their wettability which was poor in comparison to hydrophilic hydrogel materials. However, the wettability of the material could be improved by the addition of from 0.1%to 10% by weight of one or more hydrophilic monomers such as methacrylic or acrylic acid to the copolymer mixture.

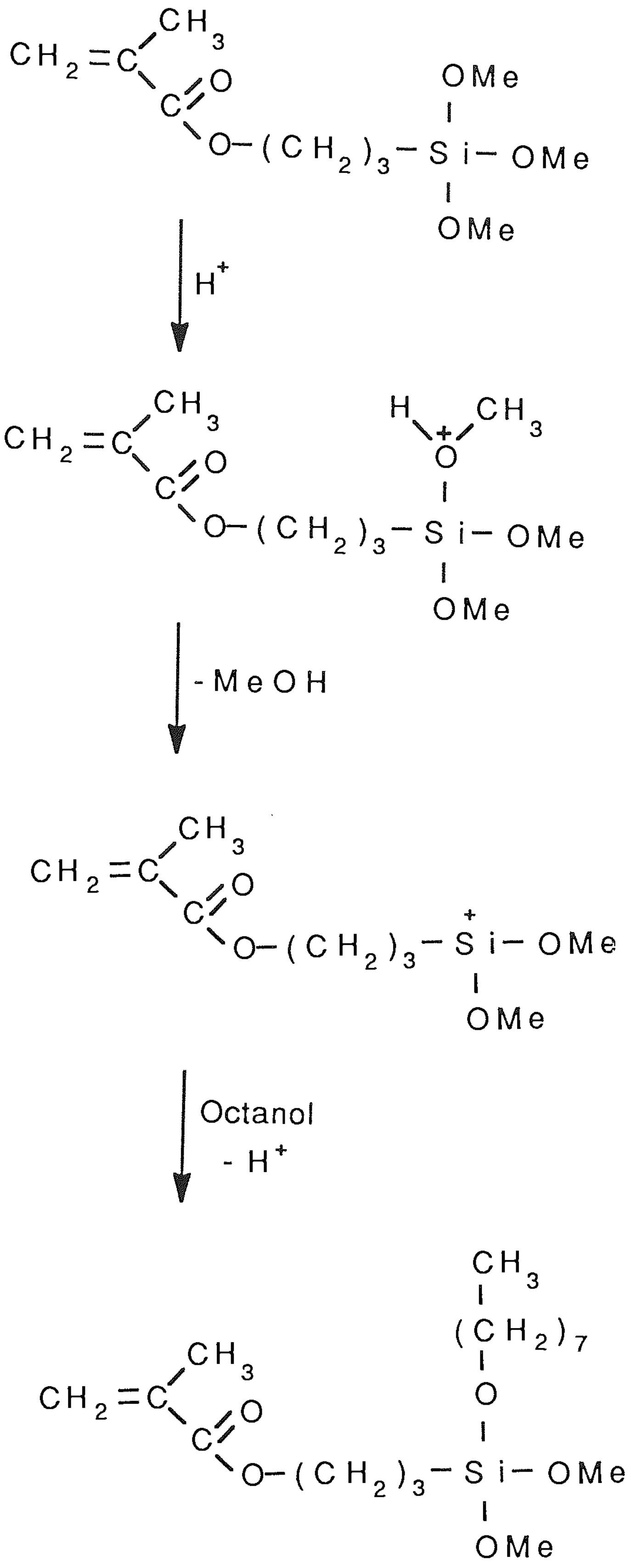
In conclusion, such materials have the great advantage in that a material with optimum properties, regarding oxygen permeability, wettability and refractive index, may be created for a particular application by altering the ratios and the chemical composition of the comonomers.

Other work has been carried out using siloxane macromers such as polydimethylsiloxane (PDMS) and methyl methacrylate to produce novel siloxane graft copolymers. Potential applications of such graft copolymers include uses as surface modifiers where increased hydrophobicity is required and as oxygen permeable membranes. However, the selectivity in permeation and mechanical strength of these polymers was found to be low due to rather long PDMS chains; polymers with short siloxane chains were found to have better selectivity in permeation and increased mechanical strength [30].

A commercially available monomer that is reportedly readily modified by an alcohol exchange reaction is 3-(methylpropenoxycarbonyl)propyltrimethoxysilane (A174). The alcohol exchange reaction may be exemplified by the reaction of A174 with octan-1-ol under acidic conditions.



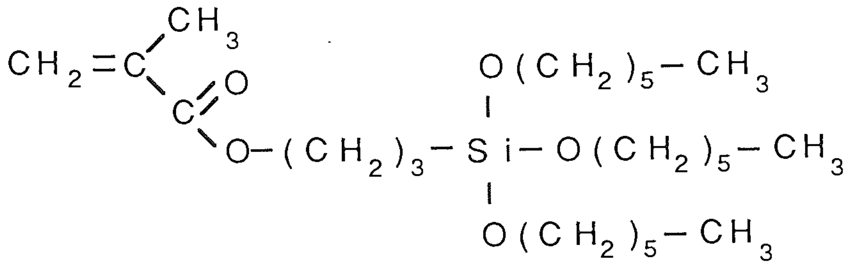
The most probable explanation for the mechanism of alcohol exchange is:



Other exchange reactions can also be carried out using alcohols such as pentan-1-ol, 4-allyl-2-methoxyphenol (eugenol) and hexan-1-ol.

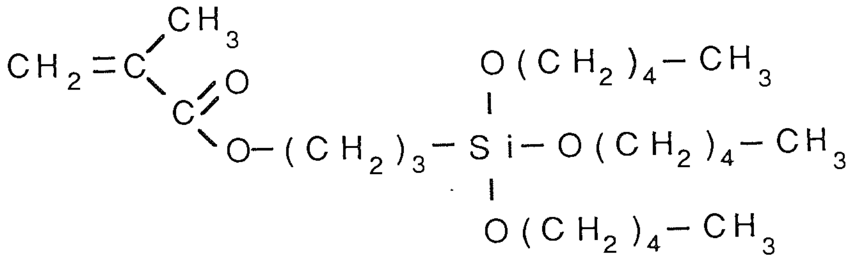
Products of these various reactions are shown below

A174 + Hexan-1-ol ⟶

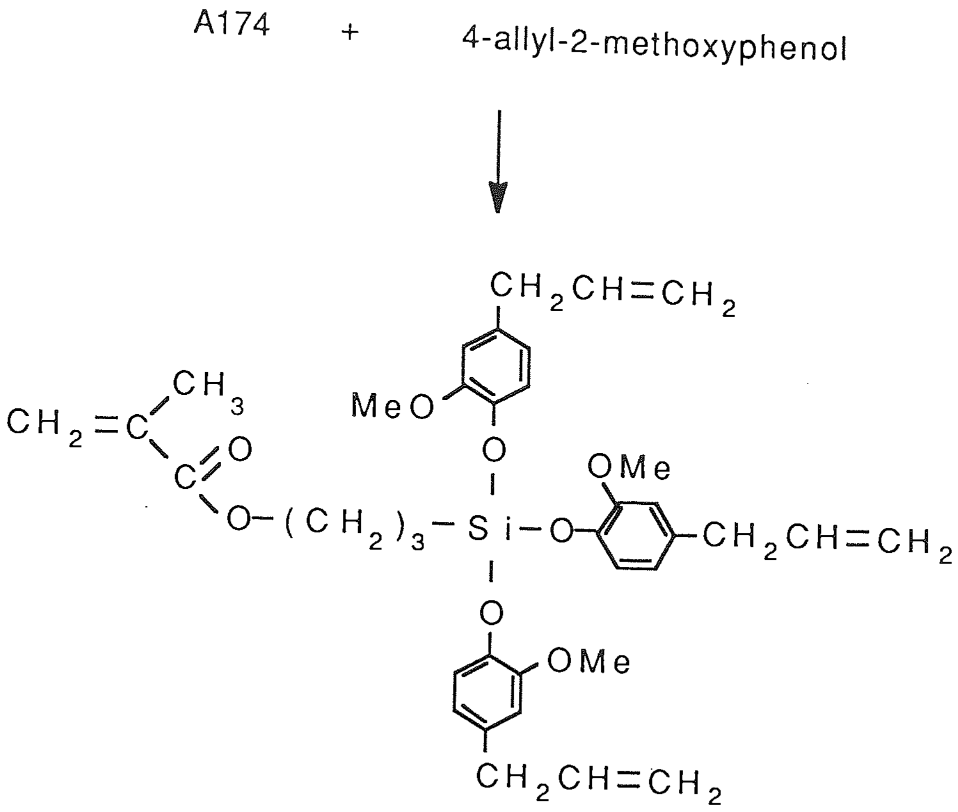


3(methylpropenoxycarbonyl)propyltrihexoxysilane

A174 + Pentan-1-ol ⟶



3(methylpropenoxycarbonyl)propyltripentoxysilane

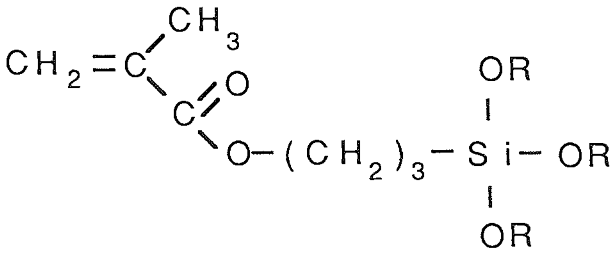


3(methylpropenoxycarbonyl)propyl-4-allyl-2-methoxyphenoxysilane

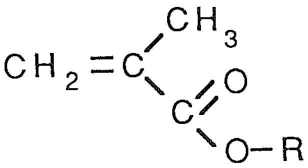
It can be seen that, potentially this alcohol exchange reaction can be modified to produce a range of monomers in which the substituent group on the silicon atom can be varied almost at will, whilst still maintaining a reactive site for polymerisation, the vinyl group. Furthermore, the reactivity of the double bond should be unaffected by the presence of the Si-O-R groups if the mechanism of polymerisation involves free radical addition conditions. The versatility of the alcohol exchange reaction would suggest that it should be possible to attach at that point in the monomer substituents that might generate polymers and/or copolymers with properties designed to improve oxygen permeability, liquid crystalline effects and reactive sites for catalyst attachment.

3.2. Polymer and copolymer synthesis

The monomer, A174, and its analogues obtained from the alcohol exchange reaction have the structure



There are two distinct sites in these monomers, those based on the Si-O-R which are potentially the source of different physical properties and



the methacrylate unit.

Methyl methacrylate may be polymerised free radically and under certain circumstances anionically. It seems appropriate therefore to review briefly the mechanisms and kinetics of free radical polymerisation at this stage.

3.2.1. Free radical polymerisation

Free radical polymerisation proceeds by a kinetic chain mechanism that involves three major steps. These are:

(i) Initiation

(ii) Propagation

and (iii) Termination

3.2.1.1. Initiation

Initiation is the reaction or reactions in which a propagating free radical is formed. Initiation normally involves two steps (a) decomposition of the initiator molecule into primary free radicals and (b) addition of a monomer unit to the primary free radical.

3.2.1.1.1. Decomposition of the initiator molecule into primary free radicals

The reaction may be summarised as:

$$I \longrightarrow 2R^{\bullet}$$

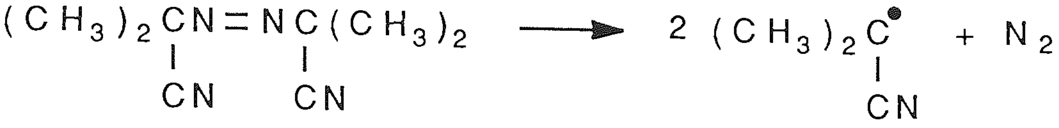
An effective initiator is a molecule which when subjected to heat, electromagnetic radiation or chemical reaction will readily undergo homolytic fission into free radicals and these species are normally characterised by having a greater reactivity than the propagating radicals. However, these radicals must be sufficiently stable to react with a monomer and create an active centre [32].

Two reactions commonly used to produce free radicals are the thermal and photochemical decompostition of:

(i) benzoyl peroxide

$$(C_6H_5COO)_2 \longrightarrow 2\ C_6H_5COO^\bullet \longrightarrow 2\ C_6H_5^\bullet + CO_2$$

and (ii) $\alpha\alpha'$ azobisisobutyronitrile



$$(CH_3)_2\underset{CN}{\underset{|}{C}}N{=}N\underset{CN}{\underset{|}{C}}(CH_3)_2 \longrightarrow 2\ (CH_3)_2\underset{CN}{\underset{|}{C^\bullet}} + N_2$$

To be useful in initiating polymerisation a compound undergoing thermal decomposition should have a first order decomposition rate constant of 10^{-5} to 10^{-6} s^{-1} at the desired polymerisation temperature, usually between 50 and 150°C [33].

Although thermal decomposition is a common method of generating free radicals it has a disadvantage in that the rate of generation of free radicals cannot be controlled readily. Photoinitiated polymerisation on the other hand can be controlled with high precision since the generation of radicals can be made to vary instantaneously by controlling the intensity of the initiating light [33].

Free radicals may also be generated as the result of oxidation-reduction reactions (REDOX REACTIONS). For example, the reaction between the ferrous ion and hydrogen peroxide in solution produces hydroxyl radicals [32,33].

$$H_2O_2 + Fe^{2+} \longrightarrow Fe^{3+} + OH^- + OH^\bullet$$

In addition, initiation can be by electrochemical means as a result of generation of free radicals at electrodes.

The stability of free radicals varies widely. Primary radicals are less stable and more reactive than secondary radicals which are, in turn, less stable than tertiary ones such as triphenylmethyl. The phenyl radical is more reactive than the benzyl radical whilst the allyl radical is quite unreactive due to the fact that it is highly stabilised by resonance and is capable only of bimolecular combination with another allyl radical. Allylic monomers are particularly prone to hydrogen abstraction,

$$\sim\!\sim\!\sim R^{\bullet} + CH_2{=}CHCH_2OCOCH_3 \longrightarrow$$

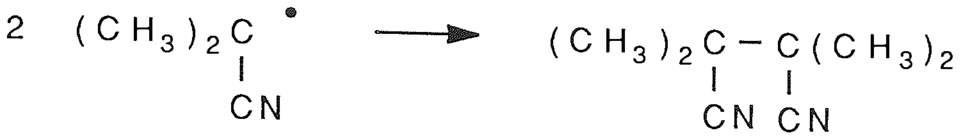
$$\sim\!\sim\!\sim RH + \overset{\bullet}{C}H_2 \overset{\cdots}{-} CH \overset{\cdots}{-} \overset{\bullet}{C}H-OCOCH_3$$

resulting in what is effectively auto-inhibition by the monomer. Propylene reacts in this manner and is reluctant to polymerise by a free radical mechanism.

Initiator efficiency

Although the decomposition of an initiator molecule can be quantitative, chain initiation can be less than 100% efficient. The efficiency with which radicals initiate chains may be estimated by comparing the amount ot initiator decomposed with the number of polymer chains formed. Most initiators used in vinyl polymerisations have efficiency factors of between 0.6 and 1.0.

The major cause of low efficiency is recombination of the radical pairs to form stable molecules before they diffuse apart. This is called the cage effect [35].



$$2\ (CH_3)_2\underset{CN}{C}{}^{\bullet} \longrightarrow (CH_3)_2\underset{CN}{C}-\underset{CN}{C}(CH_3)_2$$

Further inefficiency occurs when induced decomposition is effected by the attack of an active centre on an initiator molecule [32].

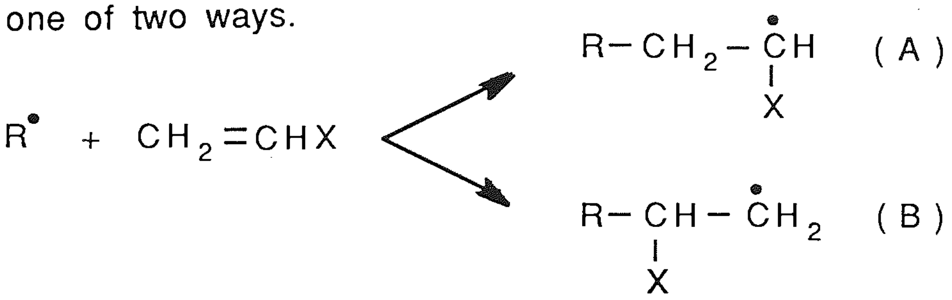
$$R^{\bullet} + R'-O-O-R' \longrightarrow R-O-R' + R'O^{\bullet}$$

This effectively produces one radical instead of three potential radical species.

3.2.1.1.2. <u>Addition of a monomer unit to the initiator</u>

Free radical polymerisation is not as specific as ionic polymerisation since most substituents (X) in the monomer $CH_2{=}CHX$ can provide some resonance stabilisation for the propagating species.

The addition of a free radical to a vinyl monomer can take place in one of two ways.



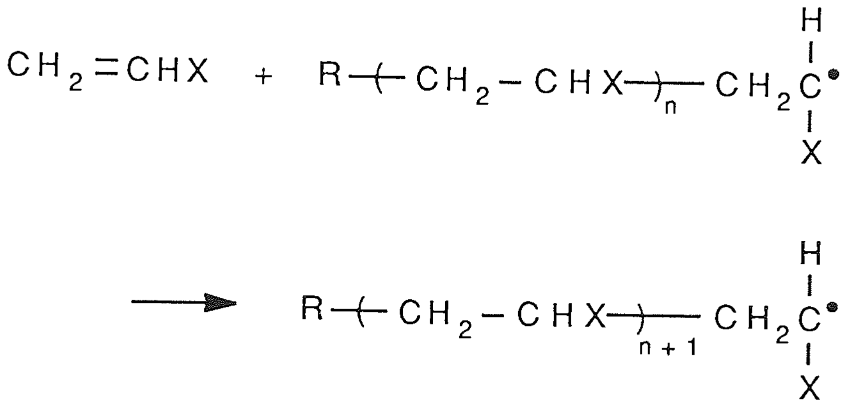
$$R^{\bullet} + CH_2{=}CHX \longrightarrow R-CH_2-\underset{X}{\overset{\bullet}{C}}H \quad (A)$$

$$R^{\bullet} + CH_2{=}CHX \longrightarrow R-\underset{X}{C}H-\overset{\bullet}{C}H_2 \quad (B)$$

The favoured reaction is the one that leads to the more stable polymer radical. Since the unpaired electron can participate in resonance with the substituent X in structure (A) but not in (B) reaction (A) is usually favoured. Steric factors also favour pathway (A).

3.2.1.2. Propagation

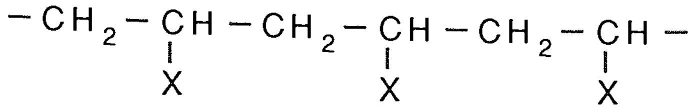
The polymer radical produced in the initation step is capable of adding successive monomer molecules to propagate the chain i.e.



$$CH_2{=}CHX + R\left(CH_2-CHX\right)_n CH_2\overset{H}{\underset{X}{C}}{}^{\bullet} \longrightarrow R\left(CH_2-CHX\right)_{n+1} CH_2\overset{H}{\underset{X}{C}}{}^{\bullet}$$

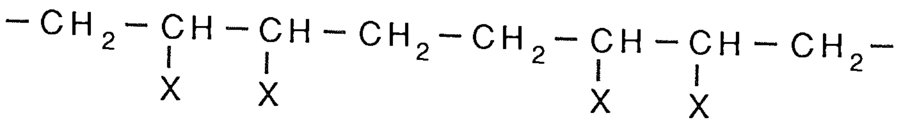
Addition of the monomer molecule to the propagating free radical will again take place so as to preferentially form the more stable of the two propagating radicals. Steric and electronic factors play an important role in the propagation reaction which must compete effectively with the termination reaction if a high molecular weight polymer is to be formed. Essentially the free radical must be sufficiently stable to be formed but also sufficiently reactive to add to another carbon-carbon double bond in order to propagate.

The occurrence of exclusive head-to-tail addition would lead to substituents on alternate atoms i.e.



$$-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}-$$

Alternative possibilities are head-to-head or tail-to-tail configurations or a random structure containing both arrangements i.e.



$$-CH_2-\underset{X}{CH}-\underset{X}{CH}-CH_2-CH_2-\underset{X}{CH}-\underset{X}{CH}-CH_2-$$

The possibility of obtaining a regular head-to-head or tail-to-tail configuration exclusively by chain polymerisation is remote and it appears that occasionally a monomer unit enters the chain in a reverse manner to provide an isolated head-to-head or tail-to-tail linkage[33]

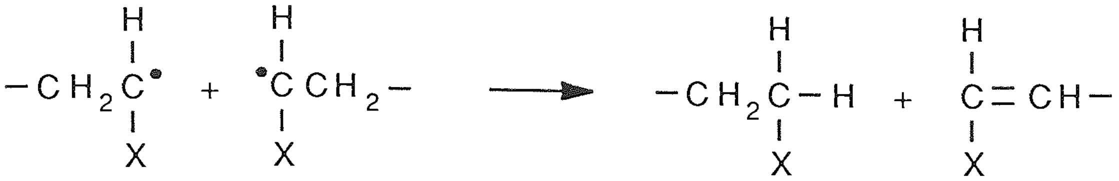
3.2.1.3. Termination

Propagation would continue until the supply of monomer was exhausted were it not for the strong tendency of free radicals to react in pairs to form a covalent bond with loss of radical activity. The termination step can take place in two ways:

(i) Combination

$$-CH_2\overset{H}{\underset{X}{C}}^{\bullet} + {}^{\bullet}\overset{H}{\underset{X}{C}}CH_2- \longrightarrow -CH_2\overset{H}{\underset{X}{C}}-\overset{H}{\underset{X}{C}}CH_2-$$

(ii) Disproportionation



$$-CH_2\overset{H}{\underset{X}{C^\bullet}} + {}^\bullet\overset{H}{\underset{X}{C}}CH_2- \longrightarrow -CH_2\overset{H}{\underset{X}{C}}-H + \overset{H}{\underset{X}{C}}=CH-$$

Studies of the number of initiator fragments per molecule showed that polystyrene terminates predominantly by combination whereas poly(methyl methacrylate) terminates entirely by disproportionation at polymerisation temperatures above 60°C and partly by each mechanism at lower temperatures [36].

Short chains are produced if the radical concentration is high because the probability of radical interaction is correspondingly high. Hence the radical concentration should be kept small if long chains are required.

3.2.1.4. Chain transfer

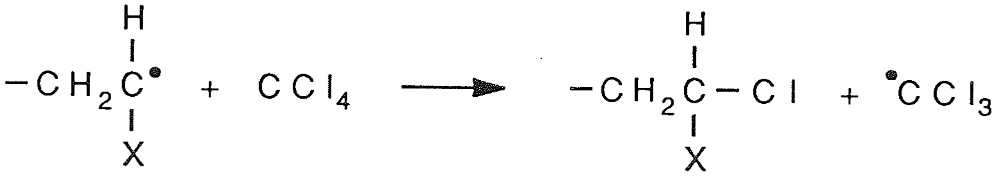
Termination in a free radical polymerisation normally occurs by collision between two active centres attached to polymer chains but the chain length of the product in many systems is lower than one would expect if this was the mechanism solely responsible for limiting the kinetic chain length [32]

Premature termination of the propagating chain may take place by a transfer of activity to another species through a collision. This is a competitive process involving the abstraction of an atom by a chain carrier from an inactive molecule XY with replaceable atoms, and is dependent on the strength of the X-Y bond.

$$\sim\!\sim\!\sim M^{\bullet}_{m} + XY \longrightarrow \sim\!\sim\!\sim M_{m}X + Y^{\bullet}$$

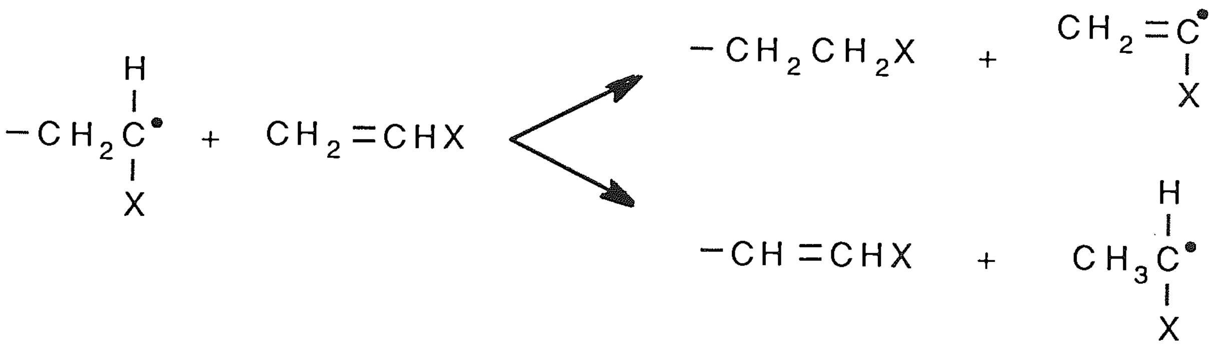
The free radical is not destroyed in the reaction: its activity is merely transferred to another polymer chain; if the new species is sufficiently active another chain will emanate from the new centre. This type of reaction is known as chain transfer.

If the molecule is saturated like a solvent or another additive the atom must be transferred to the radical i.e.



$$-CH_2\overset{H}{\underset{X}{C^{\bullet}}} + CCl_4 \longrightarrow -CH_2\overset{H}{\underset{X}{C}}-Cl + {}^{\bullet}CCl_3$$

If the molecule is unsaturated like a monomer the atom transferred (usually hydrogen) can go in either direction i.e.



$$-CH_2\overset{H}{\underset{X}{C^{\bullet}}} + CH_2{=}CHX \longrightarrow -CH_2CH_2X + CH_2{=}\underset{X}{C^{\bullet}}$$

$$-CH_2\overset{H}{\underset{X}{C^{\bullet}}} + CH_2{=}CHX \longrightarrow -CH{=}CHX + CH_3\overset{H}{\underset{X}{C^{\bullet}}}$$

The major effect of chain transfer to a saturated small molecule such as solvent, initiator or deliberately added chain transfer agent such as alkyl mercaptan i.e.

$$\sim\sim CH_2CHX^\bullet + RSH \longrightarrow \sim\sim CH_2CH_2X + RS^\bullet$$

$$RS^\bullet + CH_2{=}CHX \longrightarrow RSCH_2CHX^\bullet$$

is the formation of additional polymer molecules for each radical chain initiated.

Transfer to a polymer and transfer to a monomer with subsequent polymerisation of the double bond leads to the formation of branched molecules.

The efficiency of compounds as chain transfer agents varies widely with molecular structure. Aromatic hydrocarbons are rather unreactive unless they have benzylic hydrogens. Aliphatic hydrocarbons are more reactive when substituted with halogens.

3.2.1.5. Inhibition and Retardation

A retarder is defined as a substance that can react with a free radical to form products incapable of adding to a monomer. If the retarder is very effective no polymer may be formed; this condition is sometimes called inhibition and the substance an inhibitor.

The distinction between an inhibitor and retarder is merely one of the degree to which polymerisaiton is prevented.

Some chain transfer agents yield radicals with low reactivity and if the re-initiation reaction is slow the polymerisation rate decreases because there is a build up of free radicals leading to increased termination by coupling. In this way the chain transfer agent acts as a retarder. Nitrobenzene acts in this way with styrene.

3.2.1.6. Kinetics of polymerisation

The three basic steps in the kinetic chain can be expressed as follows:

Initiation

$$I \xrightarrow{k_d} 2R^\bullet$$

$$R^\bullet + M \xrightarrow{k_i} RM^\bullet$$

The first step is the rate determining step. Hence the rate of initiation (ν_i) is expressed

$$\nu_i = 2k_d f\,[I]$$

f = a measure of the ability of the radicals to propagate chains

Propagation

$$RM_n^\bullet + M \longrightarrow RM^\bullet_{n+1}$$

Where the rate of propagation (ν_p) is expressed as

$$\nu_p = k_p\,[M][M_n^\bullet]$$

Termination

Termination is a bimolecular process. The rate of termination (ν_t) is expressed as

$$\nu_t = 2k_t[M_n^{\circ}]\,[M_n^{\bullet}]$$

Assuming steady state in the concentration of propagating radicals

$$2k_t[M_n^{\circ}]^2 = 2k_d f[I]$$

Therefore

$$[M_n^{\bullet}] = (fk_d\ [I]/k_t)^{1/2}$$

and

$$\nu_p = k_p(fk_d\ [I]/k_t)^{1/2}\ [M]$$

Therefore

$$\bar{\nu} = \nu_p/\nu_i = \nu_p/\nu_t = k_p{}^2[M]^2/2k_t\nu_p$$

The kinetic chain length ($\bar{\nu}$) is a measure of the average number of monomer units reacting with an active centre during its lifetime and is related to x_n through the mechanism of termination. Thus combination means that $x_n = 2\bar{\nu}$ but $x_n = \bar{\nu}$ if disproportionation is the only termination step. If actual values of x_n are required then account has to be taken of transfer reactions.

3.2.1.7. Copolymerisation

In the assessment of the properties of polymeric materials it is desirable to produce materials with properties intermediate between those of the homopolymers. In other instances the structure of the vinyl monomer ($CH_2 = CHX$) may be such that X is a very bulky group and homopolymerisation of the monomer might lead to intolerable steric interactions between the substituent groups of adjacent monomer units leading to the instability of the polymer. Both these problems may to some extent, be overcome by copolymerisation.

Copolymerisation of the two monomers $CH_2{=}CHX(M_1)$ and $CH_2{=}CHY(M_2)$ may be described for free radical polymerisation by

Initiation

$$I \longrightarrow 2R^{\bullet}$$

$$R^{\bullet} + M_1 \longrightarrow R{-}CH_2{=}\dot{C}HX \quad (\dot{R}_1)$$

$$R^{\bullet} + M_2 \longrightarrow R{-}CH_2{=}\dot{C}HY \quad (\dot{R}_2)$$

Propagation

$$R_1^{\bullet} + M_1 \xrightarrow{k_{p_{11}}} R_1^{\bullet}$$

$$R_1^{\bullet} + M_2 \xrightarrow{k_{p_{12}}} R_2^{\bullet}$$

$$R_2^{\bullet} + M_2 \xrightarrow{k_{p_{22}}} R_2^{\bullet}$$

$$R_2^{\bullet} + M_1 \xrightarrow{k_{p_{21}}} R_1^{\bullet}$$

Termination

$$\left.\begin{array}{lllll} R_1^{\bullet} & + & R_1^{\bullet} & \xrightarrow{k_{t\,11}} & \text{polymer} \\ R_1^{\bullet} & + & R_2^{\bullet} & \xrightarrow{k_{t\,12}} & \text{polymer} \\ R_2^{\bullet} & + & R_2^{\bullet} & \xrightarrow{k_{t\,22}} & \text{polymer} \end{array}\right\} \begin{array}{c}\text{Disproportionation and} \\ \text{Combination for each}\end{array}$$

The composition of the copolymer being formed at any instant is given by

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]\, r_1 [M_1] + [M_2]}{[M_2][M_1] + r_2\, [M_2]}$$

where

$$r_1 = \frac{k_{p11}}{k_{p12}} \qquad r_2 = \frac{k_{p22}}{k_{p21}}$$

In the case of copolymerisation of two monomers a variety of structures may be obtained. Some of the important types are

(i) Random copolymers

These copolymers are formed when irregular propagation occurs and the two units enter the chain in a random fashion.

Table 3.1 The reactivity ratios of monomers during free radically initiated polymerisation

M1	M2	r_1	r_2	$r_1 r_2$
Butadiene	Methyl methacrylate	0.70	0.32	0.22
	Styrene	1.40	0.78	1.1
Methyl methacrylate	Vinyl acetate	22.2	0.07	1.55
	Vinyl chloride	10	0.1	1.0
Acrylonitrile	Acrylamide	0.87	1.37	1.17
	Butadiene	2.0	0.1	0.2
	Methyl acrylate	0.84	0.83	0.70
	Styrene	0.01	0.40	0.004
	Vinyl acetate	6.0	0.07	0.42

(ii) Alternating copolymers

Such copolymers are obtained when equimolar quantities of two monomers are distributed in a regular alternating fashion in the chain.

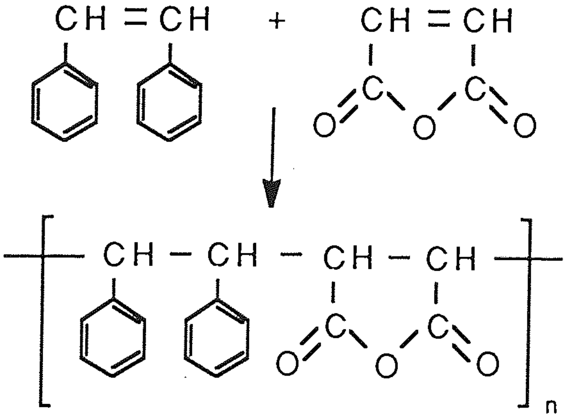
(iii) Block copolymers

Instead of having a mixed distribution of the two units the copolymer may contain long sequences of one monomer joined to another.

If $r_1 r_2 \simeq 1$ random copolymers result and if $r_1 \ll 1$ and $r_2 \ll 1$ an alternating copolymer results. If $r_1 \gg 1$ and $r_2 \gg 1$ block copolymers result but this is not usually found in free radical polymerisation. Some of the reactivity ratios r_1 and r_2 for free radical polymerisations are shown in Table 3.1.

The reactivity ratios of monomers depend on their structures. The reactivity of a free radical is known to depend on the nature of the groups in the vicinity of the radical. If in a vinyl monomer (CH_2= CHR) the group R delocalises the unpaired electron, the radical stability will increase. Thus styrene has a radical whose resonance stabilisation is high whereas vinyl acetate has a comparatively unstable radical. As a reactive monomer forms a stable free radical the radical reactivity will be the reverse of monomer reactivity. The suppression of radical activity towards a monomer is also found to be a stronger effect than the corresponding enhancement of monomer reactivity. Styrene and vinyl acetate form a poor comonomer pair since copolymerisation requires that the stable styrene radical reacts with the unreactive vinyl acetate monomer but this is a slow process and styrene tends to homopolymerise. Efficient copolymerisation tends to take place when the comonomers are either both reactive or both relatively unreactive.

Strongly alternating copolymers are formed when comonomers with widely differing polarities are reacted together. The polarity is again determined by the side group; electron withdrawing substituents decrease the electron density at the double bond in a vinyl monomer whereas electron donating groups increase the electron density. Polar forces can also help to overcome steric hindrance. For example, maleic anhydride does not form a homopolymer but can be copolymerised with stilbene to form alternating copolymers due to the strong polar interaction i.e.



Thus copolymerisation is extremely useful in situations where it is essential to modify the properties of a polymeric material to meet certain requirements. However, once the need for copolymerisation has been established, one must look closely at factors such as polarity and degree of resonance stability due to substituent groups in the monomers involved, in order to produce an efficient copolymerisation system; the reactivity ratios of comonomers depend on their structures. The structure of the resulting copolymer i.e. random, alternating or block, is also dependent on the reactivity ratios of such comonomers.

3.3. Experimental results

3.3.1. Introduction

In the literature reviewed previously it can be seen that copolymers of methyl methacrylate and silicone containing vinyl monomers have many advantageous properties and these properties can be modified either by varying the ratio of the comonomers in the copolymerisation system or by changing the nature of the siloxane; it is reported that the alkoxy group bound to the silicon atom in the monomer A174 can be varied by the alcohol exchange reaction described in section 2.6.1 so generating siloxane derivatives which have improved properties such as reactive sites for catalyst attachment. Hence it seemed reasonable to attempt the synthesis of copolymers of this type using siloxane comonomers modified by the alcohol exchange reaction, in order to produce materials with specific properites for specialist applications.

3.3.2. Modification of the siloxane containing comonomers

A typical catalyst system for the alcohol exchange reaction consisted of 14.7ml of ethanol, 16.5ml of water, and 13ml of concentrated sulphuric acid. The catalyst was used in total in a reaction where a 3:1 molar ratio of the alcohol to the siloxane (A174) was employed; the reaction system consisted of 0.1mol (24.8g) of A174 and in turn 0.3mol of each of the following alcohols:

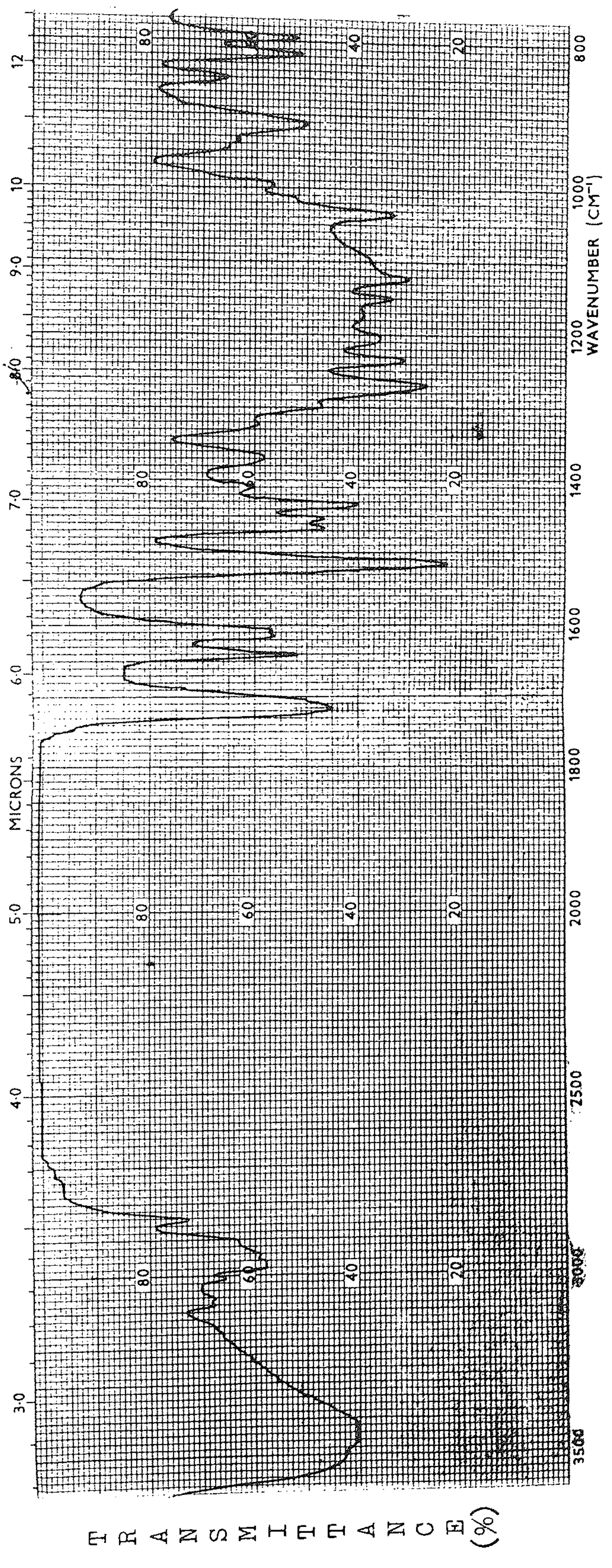

MICRONS
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
12
WAVENUMBER (CM⁻¹)
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
80
60
40
20
TRANSMITTANCE (%)

Figure 3.1

(a) Octan - 1-ol

(b) Pentan - 1-ol

(c) Hexan - 1-ol

(d) 4-allyl-2-methoxyphenol (eugenol)

The exchange reactions were carried out at 20°C for two days. On completion of this reaction the mixture was washed with water and sodium bicarbonate. 100ml of cyclohexane was then added to produce a solution of the monomer in this solvent. Purification of the comonomer was attempted by distillation under reduced pressure.

3.3.2.1. Analysis of the eugenyl derivative of A174

During the purification of the eugenyl derivative (P3D) approximately 30ml of distillate was formed in the Dean and Stark apparatus at 60°C. After distillation the reaction mixture left in the flask was analysed by IR Spectroscopy and GPC.

IR Spectroscopy

The sample was analysed by IR as a thin liquid film between sodium chloride plates. The spectrum obtained is shown in figure 3.1.

A comparison of the IR spectrum of the product with those of eugenol shown in figure 3.2 and A174 shown in figure 3.3, shows that the most notable change is the appearance of a relatively strong absorbance at 1035cm^{-1} which is typical of an aryl ether. Furthermore the new absorbance at 1270cm^{-1}

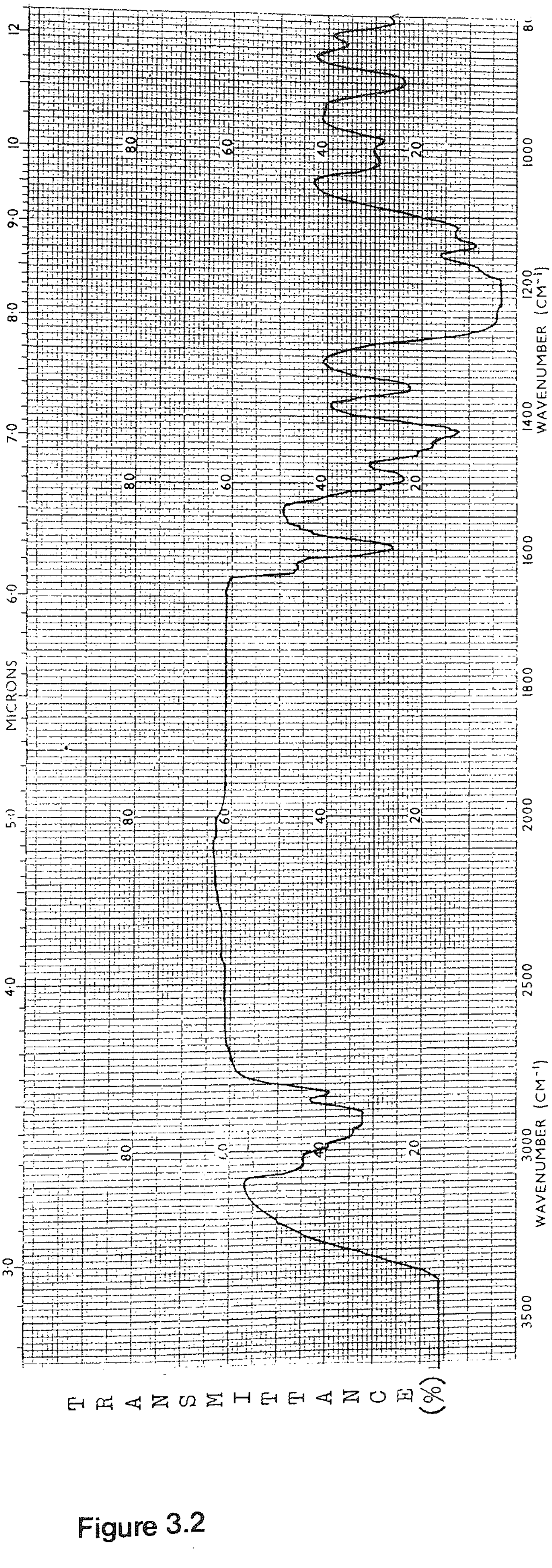

MICRONS
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
12
TRANSMITTANCE (%)
80
60
40
20
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
WAVENUMBER (CM⁻¹)

Figure 3.2

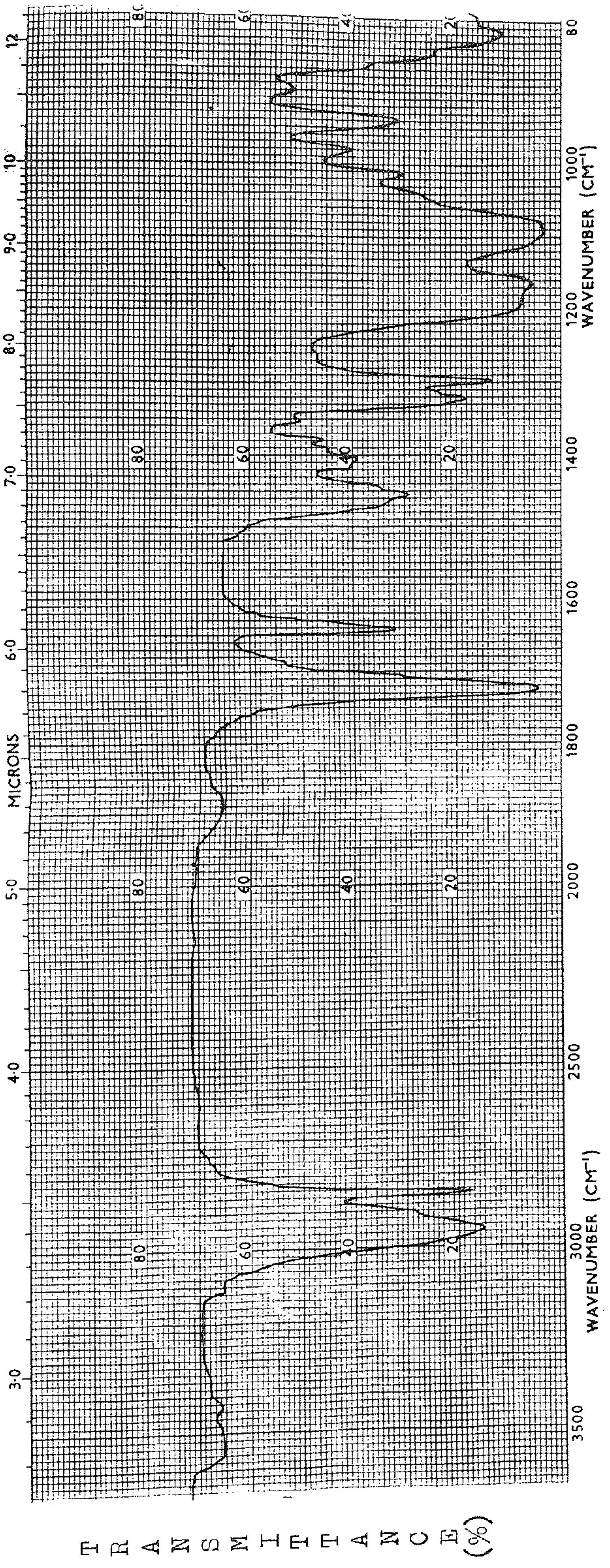
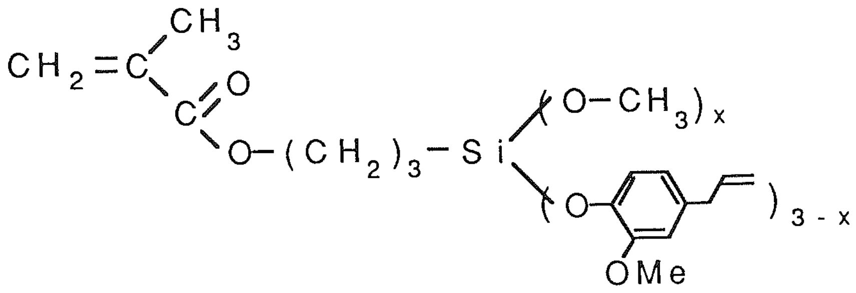

MICRONS
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
12
80
60
40
20
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
WAVENUMBER (CM⁻¹)
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (%)

Figure 3.3

could also be due to the presence of this group. The spectrum of the product also contains absorbances characteristic of both A174 and eugenol; the band at 1715cm^{-1} is characteristic of the carbonyl group of an ester, the band at 1640cm^{-1} is characteristic of the $CH_2=C<$ group and the band at 1610cm^{-1} is characteristic of the benzene ring. Thus it may be proposed that some of the reaction product shown below is formed:



A 3:1 ratio of the alcohol to A174 was used in order to produce the trisubstituted product. However, it is difficult to ascertain from IR evidence if the mono-, di-, or tri-substituted product was formed since absorbances between 1100cm^{-1} and 1200cm^{-1} in the residual reaction mixture could be due to unreacted A174 present in the mixture or the 0-CH_3 group in the mono- or di- substituted product. Furthermore, proof of the existence of unreacted eugenol by the presence of the band at 3470cm^{-1} suggests that not all the alcohol reacted to produce tri-substituted products.

GPC Analysis

The sample was analysed by GPC as a 2% solution in THF; the chromatogram is shown in figure 3.4.

It can be seen that the peaks with the two lowest elution volumes correspond to polystyrene equivalent molecular

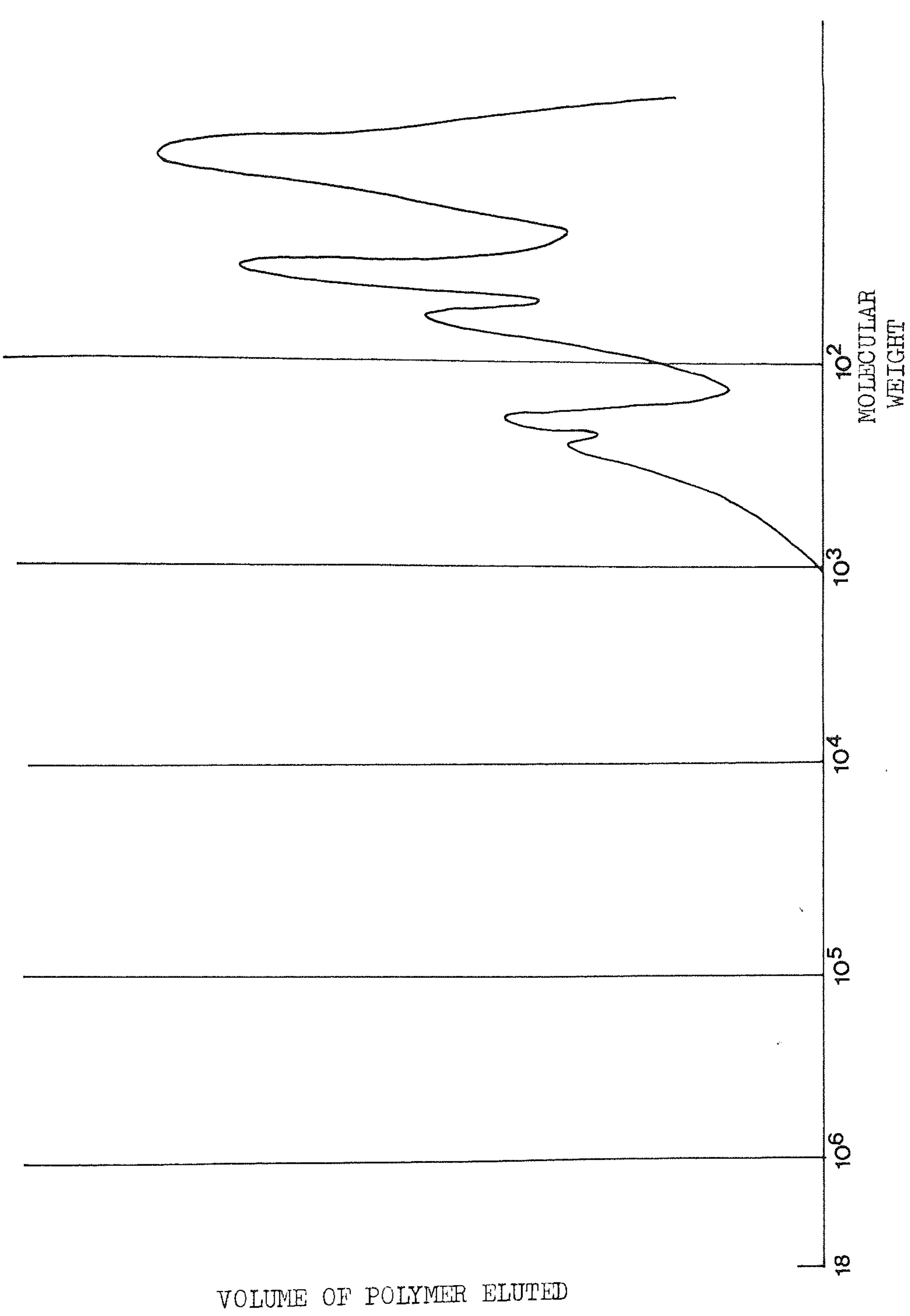

MOLECULAR WEIGHT
10^2
10^3
10^4
10^5
10^6
18
VOLUME OF POLYMER ELUTED

Figure 3.4

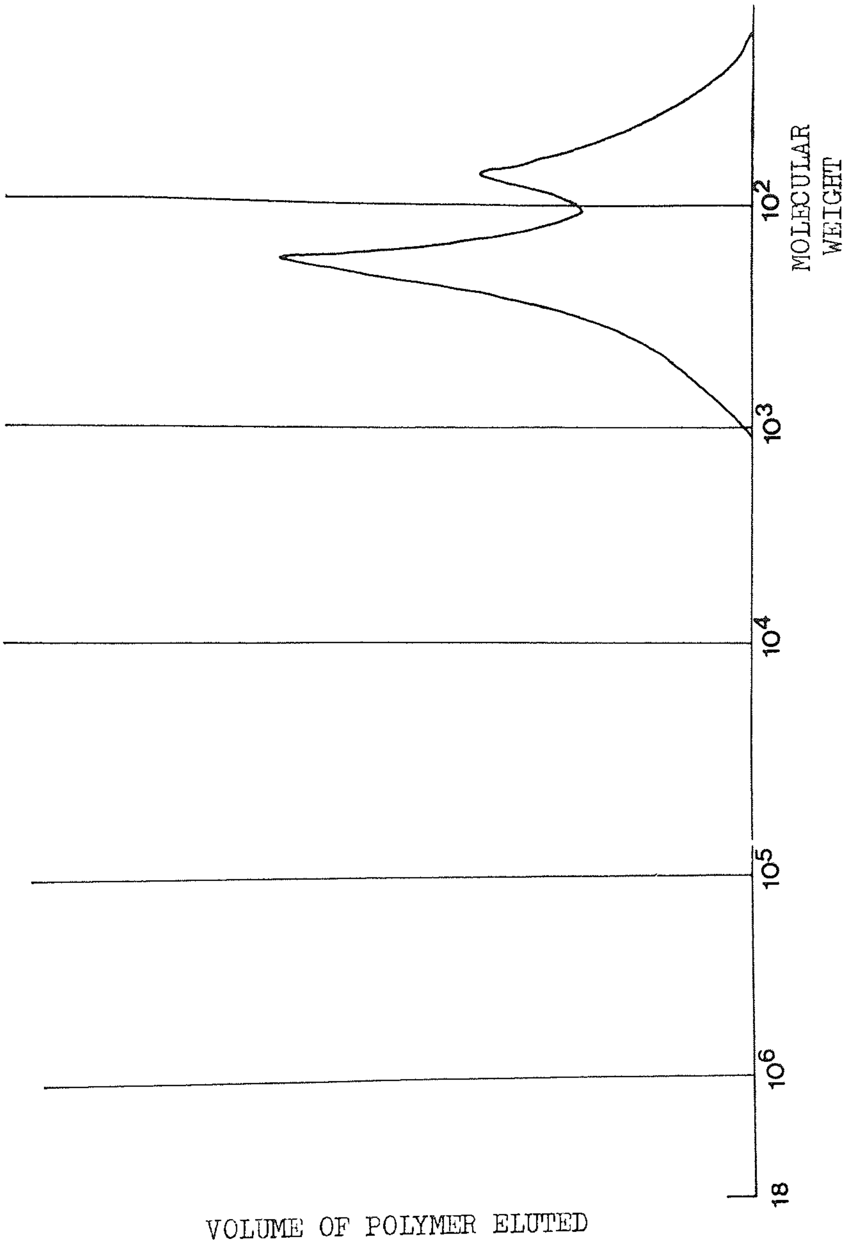

MOLECULAR WEIGHT
10^2
10^3
10^4
10^5
10^6
18
VOLUME OF POLYMER ELUTED

Figure 3.5

weights of 470 and 340 respectively and since the mono-, di- and tri-substituted products have molecular weights of 380, 543 and 644, it would seem reasonable to suggest that these two correspond to the mono- and di-substituted products. However, when the chromatogram of the product is compared with that of A174 (shown in figure 3.5) which has a molecular weight of 248, the chromatogram of this monomer shows a peak with an elution volume which corresponds to a polystyrene equivalent molecular weight of 330. Hence it would appear that some of the mono-substituted product is formed whilst the peak which corresponds to a polystyrene equivalent molecular weight of 340 is unreacted A174.

3.3.2.2. Analysis of the octyl, hexyl and pentyl derivatives of A174

During the purification of the octyl (P3A), hexyl (P3B) and pentyl (P3C) derivatives approximately 30cm^3 of distillate was formed at 55-60°C in each case. On completion of distillation the residual reaction mixture of each derivative was analysed by IR spectroscopy. In the case of the octyl derivative IR analysis was also carried out on the distillate whilst the hexyl residual reaction mixture was also analysed by GLC.

IR Spectroscopy

The samples were analysed by IR as thin liquid films between sodium chloride plates. The spectra obtained are shown in figures 3.6, 3.7 and 3.8.

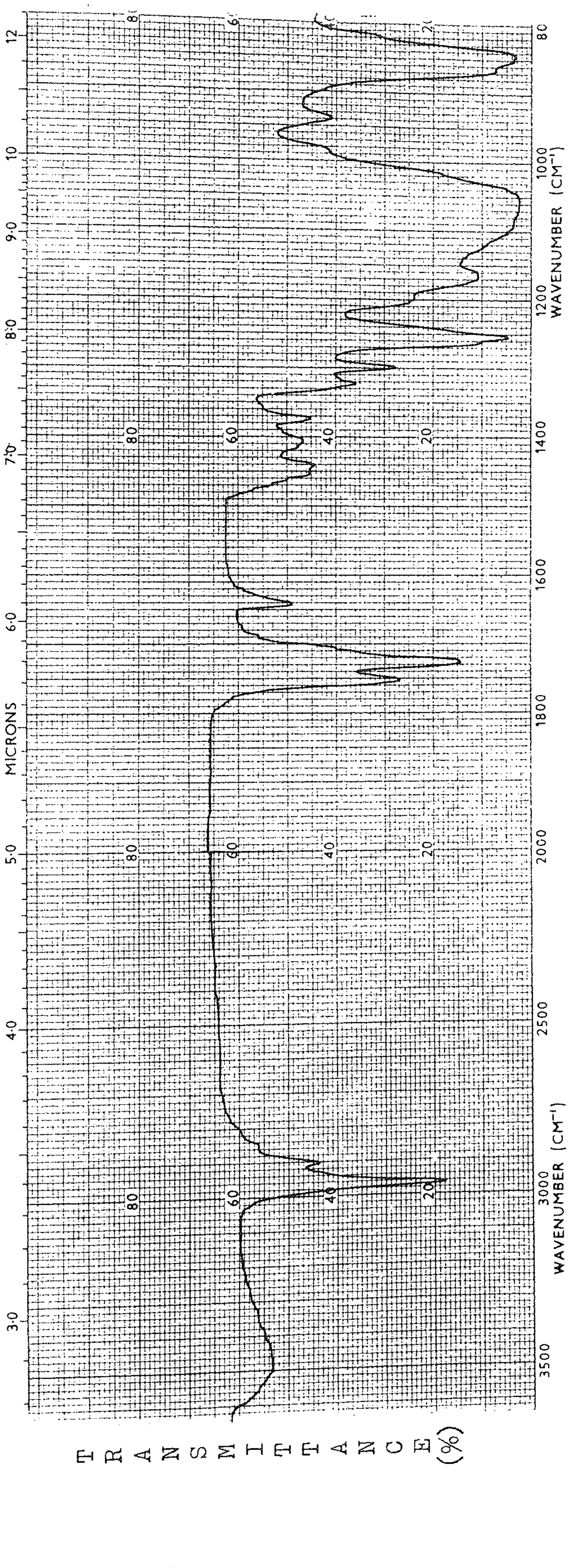

MICRONS
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
WAVENUMBER (CM⁻¹)
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
80
60
40
20
TRANSMITTANCE (%)

Figure 3.6

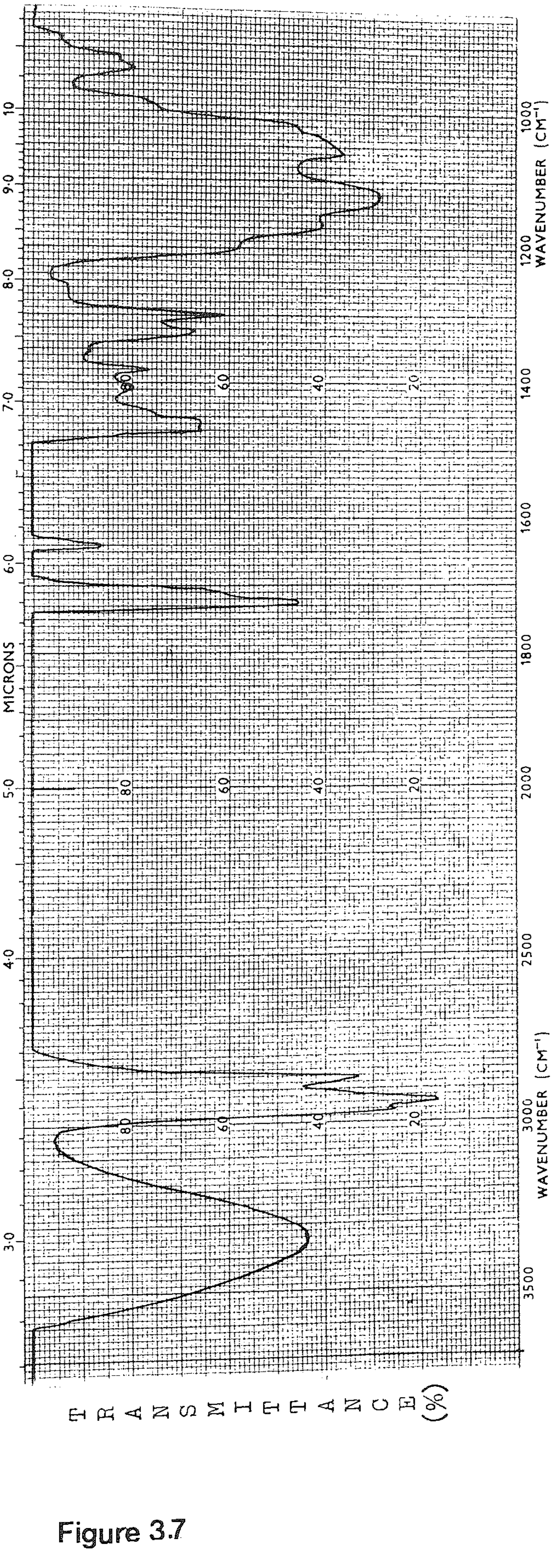

MICRONS
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
WAVENUMBER (CM⁻¹)
3500
3000
2500
2000
1800
1600
1400
1200
1000
80
60
40
20
TRANSMITTANCE (%)

Figure 3.7

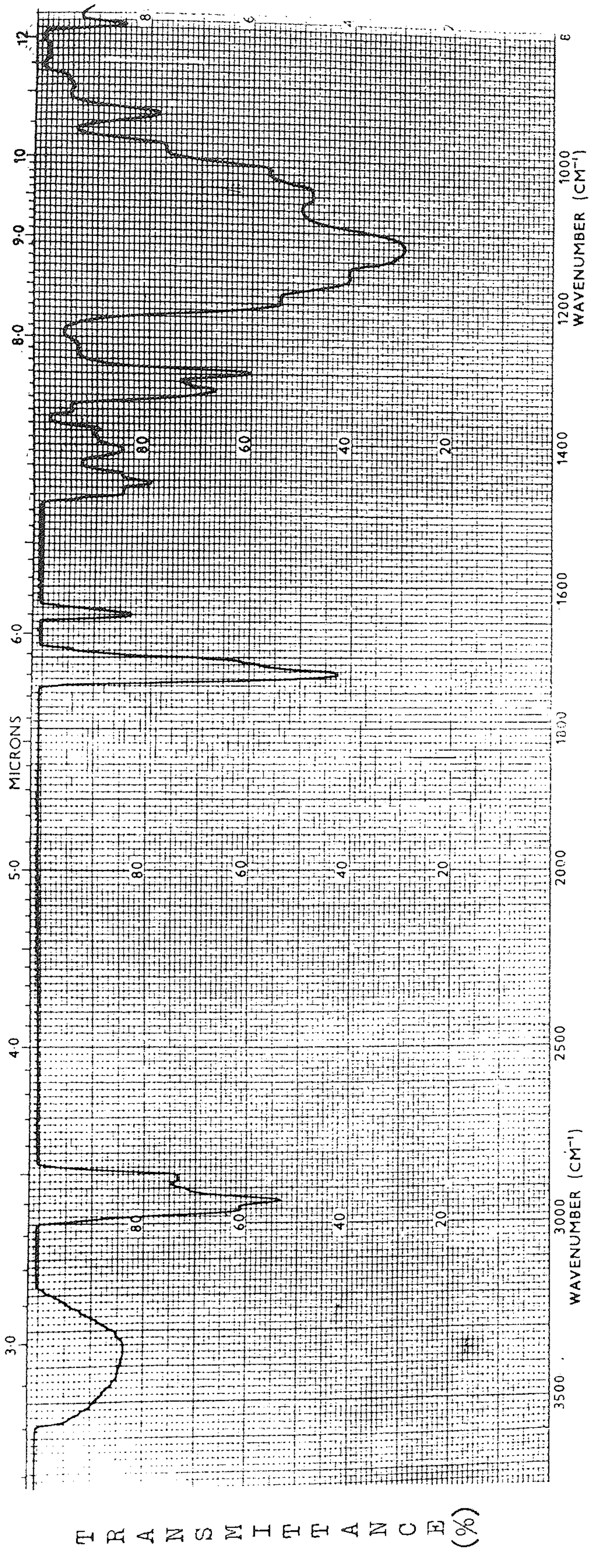

MICRONS
3·0
4·0
5·0
6·0
8·0
9·0
10
12
WAVENUMBER (CM⁻¹)
3500
3000
2500
2000
1800
1600
1400
1200
1000
80
60
40
20
TRANSMITTANCE (%)

Figure 3.8

It is very difficult to determine the extent of reaction from IR analysis since both the reactant (A174) and the expected products are aliphatic siloxanes; they differ only in the length of the alkyl chain attached to the oxygen atom.

However, the octyl derivative (P3A) (figure 3.6) shows a slightly different absorbance pattern to A174 in the region of the spectrum where aliphatic ethers are known to absorb; the product shows a very broad absorbance band between 1.040 and 1100cm^{-1} whereas A174 shows a sharper absorbance between 1080 and 1100cm$^{-1.}$ Octan-1-ol shows an absorbance at 1060cm^{-1} but the relatively weak absorbance at 3500cm^{-1} in the product proves that there was little unreacted alcohol present.

In the case of the hexyl derivative (P3B) (figure 3.7) the spectrum shows a broad absorbance at 1060cm^{-1}. However this could also be attributed to unreacted hexan-1-ol since the absorbance at 3350cm^{-1} suggests that there was some excess alcohol present. Nevertheless the absorbance is broader than one would expect if it is due to excess hexan-1-ol alone; the band extends down to 1020cm^{-1} and this cannot be attributed to A174. Furthermore, the product shows a new relatively strong absorbance at 1120cm^{-1} which is not present in either the spectrum of A174 or that of hexan-1-ol and could be due to an alkyl ether linkage.

The pentyl derivative (P3C) (figure 3.8) shows a very similar absorbance pattern to the hexyl derivative in the region of the spectrum typical of aliphatic ethers. It is, however, seen that the absorbance due to unreacted pentan-1-ol at 3360cm^{-1} is

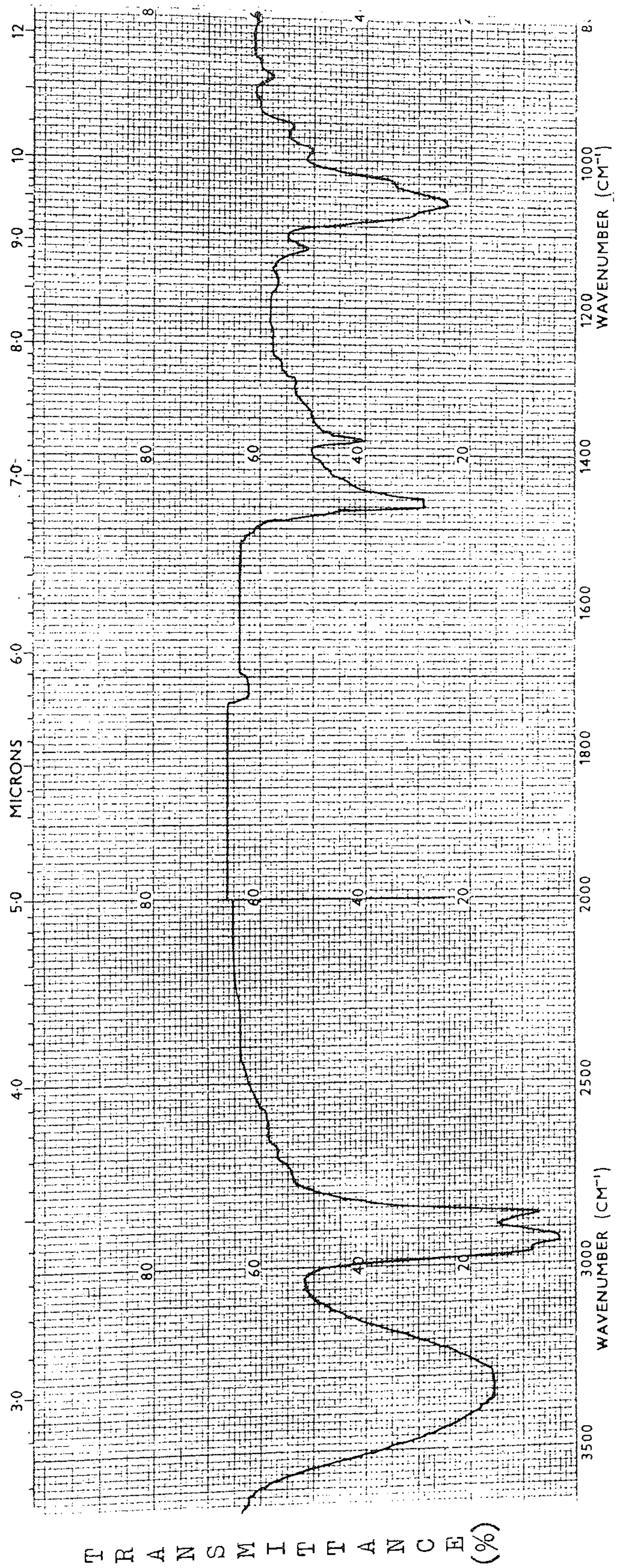

MICRONS
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
12
WAVENUMBER (CM⁻¹)
3500
3000
2500
2000
1800
1600
1400
1200
1000
80
60
40
20
TRANSMITTANCE (%)

Figure 3.9

much weaker than that of the hexyl derivative and yet the absorbances at 1060cm^{-1} and 1120cm^{-1} are of equal magnitude thus providing further evidence that the absorbance at 1060cm^{-1} in the spectra of the products is not due entirely to unreacted alcohol.

If the alcohol exchange reaction is successful methanol is formed as a by-product and is subsequently removed from the reaction mixture by distillation. Therefore IR analysis of the distillate should provide further evidence for the occurrence of the exchange reaction.

On analysis of the IR spectrum of the distillate produced during the purification of the octyl derivative (shown in figure 3.9). It is seen that it bears close relation to that published by Aldrich for octan-1-ol but could be a composite spectrum of octan-1-ol and methanol. In addition the distillate was seen to form at 55-60^{o}C under reduced pressure. This temperature seems to be a little high if the distillate consisted solely of methanol which normally boils at 65^{o}C at atmospheric pressure. Furthermore as was seen previously IR analysis showed the presence of a comparatively small amount of unreacted alcohol in the reaction mixture left in the flask after distillation. These facts could be accounted for by the fact that octan-1-ol was removed from the flask during distillation.

On comparison of the absorbances at 3500cm^{-1} in the IR spectra of the products it would appear that the hexyl derivative contained the greatest amount of unreacted alcohol. Therefore to ascertain the exact purity of the hexyl derivative, the residue remaining after distillation was analysed by GLC.

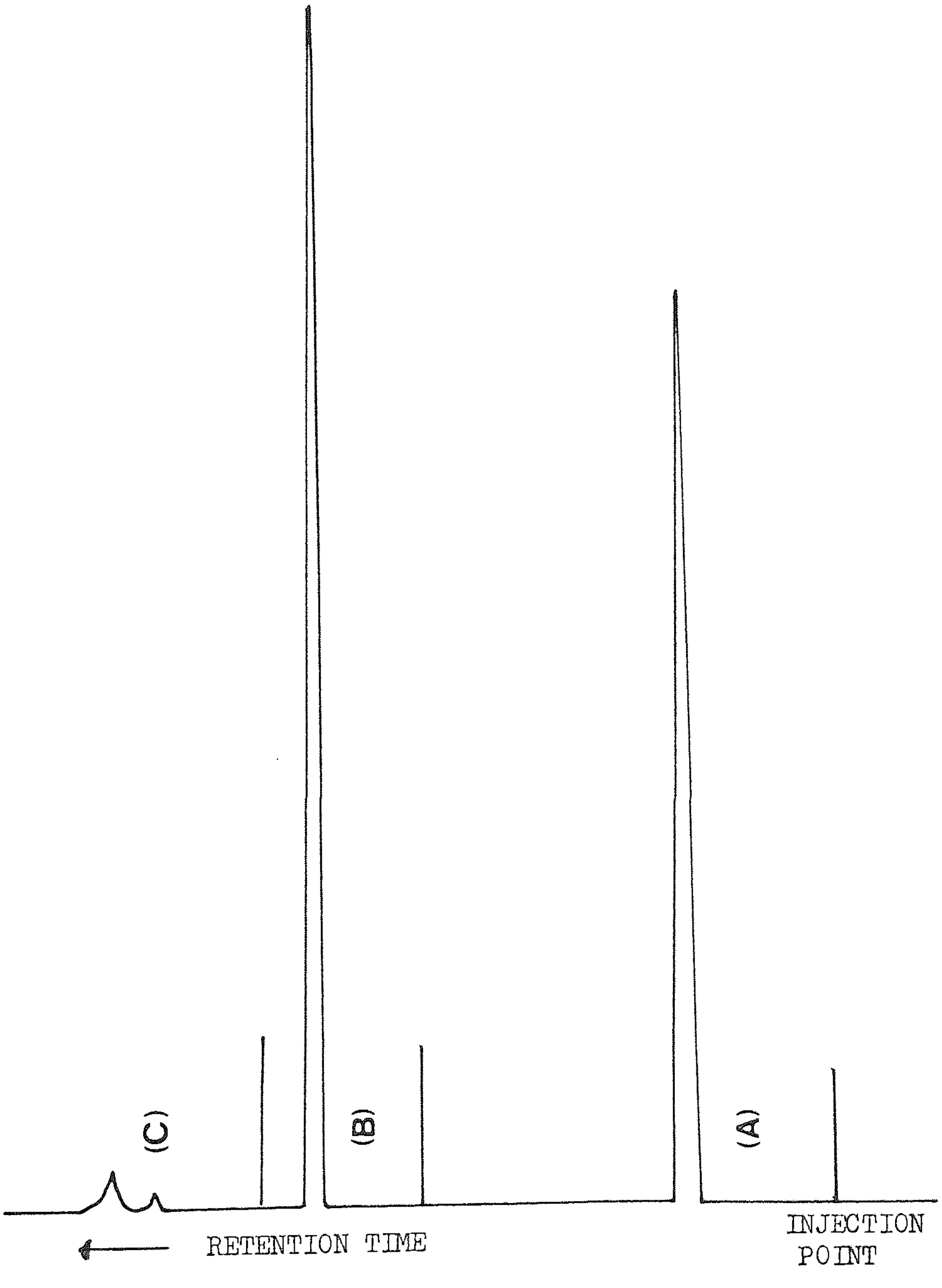


Figure 3.10

The chromatogram is shown in figure 3.10. The GLC chromatograms of hexan-1-ol and cyclohexane are also shown in figure 3.10. On comparison of the GLC trace of the product with those of cyclohexane and hexan-1-ol it is seen that the residual reaction mixture contained very little hexan-1-ol and a negligible amount of cyclohexane. This evidence correlates well with the theory that the majority of the unreacted alcohol was removed from the reaction flask by distillation. The fact that the IR absorbance at 3350cm^{-1} is much stronger for the hexyl derivative than for the pentyl and octyl derivatives could be accounted for by the remote possibility that the P3B product was not dry and that this peak is due to water.

3.3.3. Copolymerisation of siloxane derivatives with methyl methacrylate

3.3.3.1. Solution polymerisation

3.3.3.1.1. Copolymerisation of A174 and methyl methacrylate

The free radically initiated polymerisation of A174 with MMA was carried out as described in section 2.7.1.1.1. In a typical reaction system 0.05mol (12.4g) of A174 and 0.05mol (5.01g or 5.4ml) of methyl methacrylate were dissolved in sufficient toluene to give a total solution volume of 99ml. 1ml of 0.1M AZBN/toluene solution was then added as initiatior and the reaction mixture was left at 60°C for 18 hours.

After this time had elapsed the reaction mixture had not increased in viscosity and when it was poured into an excess of

Table 3.2. The reaction conditions for the preparation of copolymer sheets

TEMPERATURE AND DURATION OF REACTION	(i) 3 days at 60°C (ii) 3 hours at 90°C	WEIGHT OF INITIATOR (AZBN)	0.025g	WEIGHT OF CROSSLINKING AGENT (EGDMA)	0.05g

POLYMERISATION SOLUTION	SILOXANE COMONOMER	RATIO		WEIGHT(g)	
		MMA	SILOXANE COMONOMER	MMA	SILOXANE COMONOMER
SE$_1$	P3D	90	10	4.5	0.5
SE$_2$	P3D	80	20	4.0	1.0
SE$_3$	P3D	70	30	3.5	1.5
SE$_4$	P3D	50	50	2.5	2.5
SO$_1$	P3A	50	50	2.5	2.5
SO$_2$	P3A	20	80	1.0	4.0
SO$_3$	P3A	90	10	4.5	0.5
SO$_4$	P3A	80	20	4.0	1.0
SO$_5$	P3A	70	30	3.5	1.5
SO$_6$	P3A	60	40	3.0	2.0
SH$_1$	P3B	50	50	2.5	2.5
SM$_1$	-	100	0	5.0	0.0

methanol no polymer resulted.

The reaction was repeated using the same quantities of comonomers and initiator but in a total solution volume of 30ml. Once again polymerisation did not occur.

3.3.3.1.2. Copolymerisation of 3-(methylpropenoxycarbonyl)propyltrioctoxysilane (P3A) and methyl methacrylate (MMA)

In the copolymerisation of P3A and MMA a typical reaction system consisted of 0.005mol (2.71g) of P3A and 0.005mol (0.0501g or 0.5ml) of MMA .0.1ml of AZBN/toluene solution was added and the reaction mixture made up to 10ml with toluene. The reaction vessel was left at 60°C for 18 hours after which time the contents were poured into methanol; no precipitate of polymer was observed.

3.3.3.2. Copolymer sheet preparation

Copolymer sheet preparation was carried out as described in section 2.7.1.1.2.

Sheets were made using various ratios of siloxane comonomers to methyl methacrylate. The reaction mixtures that were employed are summarised in Table 3.2. The plates were placed in an oven at 60°C for three days and post cured at 90°C for three hours.

The copolymer sheets were removed from the plates and small sections (approximately 2g) were cut out, weighed and placed

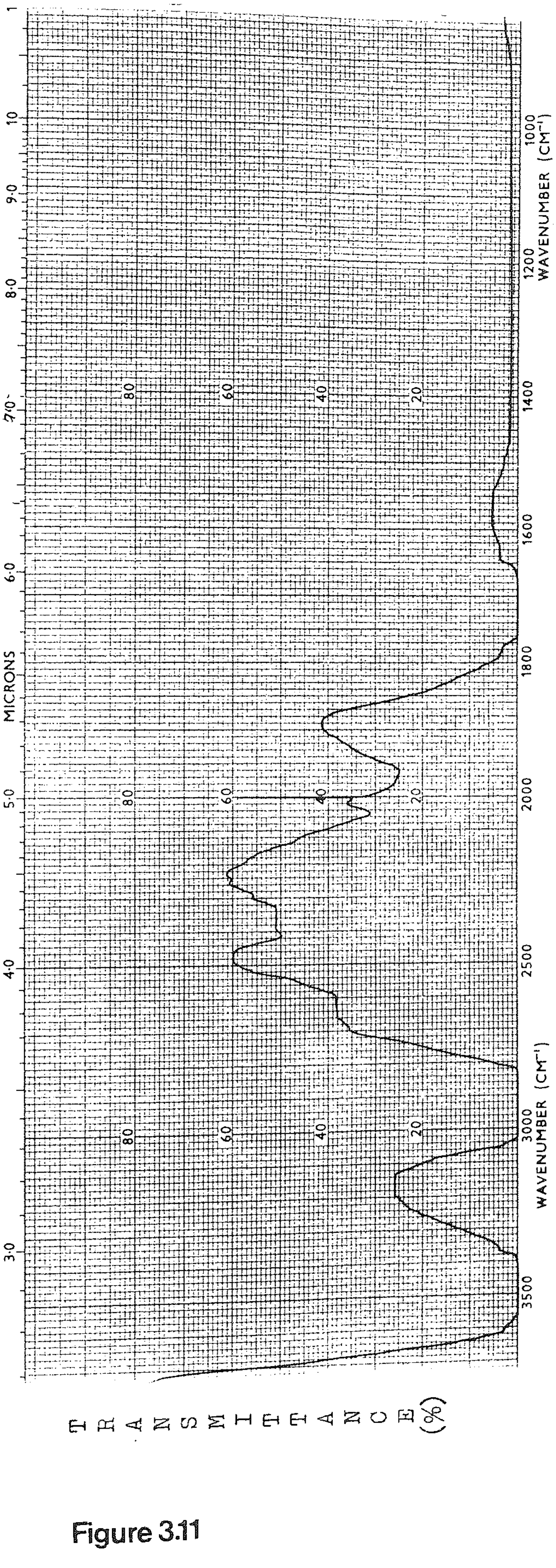

MICRONS
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
80
60
40
20
3500
3000
2500
2000
1800
1600
1400
1200
1000
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (%)

Figure 3.11

in toluene overnight. The samples were then removed, dried under vacuum and reweighed. The % loss in weight and therefore the % extraction of the copolymer sheet was then calculated.

3.3.3.2.1. Analysis of the copolymers of P3D and MMA

Extraction.

The copolymers of P3D and MMA were prepared as described above. Extraction of the copolymer sheets with toluene showed that complete copolymerisation of the monomers took place because all samples showed that no extractable material was present.

IR Spectroscopy

The polymer of sample SE_2 was analysed by IR spectroscopy. The spectrum obtained is shown in Figure 3.11. Apart from the characteristic OH absorbance at $3450cm^{-1}$ the IR spectrum shows flat peaks indicating that the sheets were too thick. Attempts were made to make thinner sheets using one polyethylene spacer but it proved impossible to release these sheets from the plates, they completely shattered on removal.

Contact angle measurements

The contact angle of water was measured on two of the copolymer sheet samples by the method described in section 2.9.6. The results obtained are shown in Table 3.3

Table 3.3

Copolymer Sheet	Contact angle (^{o})
SE_3	36
SE_4	55

The contact angles of the toluene extracted films were far lower than expected; silicone rubbers usually show contact angles of 96 ± 2 [21] and poly (MMA) a contact angle of 66 ± 2 [21]. The size of the contact angles shown by samples SE_3 and SE_4 were obviously due to residual hydrophilic (OH) groups at the surface. This provides some tentative evidence for the presence of unreacted alcohol in the monomer. However, it seems reasonable to assume that this ought to have been extracted by toluene when the films were stood overnight in the solvent.

Physical appearance

Other physical features of the copolymer films are summarised in Table 3.4.

It is possible that the brown colouration associated with the membranes SE_{1-4} was caused by the presence of unreacted eugenol but this cannot be considered as a confirmatory test.

Table 3.4

COPOLYMER SHEET	COLOUR	TEXTURE
SE_1	Light brown,opaque	Very brittle, surface rough and cracked
SE_2	Light brown, opaque	Brittle, rough surface
SE_3	Light brown, opaque	Brittle, rough surface
SE_4	Brown opaque	Softer more rubber like

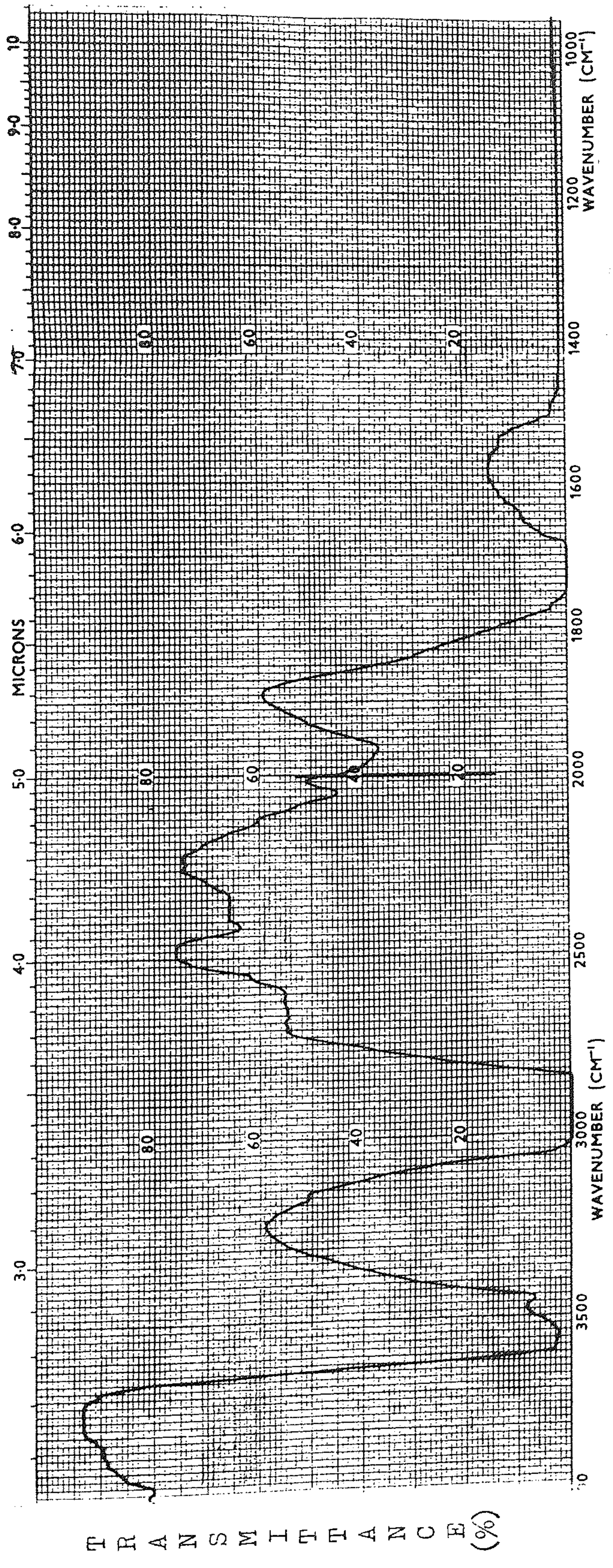

MICRONS
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
WAVENUMBER (CM⁻¹)
3500
3000
2500
2000
1800
1600
1400
1200
1000
80
60
40
20
TRANSMITTANCE (%)

Figure 3.12

3.3.3.2.2. Analysis of the copolymers of P3A and P3B with MMA

Extraction

Extractions carried out on samples of polymers SO_1 - SO_6 and SH_1 showed that there was no loss in weight. GLC confirmed the purity of the solvent on removal of the polymer samples.

IR Spectroscopy

Sample SO_1 was analysed by IR. The spectrum obtained is shown in Figure 3.12.

Flat peaks were observed showing that the membrane sample was too thick. However the absorbances at 3450 and 3550cm^{-1} are indicative of the presence of unreacted alocohol.

Physical appearance

Some structural features of the membranes are summarised in Table 3.5

As can be seen from table 3.5 the brittleness of the copolymer sheet depended on the amount of methyl methacrylate in the copolymerisation mixture.

Table 3.5

COPOLYMER SHEET	COLOUR	TEXTURE
SO_1	Transparent, colourless	Smooth surface fairly soft
SO_2	White opaque	Smooth surface very soft
SO_3	Transparent, colourless	Very brittle smooth surface
SO_4	Transparent, colourless	Brittle smooth surface
SO_5	Transparent, colourless	Quite brittle smooth surface
SO_6	Transparent, colourless	Fairly soft smooth surface
SH_1	Transparent, colourless	Fairly soft smooth surface

3.3.3.2.3. Analysis of a sheet of poly(MMA)

The sheet of poly(MMA) was seen to be more brittle than any of the other membranes, was colourless, transparent and had a smooth surface.

3.4. Discussion and conclusions

Although it has been reported that an exchange reaction readily occurs between A174 and a variety of alcohols many difficulties were encountered when attempts were made to carry out this reaction. One of the major problems was the impurity of the product. A 3:1 ratio of alcohol to A174 was used in order to form the tri-substituted product. However, proof of the inefficiency of the reaction was provided by GPC analysis of the purified comonomer which showed that (a) the reaction was only successful in forming the mono-substituted product and (b) that there was a comparitively large amount of unreacted A174 present; A174 has a relatively high boiling point making it too involatile to be distilled even under reduced pressure. It proved very difficult to estimate the exact amount of unreacted alcohol present in the purified reaction mixture. IR analysis showed that although the majority of the alcohol present was removed by distillation a certain amount still remained in the residual mixture in the flask. GLC analysis, however, provided conflicting evidence and it may be concluded that although the purified comonomer contained some unreacted alcohol it is possible that water was also present which, therefore, masked the true intensity of the IR absorbances due to the alcohol.

It does seem unusual that the distillate was formed at the same temperature during the purification of each of the comonomer mixtures but it is possible that the pressure in the distillation apparatus was adjusted to account for the difference in boiling points of the various alcohols.

Attempts to polymerise the siloxane comonomers presented some inconsistencies. The fact that copolymerisation of the siloxane derivative and methyl methacrylate occurred during the formation of a copolymer sheet but not in solution can possibly be accounted for by the fact that a greater quantity of initiator was used in sheet formation than in solution polymerisation.

A174 almost certainly contained an inhibitor although attempts to remove it resulted in hydrolysis when sodium hydroxide or ferrous sulphate solutions were used, or polymerisation in the case of strong heating during a distillation process. Therefore, it would appear that in the case of copolymer sheet formation sufficient initiator was added to react with both the inhibitor and to initiate polymerisation. The fact that hydrolysis of A174 occurred on addition of aqueous solutions of sodium hydroxide or ferrous sulphate leads one to believe that hydrolysis of this monomer could have occurred during the exchange reaction therefore accounting for the relatively strong IR absorbance in the region of the spectrum typical of alcohols.

Studies of the properties of copolymer sheets gave further proof of the impurity of the siloxane comonomers prior to polymerisation; results of the contact angle measurements can only be accounted for by the presence of hydrophilic groups such as unreacted alcohol. Nevertheless, samples of the copolymer sheets were placed in toluene to extract any unreacted material. The failure of this technique can possibly be attributed to the length of time that the films were allowed to stand in the solvent; eugenol and A174 for example, are comparitively large molecules and it may take considerably longer than one day to extract these materials from a copolymer sheet.

It may be concluded from the work carried out that the alcohol exchange reaction is not a successful method of modifying the structure and properties of the siloxane monomer A174. Furthermore although it was shown that the brittleness of the copolymer sheets could be controlled by varying the amount of methyl methacrylate present it was very difficult to assess the other properties of the sheets due to the inefficiency of the exchange reaction and therefore the impurity of the siloxane comonomer.

CHAPTER FOUR

METALLATION

4. Metallation

4.1. Grignard Formation

4.1.1. Introduction

The synthesis and use of organomagnesium halides, Grignard reagents, were devised early in this century by the French chemist Victor Grignard who for that reason shared the Nobel prize for chemistry in 1912 [37, 38, 39.] . In 1900 Grignard discovered that bromoethane reacts with magnesium suspended in dry ether [40] in a reaction that is vigorously exothermic. The magnesium dissolves and an ether soluble product known as a Grignard reagent is formed.

$$CH_3-CH_2-Br \ + \ Mg \xrightarrow{\text{dry ether}} CH_3-CH_2-MgBr$$

Grignard reagents can be formed from alkyl (1^o, 2^o or 3^o), allyl, aralkyl (e.g benzyl) or aryl (phenyl or substituted phenyl) halides where the halogen may be either Cl, Br or I. However, arylmagnesium chlorides have to be synthesised in THF [38]. Di - Grignard reagents have also been prepared using 2,2' dibromodibenzyl in THF [41].

Although Grignard reagent syntheses are normally performed in ethereal solvents, preparations have been carried out in hydrocarbon solvents in the presence of complexing agents such as triethylamine [42].

4.1.2 Mechanism

As a result of stereochemical [43], kinetic [44], CIDNP [45, 46] and product studies, it is known that alkyl free radicals are intermediates in the formation of Grignards. That the synthesis was not an ionic process was demonstrated by the fact that when magnesium dissolves in an ethereal solution of ethyl bromide the solution has a very low conductivity. Furthermore the formation of biphenyl in the reaction of magnesium with bromobenzene and the disproportionation and coupling products observed in the reaction of ββ'- di methylphenethyl chloride with magnesium have been interpreted to involve free radical intermediates [43].

Two principal mechanisms have been put forward [43, 44] for the formation of Grignard reagents.

Scheme one involves a rate limiting electron transfer from the magnesium surface to the alkyl halide followed by collapse of the ion pair [45, 47] e.g.:

$$\begin{tikzcd} RX + Mg_{(s)} \arrow[r] & {[RX^{-\bullet}Mg^{+}_{(s)}]} \arrow[d, "fast"] \\ RMgX + Mg_{(s)} & {[R^{\bullet}\quad X\dot{M}g_{(s)}]} \arrow[l] \end{tikzcd}$$

It has also been suggested that the formation of dialkyl magnesium is indicative of a free radical reaction. Instead of R-Mg-X being eliminated from the surface of the magnesium, the alkyl radical reacts with another magnesium atom as shown below [47].

$$R^{\bullet} + \dot{M}gX_{(s)} \xrightarrow{Mg_{(s)}} R{-}Mg^{\bullet}_{(s)} \xrightarrow{R^{\bullet}} R_2Mg$$

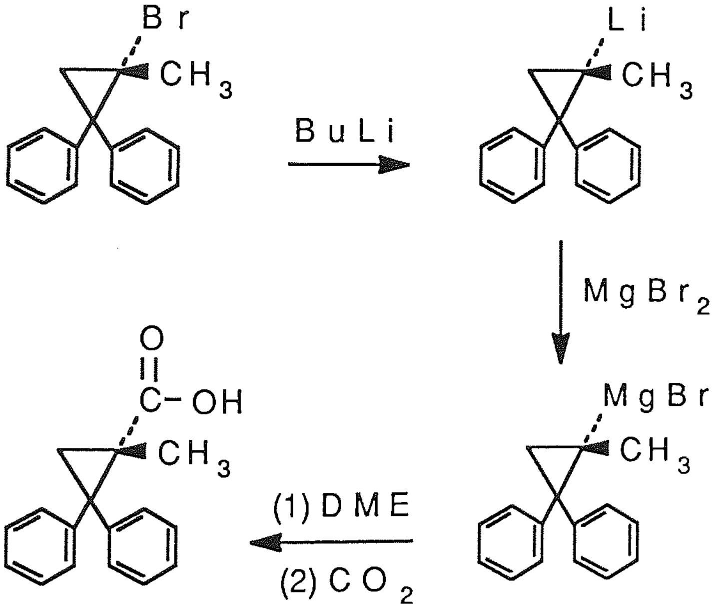
Further reaction with another alkyl radical results in the formation of R_2Mg.

On the other hand, scheme two constitutes a one step process in which direct transfer of the halogen to the magnesium is involved in the activation process [46,47].

$$RX + Mg_{(s)} \longrightarrow \left[R^{\bullet} \quad X\dot{M}g_{(s)} \right] \xrightarrow{\text{fast}} RMgX + Mg_{(s)}$$

The two proposals were studied with regard to stereochemical evidence using the optically active 1-methyl-2, 2-diphenylcyclopropyl halide system [43, 48]. According to scheme one a radical anion is produced in close association with a univalent magnesium cation. Such a tight anion radical - cation radical pair may collapse directly to the Grignard or collapse may proceed via a loose radical pair. Thus if the radical ion complex collapses directly to the Grignard retention of configuration and optical purity is expected due to the close proximity of the ion radical pair in the complex. However, in scheme two a loose radical pair is formed directly from magnesium and the halide. In this type of loose radical pair the R group of RX is sufficiently separated to permit rotation and therefore racemisation. Studies were made using different halides and solvents. The optical purity of the carbonated Grignard was seen to increase in the order I<Br<Cl. This is consistent with the significance of formation of the loose radical pair being determined by the strength of the carbon halogen bond. However, as the halogen is changed from iodide to bromide to chloride not only does the bond strength increase but more energy is required to add an additional electron to the carbon halogen bond. As a result the lifetime of the radical ion

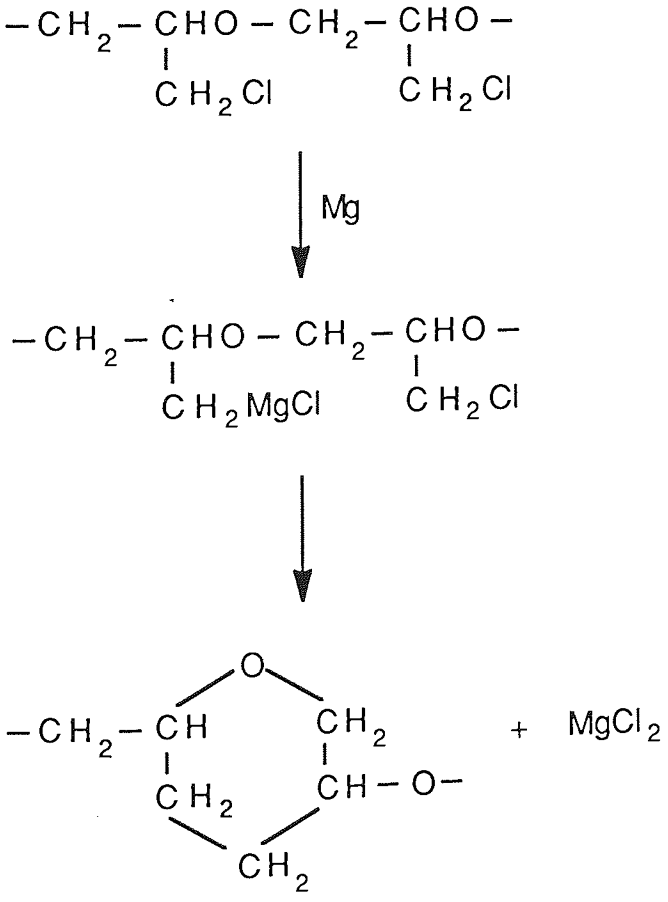
intermediate decreased in this order with the consequence that there was less loose radical pair formed and thus less racemisation. Further studies were also made of Grignard formation of the bromide in ether and THF. From the literature on aromatic radical anions ether is one of the poorer solvents for the formation of such species from alkali metals whilst THF is effective in promoting their formation [43]. Hence ether was not able to stabilise the intermediate as effectively as THF resulting in a greater formation of the loose radical pair in this solvent. In addition, to prove that any racemisation occurred during Grignard formation and not afterwards the following experiment was performed [48]



When 1-methyl-2,2-diphenylcyclopropyllithium was added to an ethereal solution of anhydrous magnesium bromide, the intense yellow colour characteristic of the lithium reagent rapidly disappeared. Carbonation of the reaction mixture then yielded optically pure 1-methyl-2,2-diphenylcyclopropanecarboxylic acid. The occurrence of lithium-Grignard exchange in this reaction was proved by treating the reaction mixture with 1,2 dimethoxyethane (DME) before carbonation as it had been shown that 1,methyl-2,2-diphenylcyclopropyllithium is decomposed by DME whilst the corresponding Grignard is stable to this solvent. However after addition of DME subsequent carbonation still yielded the corresponding acid with complete retention of optical activity and configuration. Thus such results show that once formed the 1-methyl-2,2-diphenylcyclopropyl Grignard reagent is optically stable [48].

4.1.3 Grignard formation of polymeric reagents

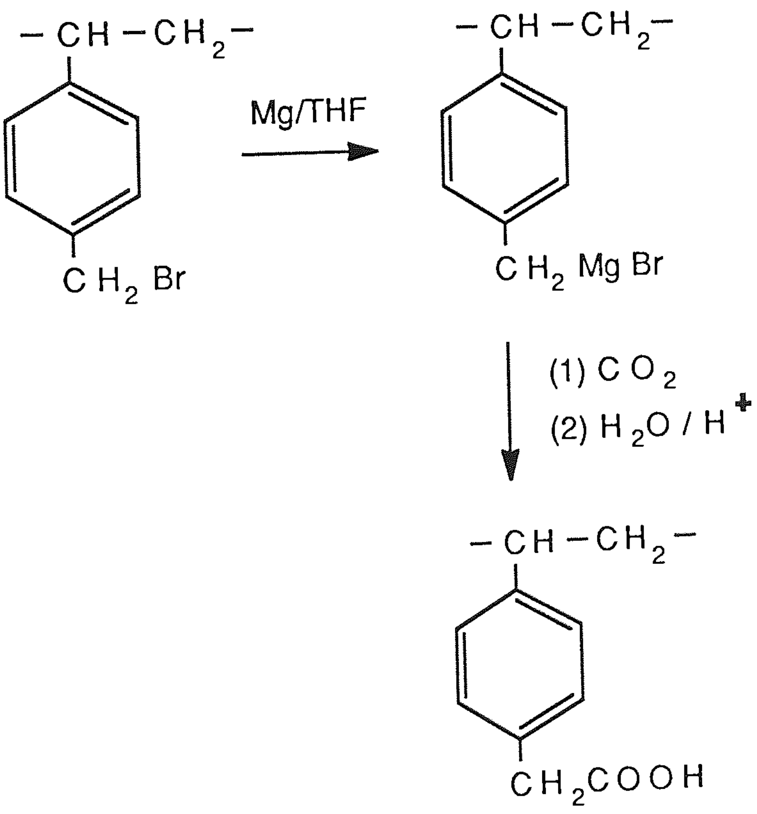
Minoura el al studied the reaction of poly(epichlorohydrin) with magnesium in THF in the hope of obtaining a polymeric Grignard reagent [49]. The polymeric Grignard reagent was not obtained but they found that dechlorination occurred. The Grignard intermediate coupled with the adjacent chloromethyl group eliminating magnesium chloride.



The most probable reason for this reaction taking place in this way is that elimination of $MgCl_2$ resulted in the formation of an unstrained six membered ring.

Poly(epichlorohydrin) has also been reacted with benzylmagnesium chloride and allylmagnesium chloride. It was found that in both cases the chlorine atom in the polymer could be substituted by benzyl and allyl groups [49] confirming that poly (epichlorohydrin) is susceptible to this type of displacement reaction.

There has been success in the formation of the Grignard reagent of poly(vinylbenzylbromide) [50]



Confirmation of the formation of the Grignard was achieved by adding dry ice; proof of formation of the corresponding carboxylic acid was obtained from IR evidence.

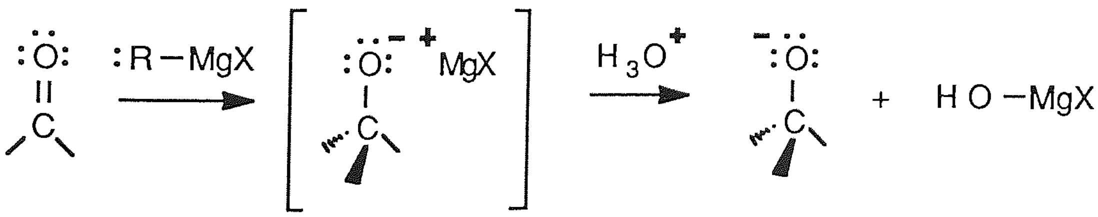
It has also been found that no detectable reaction took place between poly(bromostyrene) and magnesium [50]. During the formation of the Grignard reagent from the monomer p-bromostyrene some polymeric products were obtained when the reaction mixture was heated. However, identification of the structure of such products and proof of the existence of a polymeric Grignard reagent was not possible [50].

4.1.4. Reactions of Grignards

Grignard formation is a very useful synthetic tool owing to the polarity of the C-Mg bond which is approximately 35% ionic in character [39]. Grignard reagents react with many different types of functional groups.

4.1.4.1. Reaction with carbonyl groups

Grignard reagents (RMgX) add to carbonyl compounds according to the following scheme:

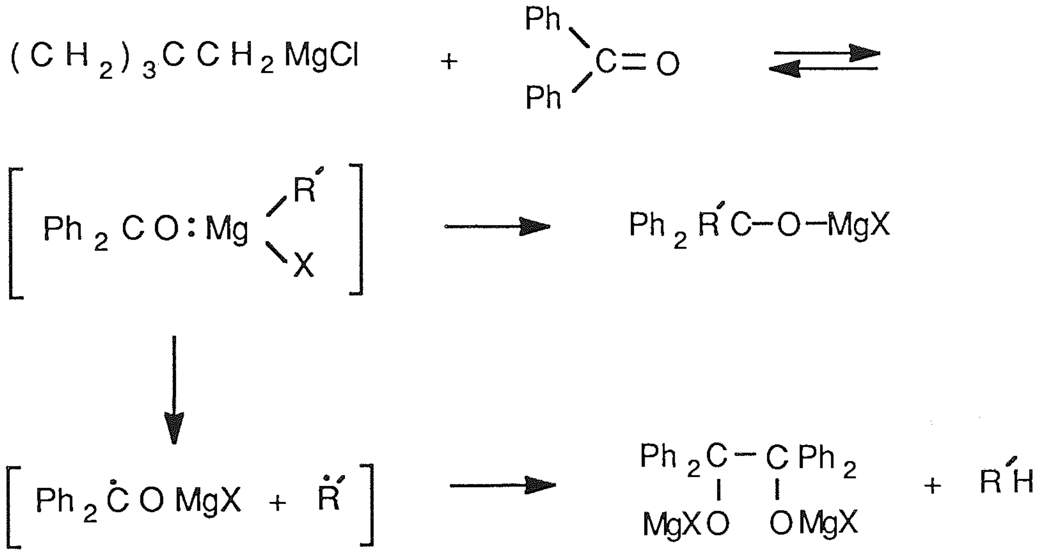


Nucleophilic Grignard reagents react as if the alkyl groups were carbanions and undergo addition reactions to carbonyl compounds.

However, there are reports that radical processes could also be involved. There is evidence for the presence of free radicals in the reactions of the Grignard of neopentyl chloride with benzophenone in THF [51, 52]. The reaction is thought to proceed via two competing reactions

(i) the usual polar reaction affording the 1,2 adduct as major product.

(ii) a radical reaction involving the ketyl radical as intermediate

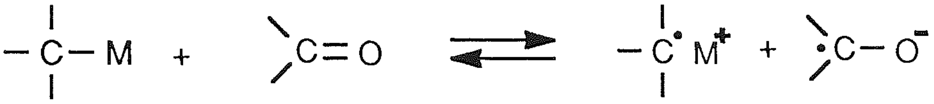


Although the main reaction product was the expected 1,1 diphenyl-3,3-dimethylbutanol, benzopinacol was isolated in 20% yield and a corresponding amount of neopentane, although not isolated, was shown to be present from NMR studies on the unhydrolysed reaction mixture. The latter two products are characteristic of a free radical process. It is thought that the steric bulk of the neopentyl group (R') retards the normal addition reaction so that radicals formed in the process are able to escape from the solvent cage. The neopentyl radical can then react with the solvent to give neopentane and the ketyl can dimerise to give the magnesium halide salt of benzopinacol. However the formation of such radicals is best considered as a two step process involving electron transfer followed by collapse of the ion pair [52]

$$RMgX + Ph_2CO \longrightarrow [RMgX^{\bullet +} \; Ph_2C\dot{O}^{-}]$$

$$\longrightarrow [R^{\bullet} \; Ph_2\dot{C}OMgX]$$

Indeed a theory of a one electron transfer process producing radical anions detected by ESR has been put forward for the reactions of $\alpha\beta$ unsaturated esters, benzophenone anils, deoxybenzoins and aldehydes with RMgX [53]. Thus the one electron transfer process may be represented by the general formula.

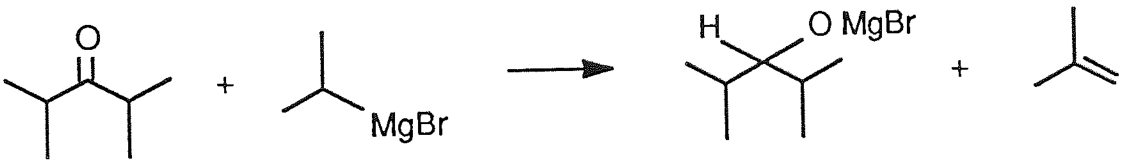


Further support of this mechanism comes from the fact that t-butylmagnesium bromide reacts with sterically hindered phenyl duryl ketone 10^5 times faster than methylmagnesium bromide [52]. This order of reactivity is not expected from the polar process but it does follow from the ease of oxidation of the t-alkyl Grignard reagent as measured by electrochemical techniques.

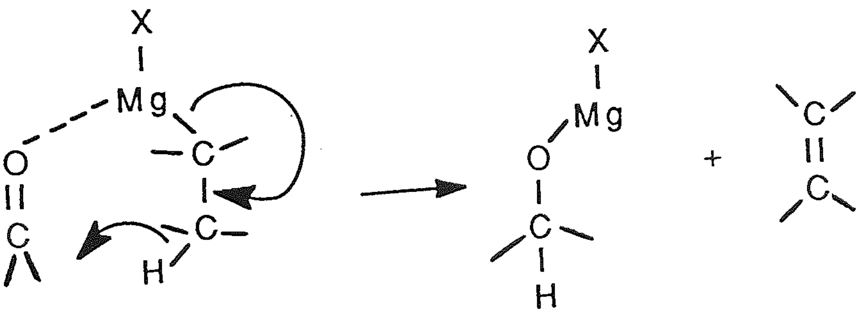
Although one would expect the more ionic alkali metal compounds such as organolithium compounds to favour the polar 1,2 addition reaction there is evidence for ketyl formation in sterically hindered systems. For example with tritylsodium and benzophenone in ether solution the observed green colour was attributed to the following equilibrium [54].

$$\begin{tikzcd}(C_6H_5)_3C\,Na + (C_6H_5)_2C{=}O \arrow[d, shift right] \\ (C_6H_5)_3\dot{C} + (C_5H_6)_2\dot{C}\,O\,Na \arrow[u, shift right]\end{tikzcd}$$

In addition to formation of radical products other side reactions may occur in the reaction of a Grignard reagent with a carbonyl group. In cases where the reagent possesses a β-hydrogen atom the reaction is subject to the occurrence of reduction as a side reaction [55(a)]. With aliphatic Grignard reagents the hydrocarbon residue is dehydrogenated to an oleofin



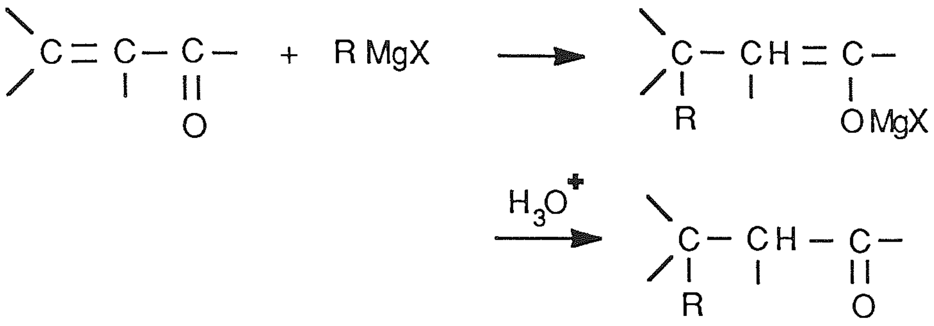
This reaction can be formulated as an alternative mode of reaction of a Grignard reagent coordinated to a carbonyl group.[56]



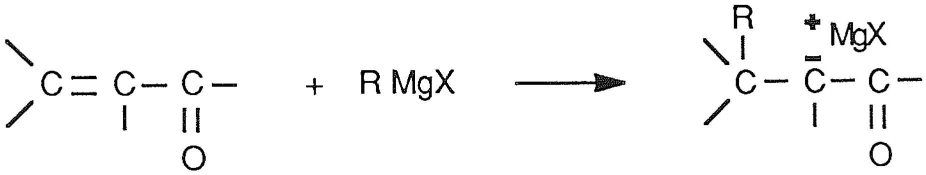
An increase in the bulk of the alkyl group results in an increase in reduction and enolisation.[54]

In the case of conjugated unsaturated systems such as methyl methacrylate 1,4 and 3,4 addition can also occur.

1,4 addition



3,4 addition

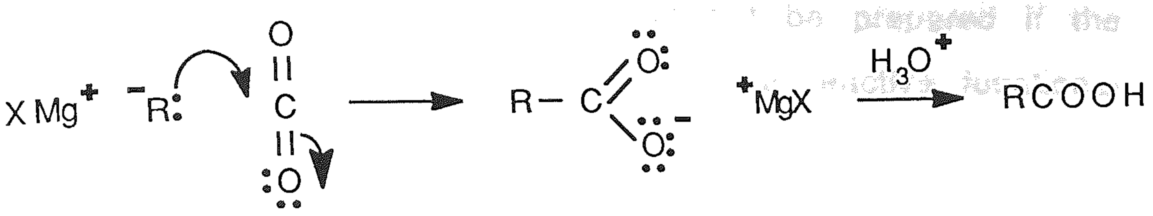


Usually 3,4 addition is the most favoured pathway and takes place in preference to addition to the carbonyl group.

Often organolithium derivatives are more preferable to Grignard reagents since they are less prone to side reactions than Grignard reagents [54, 55(a)]

4.1.4.1.1. Reaction with carbon dioxide

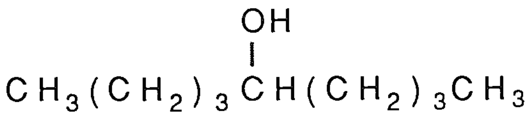
Grignards react with carbon dioxide to give carboxylate salts which can be protonated to give carboxylic acids. [57]. The mechanism of the carboxylation reaction is nucleophilic attack by the organomagnesium halide on one of the C=O bonds of CO_2 yielding the product



4.1.4.1.2. Reaction with esters

The reaction between a Grignard and esters is best exemplified using ethyl formate as a substrate [57]

$$2CH_3(CH_2)_3MgBr + HCOC_2H_5$$



$$\xrightarrow{\text{ether}} \xrightarrow{H_3O^+} CH_3(CH_2)_3\overset{OH}{\overset{|}{C}}H(CH_2)_3CH_3$$

5-nonanol

4.1.4.2. Side reactions

The Grignard reaction has limitations in that it must be carried out under anhydrous conditions because of the following reaction: [37]

$$2\ C_6H_5MgBr + 2\ H_2O$$

$$\longrightarrow 2\ C_6H_6 + Mg(OH)_2 + MgBr_2$$

Oxygen must also be excluded i.e.

$$RMgX + O_2 \longrightarrow R-O-O-Mg$$

$$\xrightarrow{RMgX} 2\ ROMgX \xrightarrow{H_3O^+} 2\ ROH$$

Furthermore a Grignard reagent cannot be prepared if the organohalogen precursor also contains a reactive functional group such as an alcoholic or a carbonyl group.

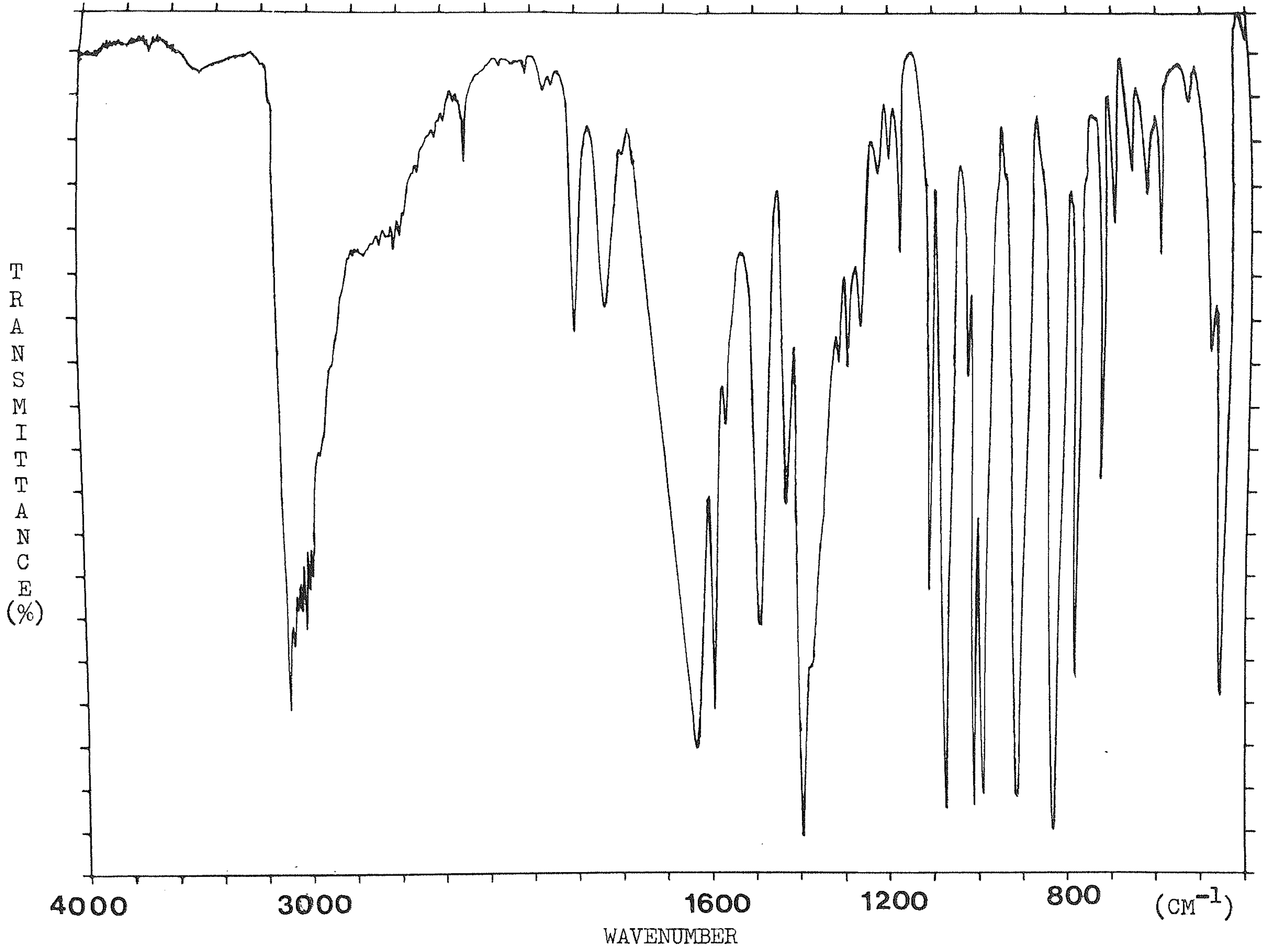


Figure 4.1

4.1.5. Experimental results

4.1.5.1. Introduction

Since work has been carried out on the successful Grignard formation of poly(vinylbenzylbromide) in THF, and bromostyrene monomer is known to react readily with magnesium to form the Grignard derivative, it seemed feasible to attempt the synthesis of the Grignard reagent of poly-(bromostyrene) even though the failure of this reaction is reported in the literature.

Grignard reagents are known to react readily with all types of carbonyl compounds. Consequently it seemed fair to assume that subsequent reaction of the Grignard reagent of poly-(bromostyrene) with carbon dioxide or ethyl formate would lead to the formation of the carboxylic acid derivative or aldehyde respectively.

4.1.5.2. Preparation of poly(bromostyrene)

4.1.5.2.1. Analysis of p-bromostyrene

The monomer was analysed by FT IR as a neat liquid and the spectrum is shown in figure 4.1

4.1.5.2.2. Polymerisation of p-bromostyrene

p-Bromostyrene was polymerised free radically using benzoyl peroxide as initiator as described in section 2.7.1.2. A reaction mixture of 25g (0.136mol) of p-bromostyrene and 0.32g (0.00136mol) of recrystallised benzoyl peroxide was used and

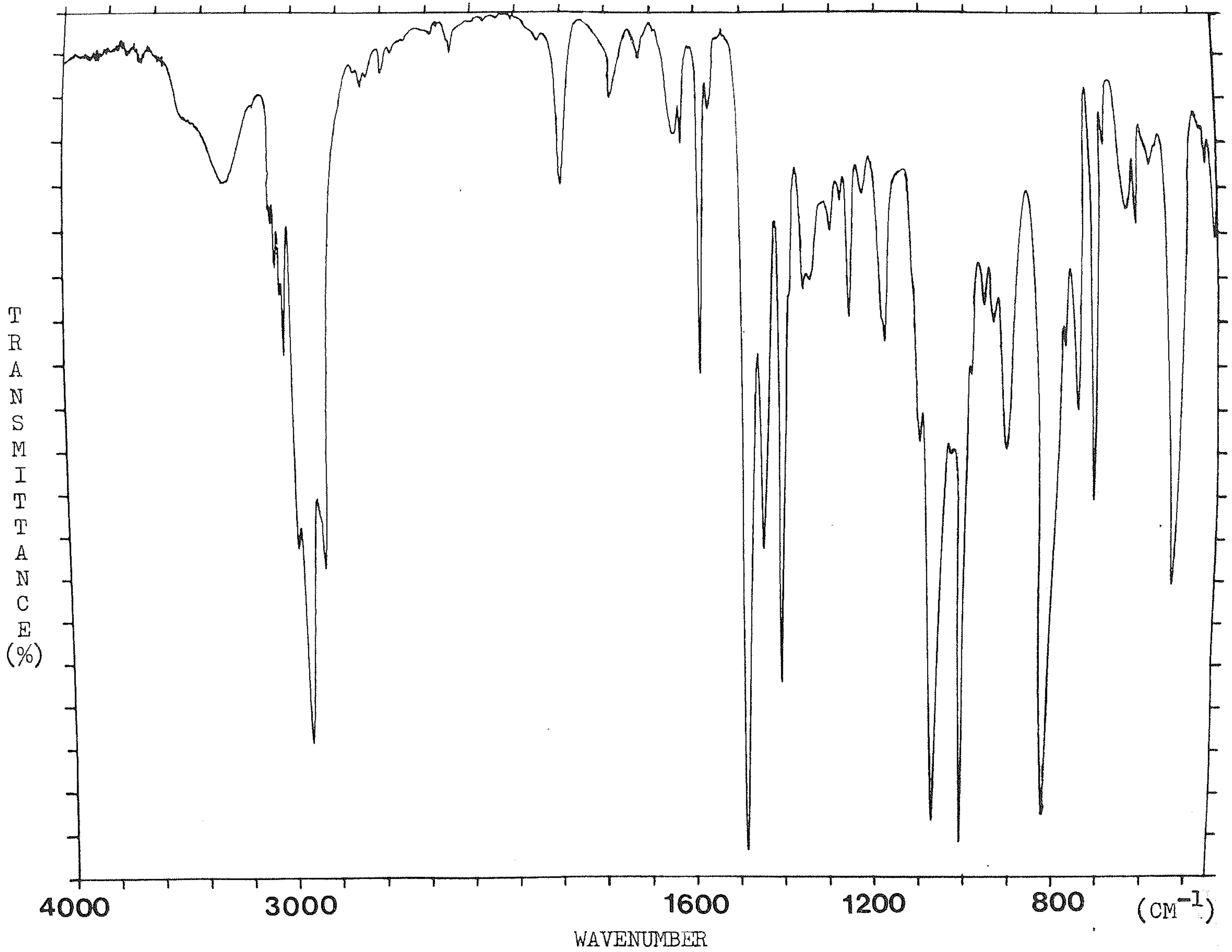


Figure 4.2

added to 25ml of toluene.

On completion of polymerisation the polymer was precipitated by pouring the reaction mixture into methanol. The polymer was then dried under vacuum and purified by dissolving in THF; the solution was then added to a stirred methanol solution to produce a fine polymer precipitate. The polymer was dried once again and weighed. The yield of polymer was seen to be 17.3g.

4.1.5.2.3. Analysis of the polymer

The polymer sample was analysed by FT IR, NMR and GPC.

IR analysis

The polymer sample was analysed as a film cast from a solution of the polymer in THF. The spectrum obtained is shown in figure 4.2

On comparison of the spectrum of the polymer with that of the monomer the most notable change is the disappearance of absorbances at 988cm^{-1} and 1630cm^{-1} due to the $CH=CH_2$ group. There is also a sharp reduction in intensity of bands at 913cm^{-1} and 3089cm^{-1}, also due to alkene groups. In addition bands at 1450cm^{-1}, 1486cm^{-1}, 2853cm^{-1} and 2927cm^{-1} which are due to saturated CH and CH_2 groups have increased in intensity.

Thus all the evidence suggests the disappearance of the $CH=CH_2$ group and an increase in the amount of saturated CH and CH_2 groups which one would expect in a successful addition

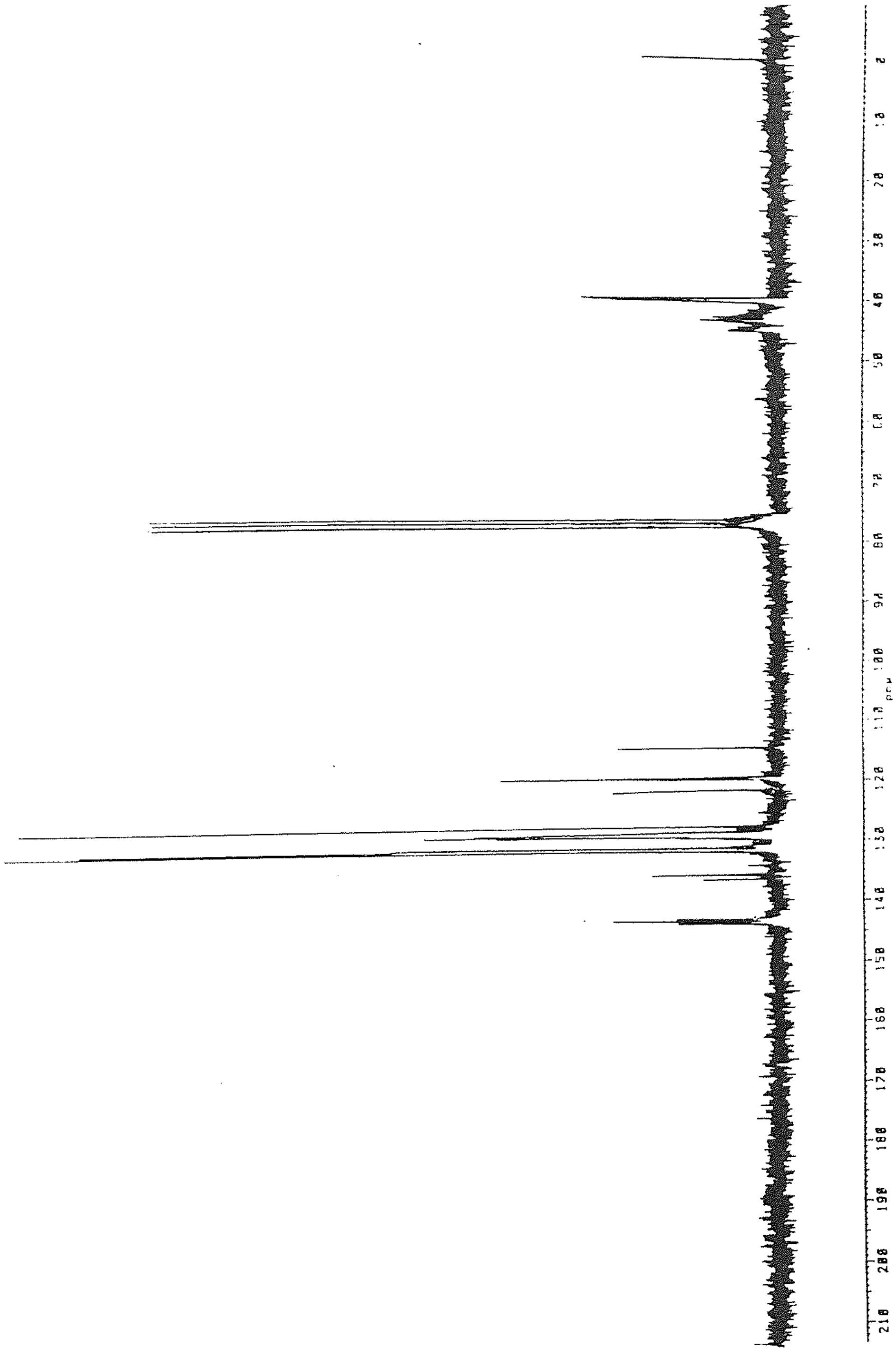
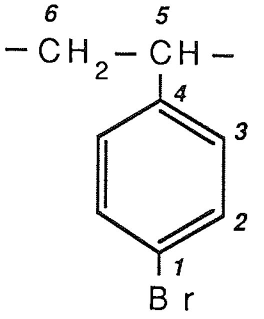

0
10
20
30
40
50
60
70
80
90
100
110
ppm
120
130
140
150
160
170
180
190
200
210

Figure 4.3

polymerisation reaction.

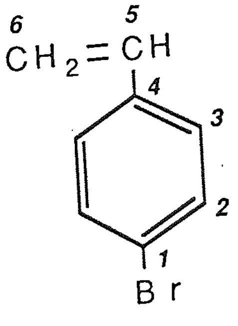
NMR analysis

The polymer sample was analysed as a solution in $CDCl_3$ solvent. The spectrum obtained is shown in figure 4.3. ^{13}C NMR was used to detect the number of non-equivalent carbon atoms in the sample. The polymer can be written as follows:



The non-equivalent carbon atoms are numbered. Both the expected and the obtained chemical shift values for each of these carbon atoms are shown in table (A) in appendix 1.

The polymer produced may, however, also have contained some unpolymerised p-bromostyrene monomer. The monomer is represented as:



The non equivalent carbon atoms are again numbered and both the obtained and expected chemical shifts for these carbon atoms are shown in table (B) in appendix 1.

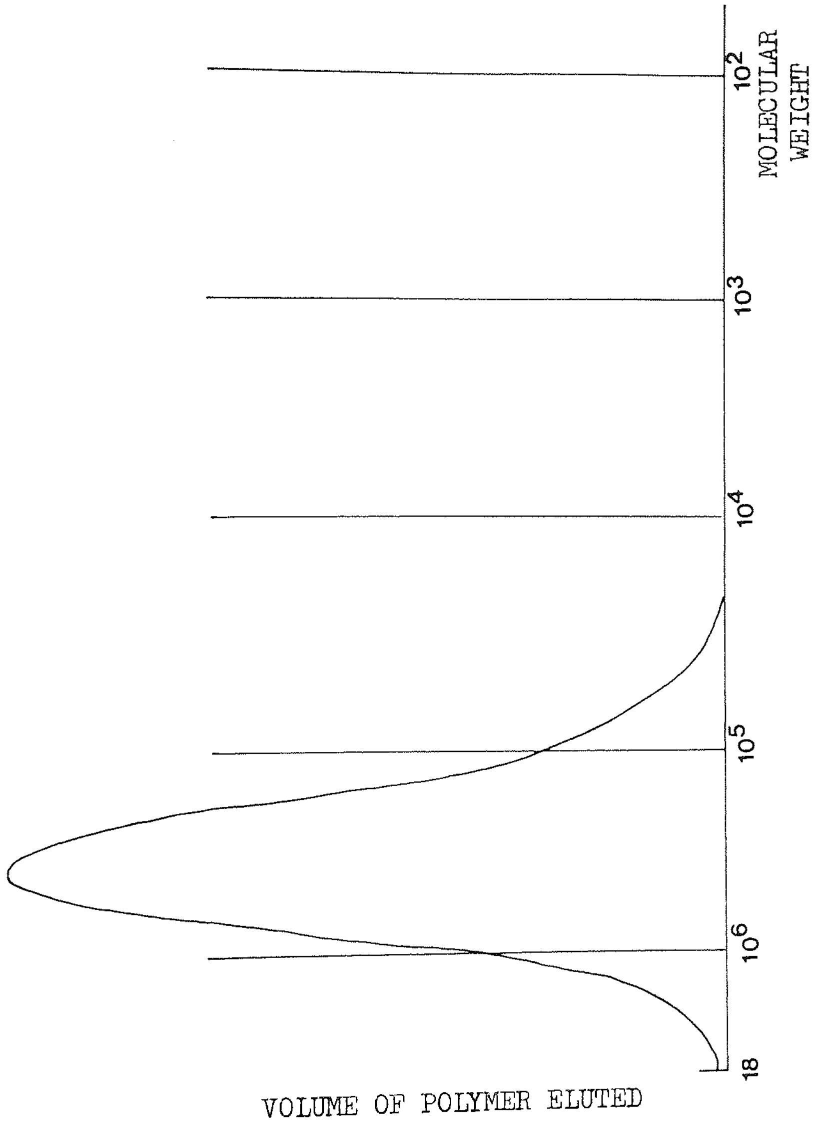

MOLECULAR WEIGHT
10^2
10^3
10^4
10^5
10^6
18
VOLUME OF POLYMER ELUTED

Figure 4.4.

Analysis of the NMR spectrum obtained confirms the presence of unreacted p-bromostyrene monomer in the polymer sample as shown by absorbances at 115 and 136 δ.

The chemical shift at 143 δ shows some evidence for the polymer being an atactic material since the absorbance here is a triplet, corresponding to isotactic, syndiotactic and atactic triads.

GPC analysis

The polymer sample was analysed as a 2% solution in THF. The chromatogram obtained is shown in figure 4.4.

Analysis of the chromatogram showed the polymer to have a number average molecular weight ($\bar{M}_n$) of 261000 and a weight average molecular weight ($\bar{M}_w$) of 419000. The polydispersity ($\bar{M}_w/\bar{M}_n$) of the material was determined as 1.6 which one would expect of a free radically produced polymer when only termination occurs.

4.1.5.3. Grignard formation and carboxylation

Poly(bromostyrene) was converted to the corresponding Grignard compound as described in section 2.8.1.1. In a typical reaction system lg of polymer dissolved in 20ml of THF and lg of 1,2,dibromoethane were added to 0.4g of magnesium turnings contained in 20ml of THF. Once Grignard formation was complete the reaction mixture was poured into a slurry of solid carbon dioxide in THF; an excess of solid CO_2 was used in order to prevent side reactions. Once effervescence had ceased 25ml

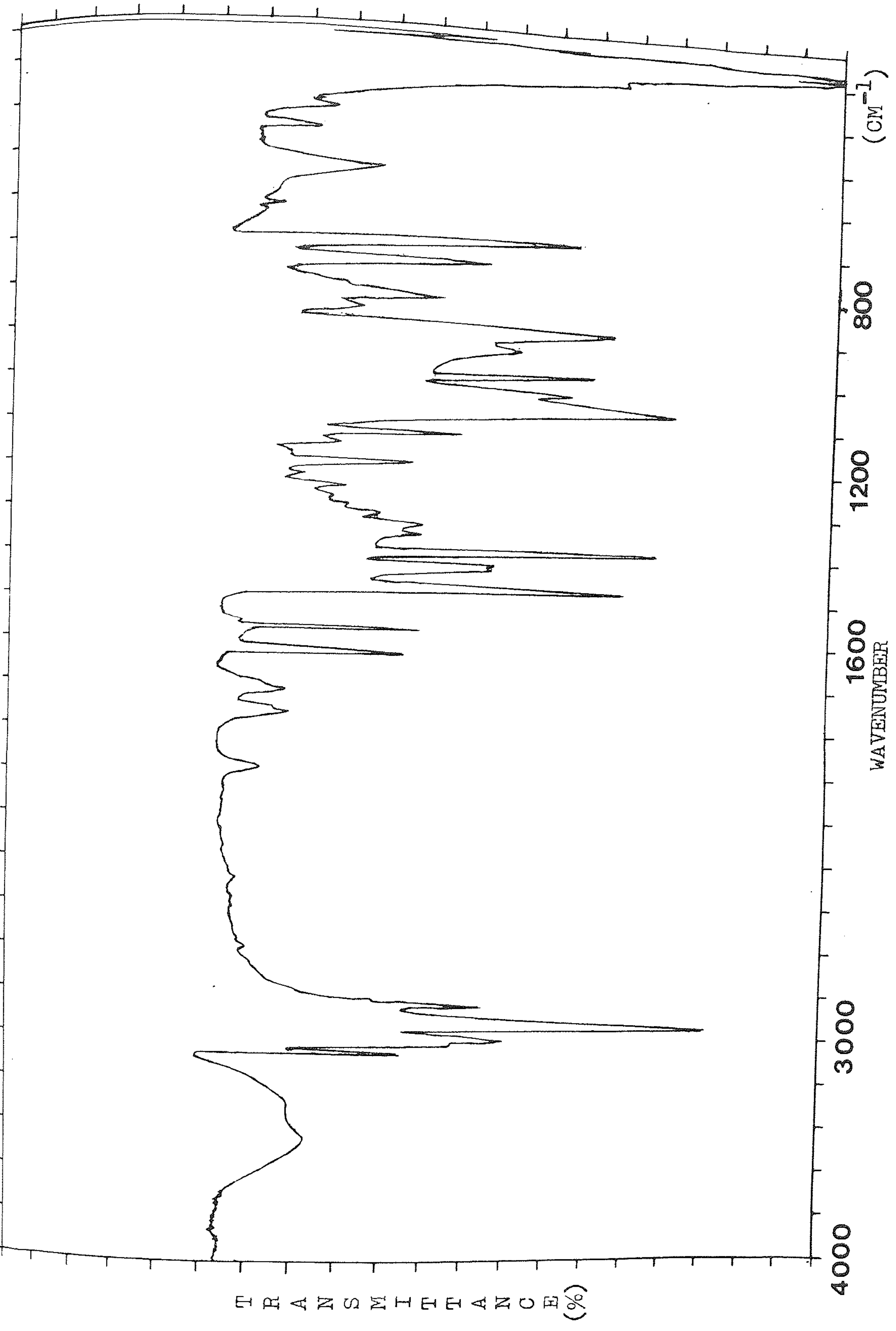


Figure 4.5

of IM hydrochloric acid, diluted with 25ml of THF, were added to remove any excess magnesium. The polymer product was precipitated by pouring the reaction mixture into an excess of methanol. The polymer was then dried under vacuum and purified by dissolving in THF and reprecipitating into methanol.

4.1.5.3.1. Analysis of the product

The polymer product was analysed by FT IR, NMR, and GPC.

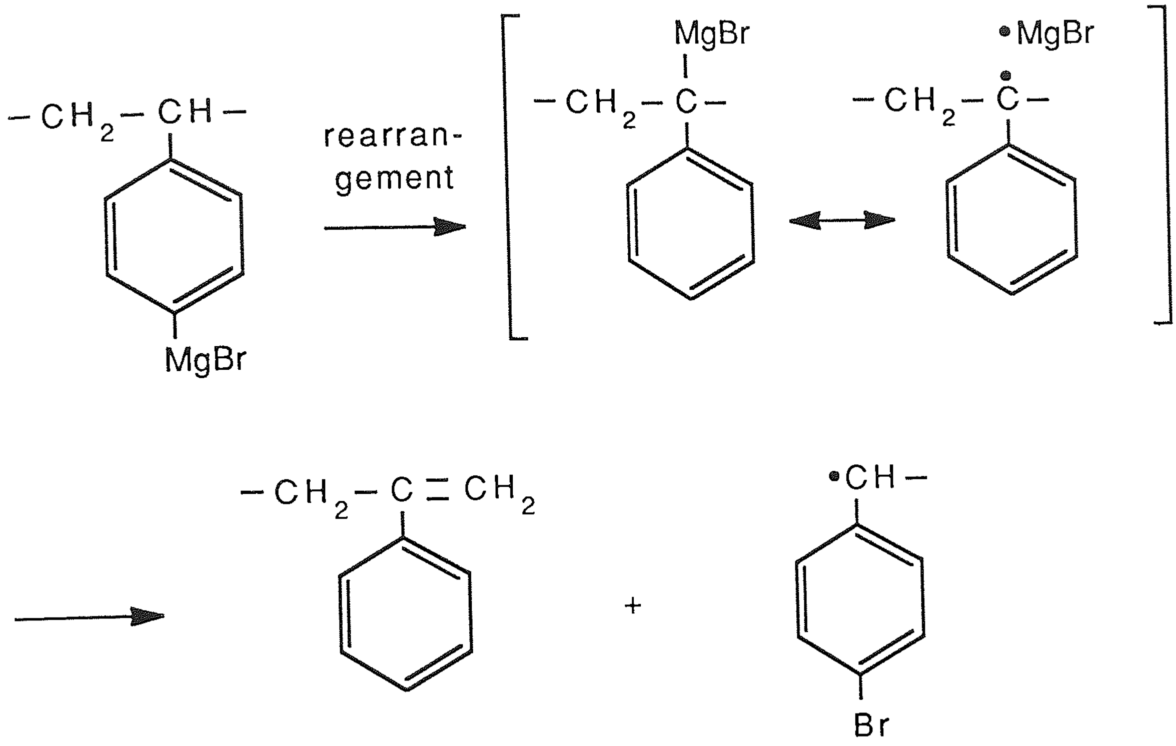
IR analysis

The polymer was analysed by IR as a film cast from a THF solution onto sodium chloride plates. The spectrum obtained is shown in figure 4.5.

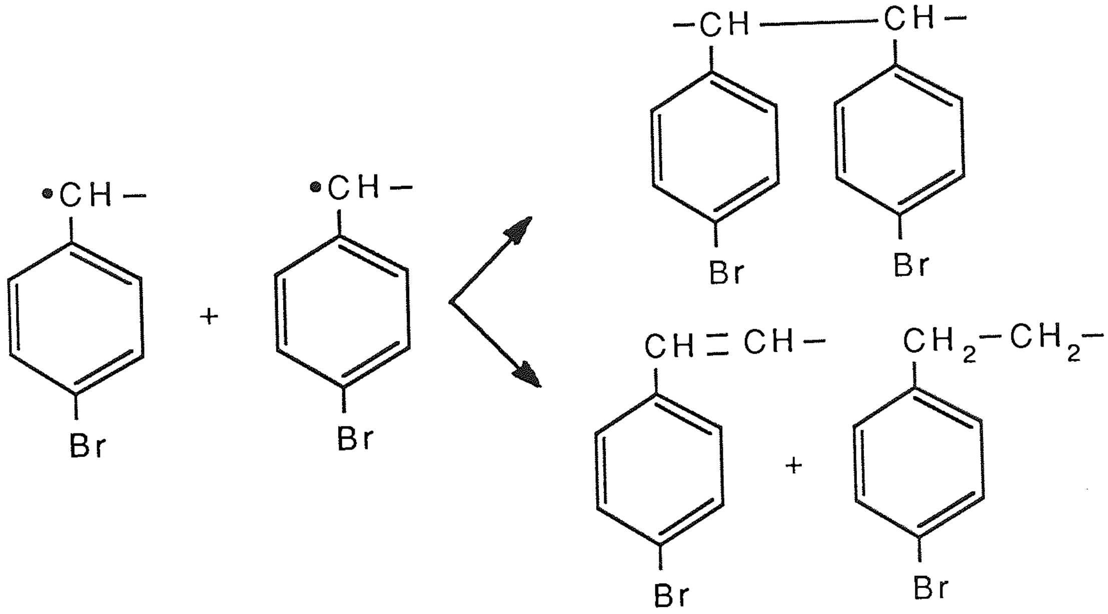
A comparison of the spectrum of the product with the spectrum of poly(bromostyrene) shows some interesting changes. The most notable change is the appearance of a band at 889cm^{-1} due to the $>C=CH_2$ group. Furthermore, there are other bands at 1391cm^{-1}, 1629cm^{-1}, and 3077cm^{-1} which are characteristic of alkene groups. In addition, there is a reduction in the intensity of the band at 2850cm^{-1} due to saturated CH groups, of the band attributed to a para-disubstituted benzene ring at 825cm^{-1} and of that due to the C-Br group at 545 cm^{-1}.

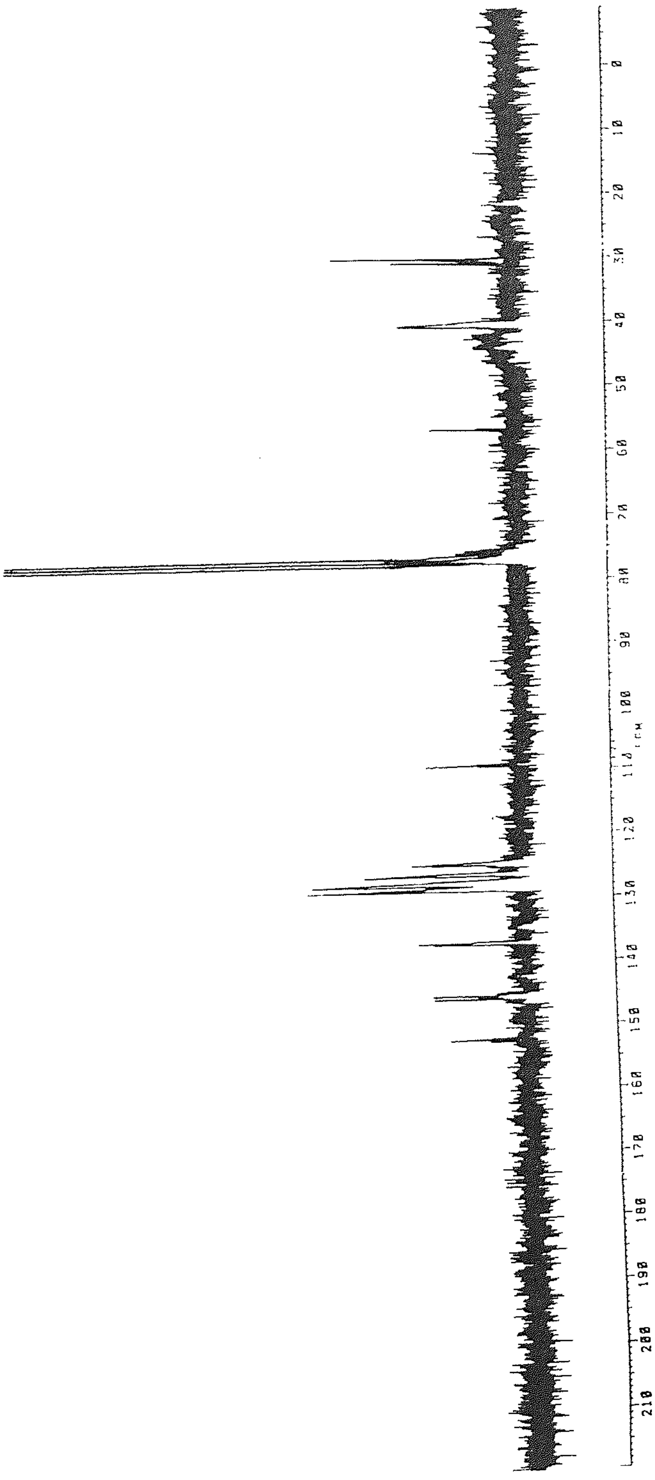
Such changes in the spectrum suggest the formation of an alkene group commensurate with the loss of the bromine atom at the para position. Such facts can be accounted for by the occurrence of the series of reactions shown in figure 4.6.

Figure 4.6



Then :

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PPM
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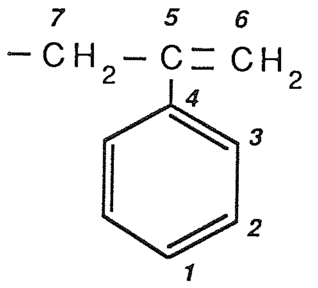
210

Figure 4.7

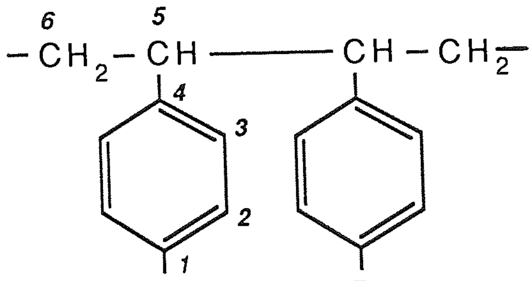
NMR analysis

The polymer sample was analysed by NMR as a solution in $CDCl_3$ solvent.

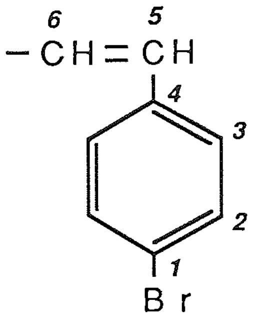
Assuming chain scission did occur by the pathway shown in figure 4.6 the expected products are shown below:



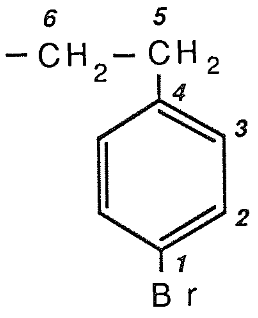
(A)



(B)



(C)



(D)

The non-equivalent carbon atoms are numbered in each product. Both the expected and obtained chemical shift values for these carbon atoms are shown in tables (C) (D) (E) (F) respectively in appendix 1.

On comparison of the NMR spectrum of the product with that of poly(bromostyrene) it is seen that chemical shifts at 30δ and 31δ appear in the product spectrum; these shifts could be due to a CH_2 group at the end of a polymer chain as shown in product (D). The appearance of these absorbances is indicative of an increased number of CH_2 end groups.

In addition the chemical shift at 57δ seems to correlate well with an expected shift of 56δ due to the backbone CH_2 in product (A) and 54δ due to the backbone CH group in product (B).

Furthermore, evidence for the formation of product (A) is provided by the chemical shifts at 109δ and 152δ which can be attributed to terminal alkene groups in product (A).

Thus, in conclusion,all the evidence points towards the occurrence of chain scission. Chemical shifts of the product correlate comparatively well with those expected of product (A) which is one of the major products formed by rearrangement and chain scission. There is also evidence that there was some formation of products (B) (C) and (D) due to the presence of absorbances which could be due to certain atoms in these products. There is particular evidence for the formation of product (D) by the bands at 30 and 31δ. Again this fact supports chain scission; an increased number of shorter chains having CH_2 end groups are produced by a disproportionation mechanism of one of the products of rearrangement and chain scission.

Therefore NMR evidence correlates well with IR evidence in favour of rearrangement and chain scission by the mechanism shown in figure 4.6.

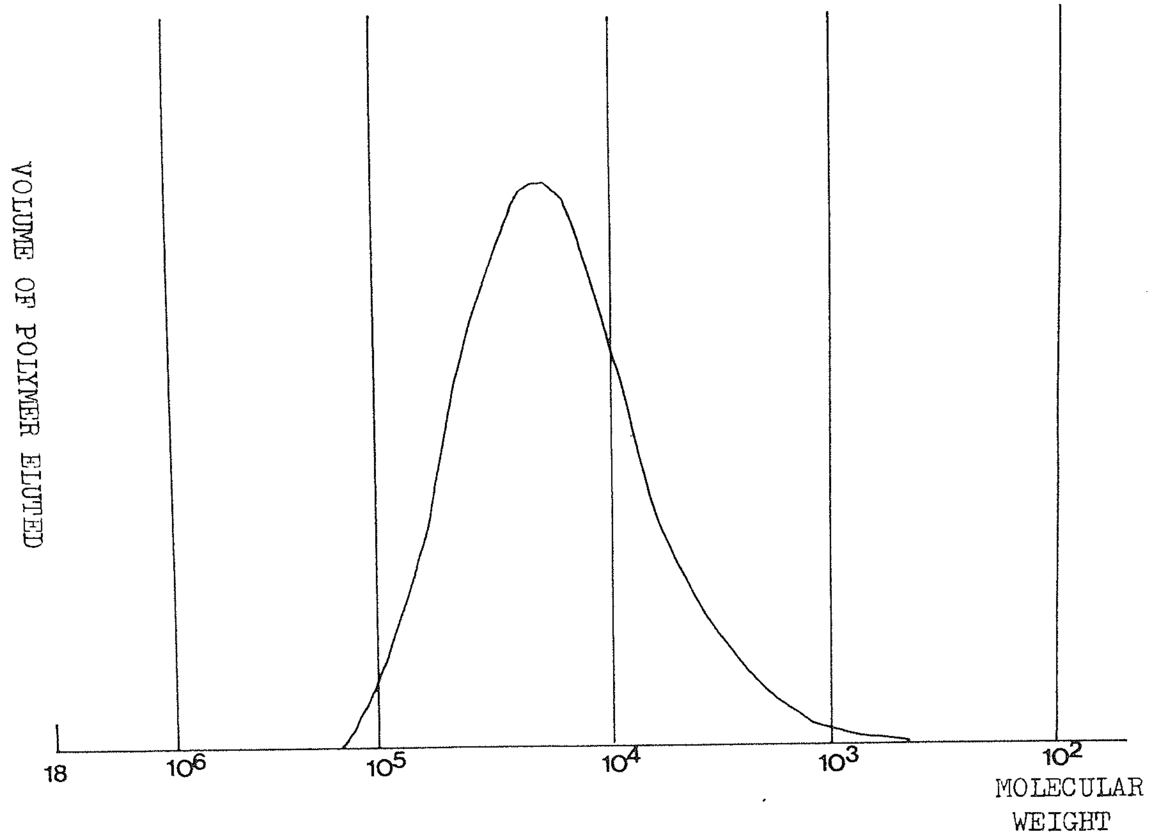

VOLUME OF POLYMER ELUTED
18
10^6
10^5
10^4
10^3
10^2
MOLECULAR WEIGHT

Figure 4.8

the product by GPC, NMR and IR. This does, however, serve to illustrate that the chain scission mechanism was independent of the activating agent (iodine or 1,2,dibromoethane) employed.

4.2 Lithiation

Lithiation may be defined as the creation of organometallic compounds containing lithium, in particular compounds that contain a carbon-metal bond. Such organometallics are characterised by the fact that the carbon-lithium bond may be purely ionic if a strong electron donor is present in the system, or substantially covalent if this is absent.

Lithiation of organic compounds may be effected by three principal routes

(i) the reaction of the compound with metallic lithium

(ii) the reaction of the compound with butyllithium; in some cases a complexing base, such as N,N,N',N'-tetramethylethylenediamine (TMEDA) or potassium t-butoxide is present

(or)

(iii) the reaction of the compound with lithium amides.

The substrate to be lithiated may either contain a carbon-halogen bond or possess a "labile" hydrogen atom. In the former case the reaction is similar to the formation of a Grignard reagent by the reaction of an alkyl or aryl halide with magnesium. In the case of lithiation reactions using metallic lithium there is some evidence to suggest that a trace of metallic mercury acts as a catalyst for the reaction. When an organic compound with a labile hydrogen is reacted with butyllithium, then the reaction is more closely related to the reaction between an acid and a base

$$\mathrm{R{-}H} + \mathrm{Bu}^{-}\,{}^{+}\mathrm{Li} \longrightarrow \mathrm{R{-}Li} + \mathrm{BuH}$$

The ease with which this proton is displaced will be determined by:

(i) the acidity of the proton undergoing reaction which will be related to,

(ii) the stability of the product anion compared to the stability of the reacting butyl anion.

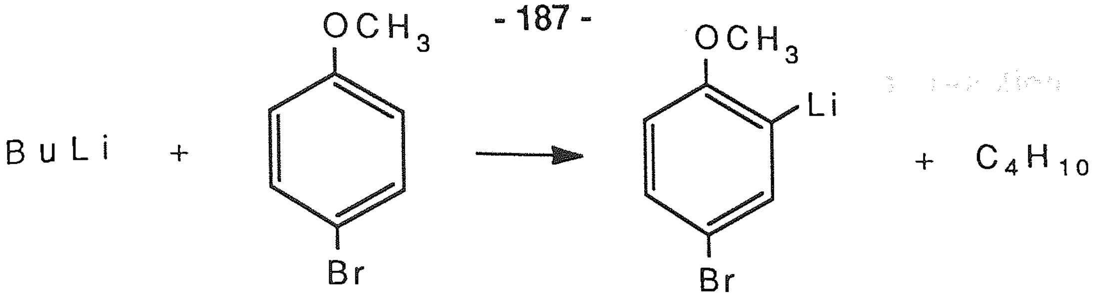
These interrelated factors will depend upon the parts played by steric and electronic, inductive and resonance effects. Those effects that lead to a more stable anion than the butyl anion will promote lithiation reactions. These factors will now be reviewed in some detail.

4.2.1. Hydrogen - lithium exchange

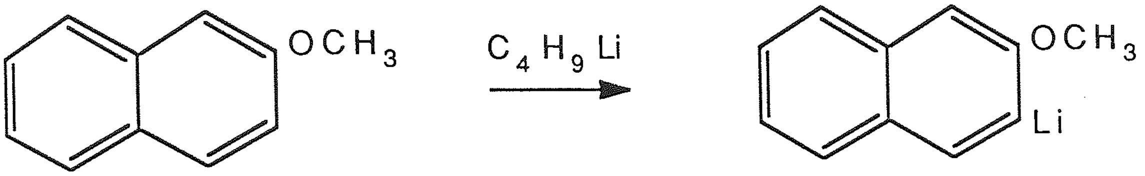
4.2.1.1. Lithiation by metal alkyls

4.2.1.1.1. Metallation of the benzene ring

There are a number of reports of reactions where lithium-hydrogen exchange occurs involving the hydrogen atom on a benzene ring; m- and p-brominated anisoles have been observed to undergo hydrogen-lithium exchange, in some cases in preference to halogen-metal exchange, when butyllithium is used as a metallating agent [58]

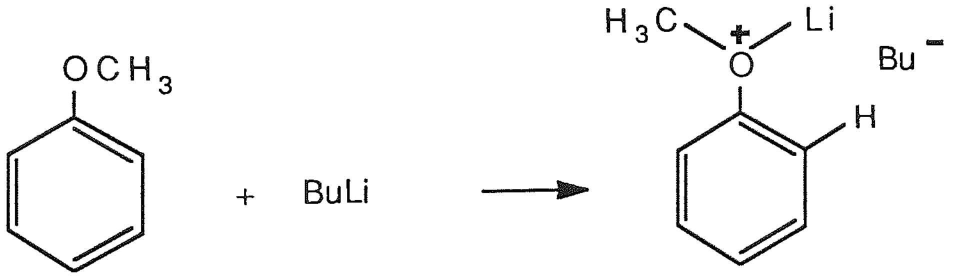


Another example is the lithiation of 2-methoxynaphthalene [59]

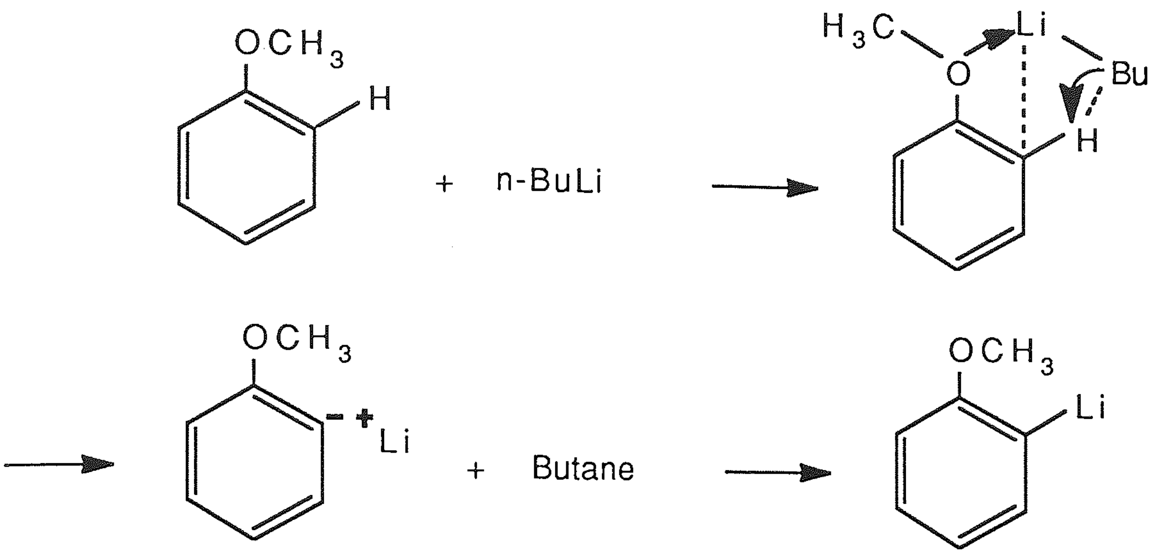


In such reactions ortho metallation is generally observed.

It is possible that a "protophilic" substitution is involved; the carbanionic portion of the organo-metallic reagent behaves as a nucleophile and attacks the most acidic hydrogen [60]. If one of the lone pairs of electrons on the oxygen atom coordinates with lithium, the carbon-lithium bond will be heterolytically cleaved and the lithium will coordinate as a lithium cation



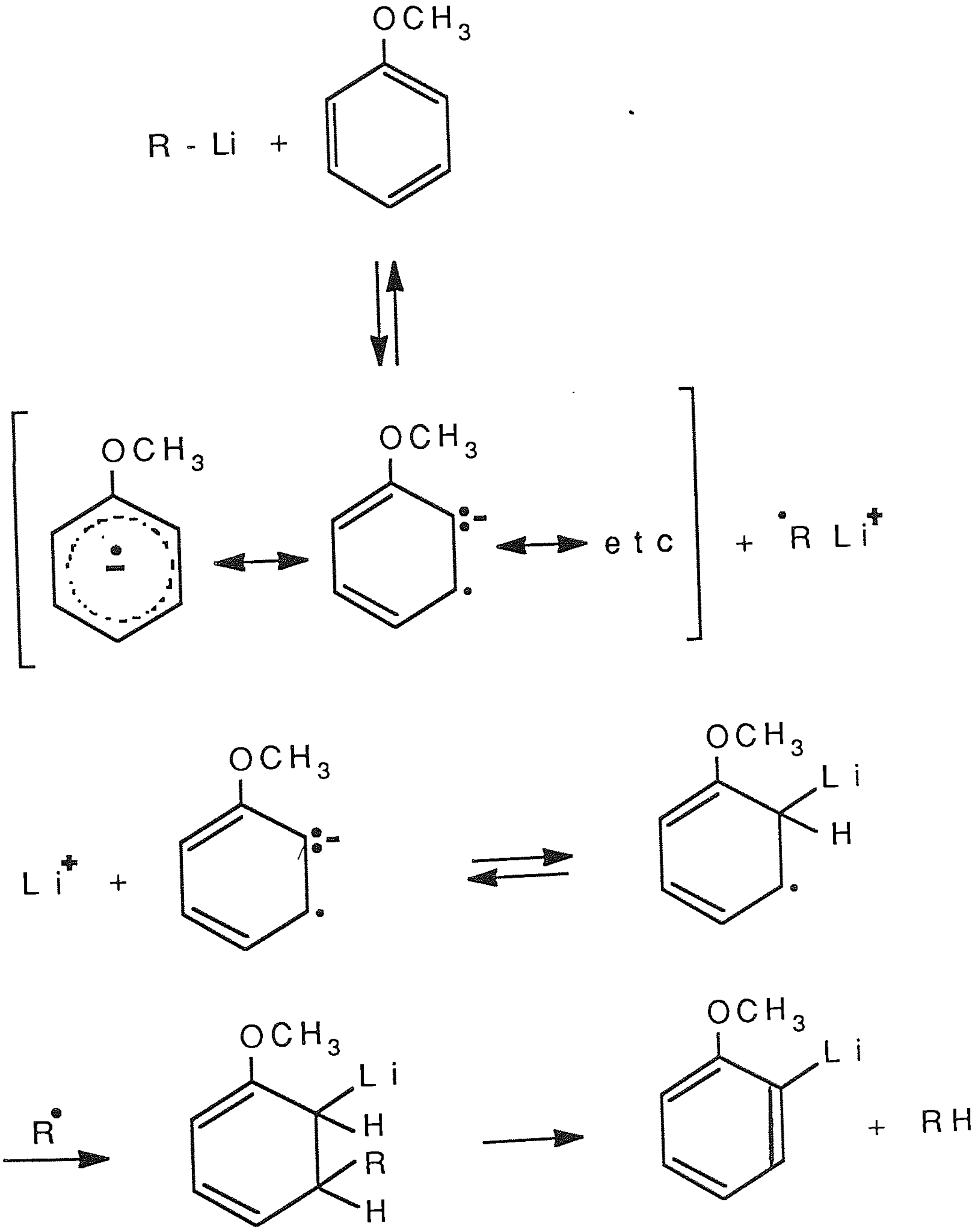
The complex is most likely to be present as a close contact ion pair with the butyl anion held in close proximity to the ortho-hydrogen atom of the benzene ring. This ortho hydrogen is now much more acidic than in neutral methoxybenzene (anisole) because the complexed methoxy group is electron withdrawing due to the fact that the lone pair coordinated to the lithium is unavailable for interaction with the ring π system [55(b), 59, 60]. The butyl anion thus removes the acidic ortho-hydrogen and the lithium cation migrates towards the resulting area of high electron density. The reaction is summarised as follows:



In this case the methoxy group has activated the ring towards metallation whereas the ring protons in benzene are not usually susceptible to abstraction by the butyl group.

Alternatively the reaction mechanism may be regarded as primarily electrophilic attack by the lithium cation. For example in the case of metallation of benzotrifluoride the start of the process is considered to be the attraction of the metal component for electrons. If such electrons are found on one of the three fluorine atoms coordination occurs and the succeeding migration of a proton and metal lead to ortho substitution; if the electrons are found in the aromatic nucleus, direct substitution occurs at the meta position because of the influence of the trifluoromethyl group. Such places of high electron density are attacked in the ratio of about five to one which accounts for the observed ratio of reaction products[61] of 5 parts ortho-metallation to one part meta-substitution.

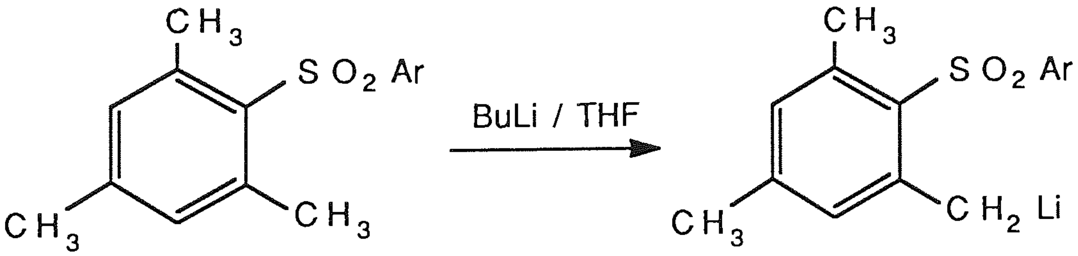
To account for the steric insensitivity of the reaction of alkyllithium reagents with substrates possessing bulky substituents such as $OCMe_3$ another mechanism was proposed involving a one electron transfer from the carbanion portion of the substrate forming a radical anion intermediate [56(b), 62].



The greater concentration of the ortho isomer found on analysis of the product distribution between isomeric forms was explained by the fact that there is additional stability afforded by the opportunity for chelation of the lithium atom with adjacent atoms (oxygen in this case).

4.2.1.1.2. Benzene ring substituent metallation

In addition to phenyl protons being replaced under some circumstances in metallation reactions, metallation has also been observed in the ∝ position of substituent groups. In some cases the protons in the ∝ position are activated towards metallation if the substituent is o- or p- to an electron withdrawing group, such as in the case of the metallation of the misitylene derivative: 55(b).



Such side chain metallation was first performed on toluene in ether solution using butyllithium, but the degree of metallation was low. 63. However, lithium-hydrogen exchange was found to be more effective using THF as a solvent and an excess of butyllithium 63. Nevertheless, metallation of toluene with alkyllithium compounds was generally unsuccessful until the discovery that tertiary amines such as TMEDA activate alkyllithium compounds in metallation reactions 64. Using such an activator Eberhardt and Butte 65 found that toluene undergoes quantitative metallation to benzyllithium with n-butyllithium. In addition to the rapid formation of

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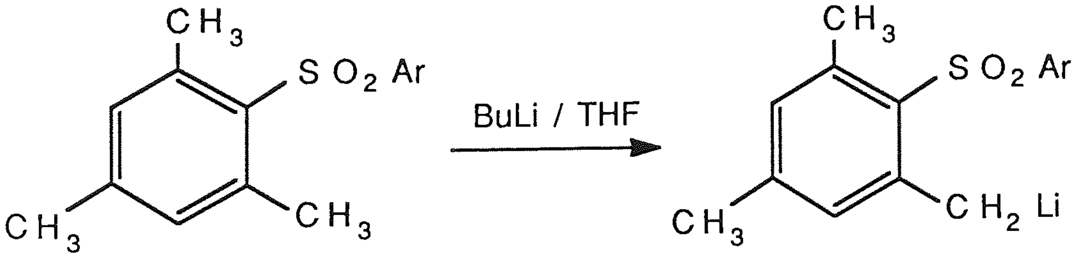
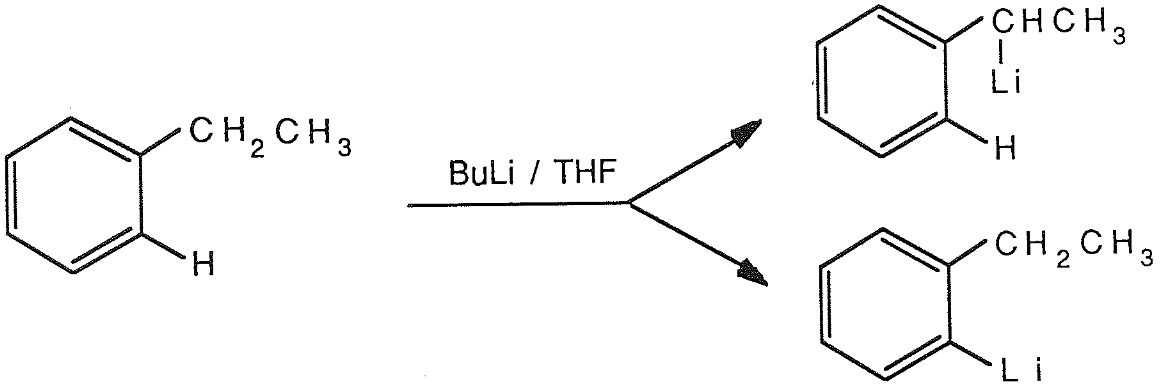


Such side chain metallation was first performed on toluene in ether solution using butyllithium, but the degree of metallation was low. [63]. However, lithium-hydrogen exchange was found to be more effective using THF as a solvent and an excess of butyllithium [63]. Nevertheless, metallation of toluene with alkyllithium compounds was generally unsuccessful until the discovery that tertiary amines such as TMEDA activate alkyllithium compounds in metallation reactions [64]. Using such an activator Eberhardt and Butte [65] found that toluene undergoes quantitative metallation to benzyllithium with n-butyllithium. In addition to the rapid formation of benzyllithium some evidence for ring metallation as a slower side reaction was put forward. [64, 66].

Work has been carried out on the effects of substitution at the benzylic carbon atom on the rate of metallation at this position. It was found that as the number of methyl groups at the benzylic carbon atom was increased the rate of side chain metallation was reduced so that reaction at ring protons became more significant.

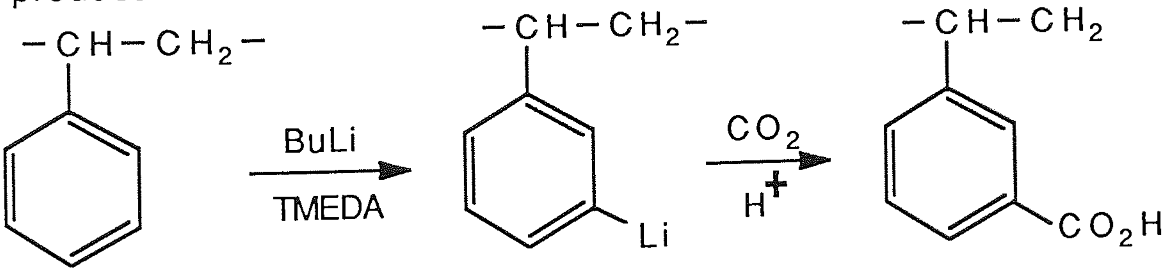


This can be explained on the basis that metallation proceeds via competitive proton abstraction leading to carbanionic transition states. In the case of ethylbenzene attack at the benzylic position is counteracted by the inductive effect of the methyl group leading to increased substitution at ring sites. In conclusion, evidence supports a mechanism involving nucleophilic attack, resulting in proton abstraction producing a carbanion intermediate, which in the case of the benzyl anion is delocalised by resonance [67].

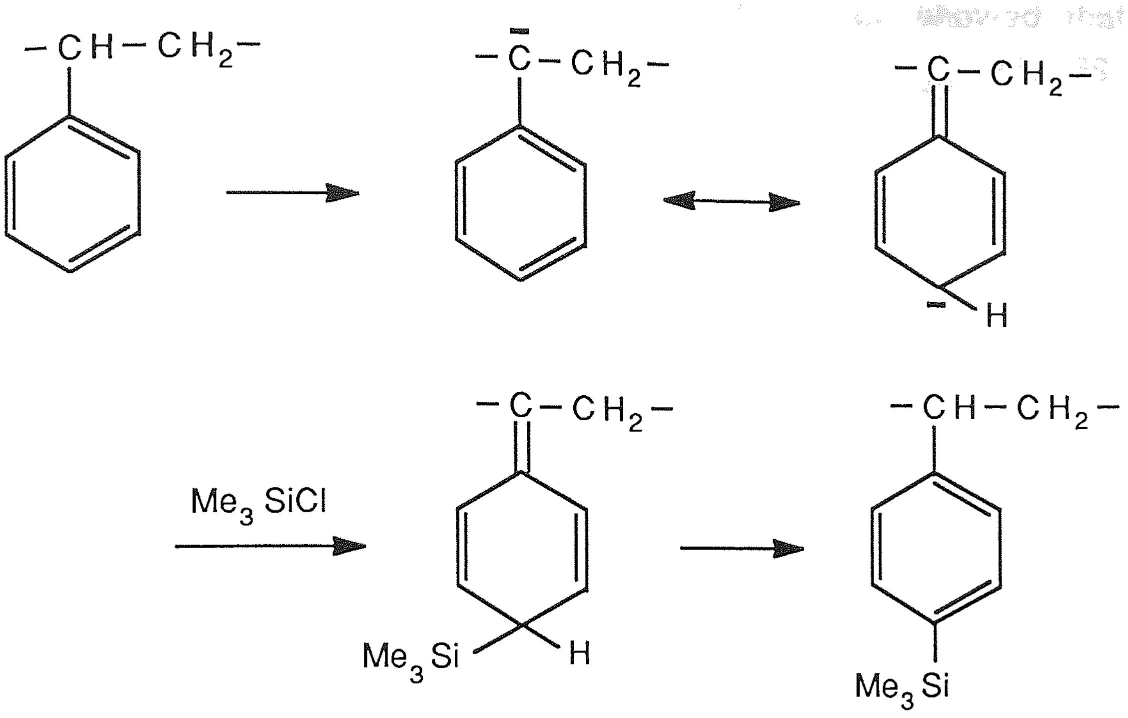
4.2.1.1.3. Metallation in polymer systems

Metallated polystyrene was first prepared by the reaction of halogenated polystyrene with alkali metals [68]. However, this method had a disadvantage in that there was a possibility of the occurrence of crosslinking by reaction between metallated and halogenated sites. This disadvantage is obviated if a non halogen containing polymer can be directly metallated with metal alkyls.

The direct metallation of polymers requires fairly acidic protons activated by a neighbouring electronegative group which itself is often reactive. Poly(phenylene ethers) can be metallated directly with butyllithium in THF without side reactions [68]. It was also found that polystyrene could be successfully lithiated using n-butyllithium activated by TMEDA[26, 69]. On analysis of the product by IR the metallation reaction was thought to involve metal-hydrogen exchange of the metahydrogen atom of the polystyrene since subsequent reaction with carbon dioxide led to the meta substituted product[26, 69].



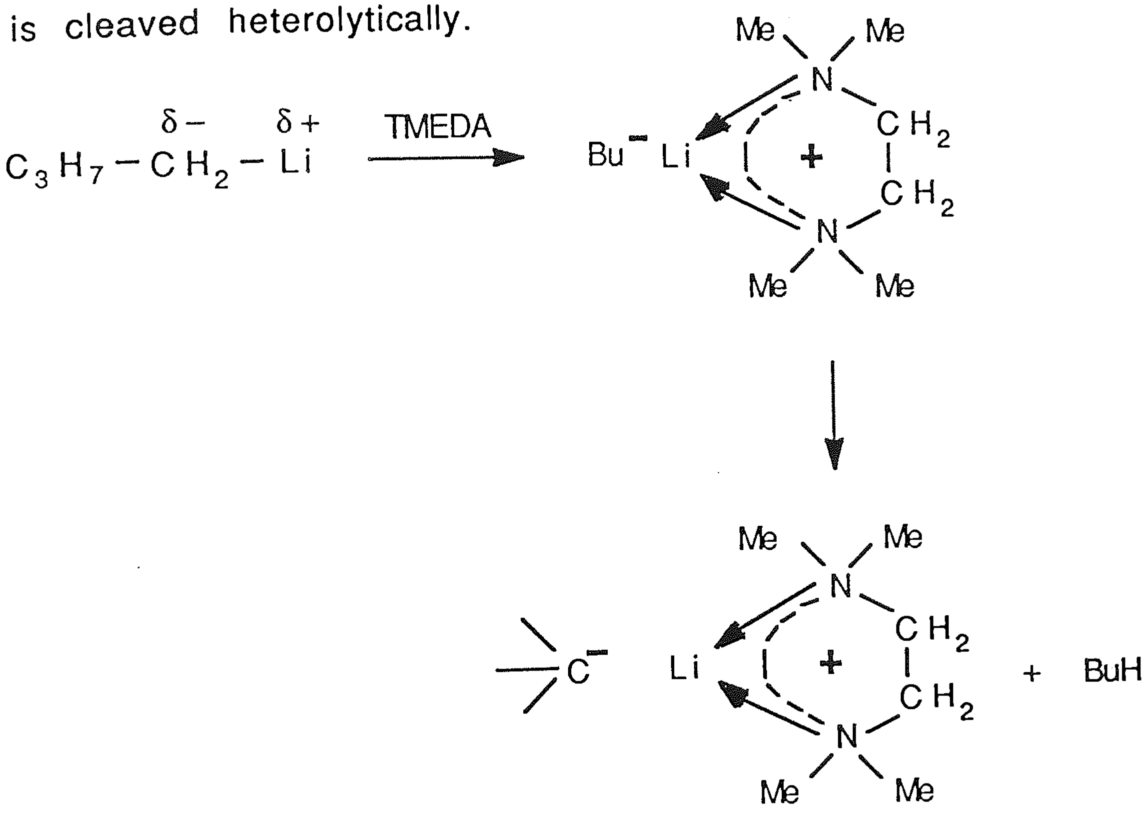
However, Chalk showed that ring substituted products could be obtained if the metallation occurred at the benzylic hydrogen, the most reactive position. The sequence of reactions involved addition followed by rearrangement to regenerate the benzene ring.



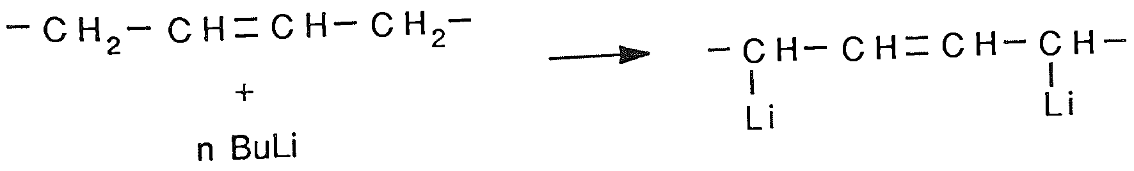
In addition to this product a substantial degree of substitution took place at the benzylic position.

However, other NMR studies suggest that polystyrene is metallated in the meta and para ring postitions with no detectable metallation at the ortho position or at the α carbon. For polystyrene in cyclohexane the coil geometry must be such that the α carbon is not accessible to the bulky n-BuLi/TMEDA complex [71]. Further evidence to support this idea is provided by the lithiation of polystyrene using sec Buli/TMEDA in place of n Buli /TMEDA. It was found by NMR analysis that once again metallation occurred chiefly in the meta and para positions of the aromatic ring with only small amounts of substitution at the α and the ortho position. The extent of lithiation was however higher than that achieved in the metallation reaction with nBuLi/TMEDA [72].

Poly(p-methylstyrene) has also been successfully lithiated using a system of n-BuLi/TMEDA in heptane. IR analysis of the product of carboxylation of the lithiated species showed that sustitution occurred mainly at the methyl group [26, 69]. n-BuLi/TMEDA is commonly used as a metallating reagent for aryl containing polymers. Activation of the butyllithium occurs because the base forms a stable complex with the lithium cation and, even in non-polar solvents, the covalent C-Li bond is cleaved heterolytically.



Other examples of the metallation of polymeric systems include the lithiation of polybutadiene by n-BuLi/TMEDA i.e.

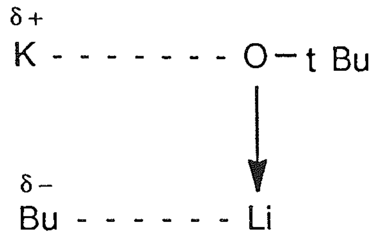


$$-CH_2-CH=CH-CH_2- + n\,BuLi \longrightarrow -\underset{Li}{CH}-CH=CH-\underset{Li}{CH}-$$

The lithium exchange reaction occurs with the allylic hydrogen and does not add to the double bond [73].

Studies have also been made of the alkyllithium initiated anionic polymerisation of butadiene using other activating agents in place of TMEDA. Alkali metal t-butoxides (KBu^tO)

were shown to behave in a similar manner to TMEDA; the rate of polymerisation was increased when either TMEDA or KBu^tO was added. Thus both agents serve to activate the alkyllithium compound. Potassium t-butoxide is a strong base and is known to complex with butyllithium; the following structure has been proposed for this complex [74].

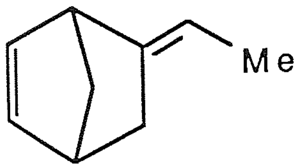


An exchange reaction which proceeds via an intermediate complex has been described [75].

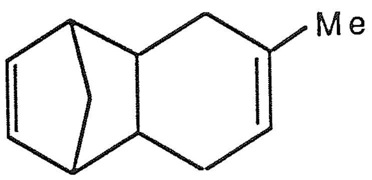
$$\mathrm{t\,Bu\,O\,K} + \mathrm{R\,Li} \longrightarrow \mathrm{R\,K} + \mathrm{t\,Bu\,O\,Li}$$

Hence such potassium alkoxides enhance the reactivity of organolithium compounds by increasing the ionic nature of the C-Li bond on formation of the complex.

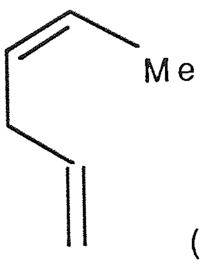
Work has been undertaken using butyllithium activated by KBu^tO to metallate ethylene - propylene terpolymers prepared from ethylidene norbornene (A), endo methylene hexa-hydro-naphthalene (B) and 1-4 hexadiene (C) termonomers[27].



(A)

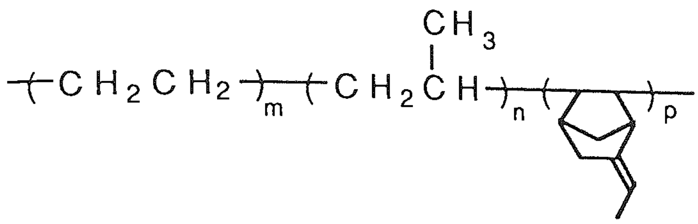


(B)

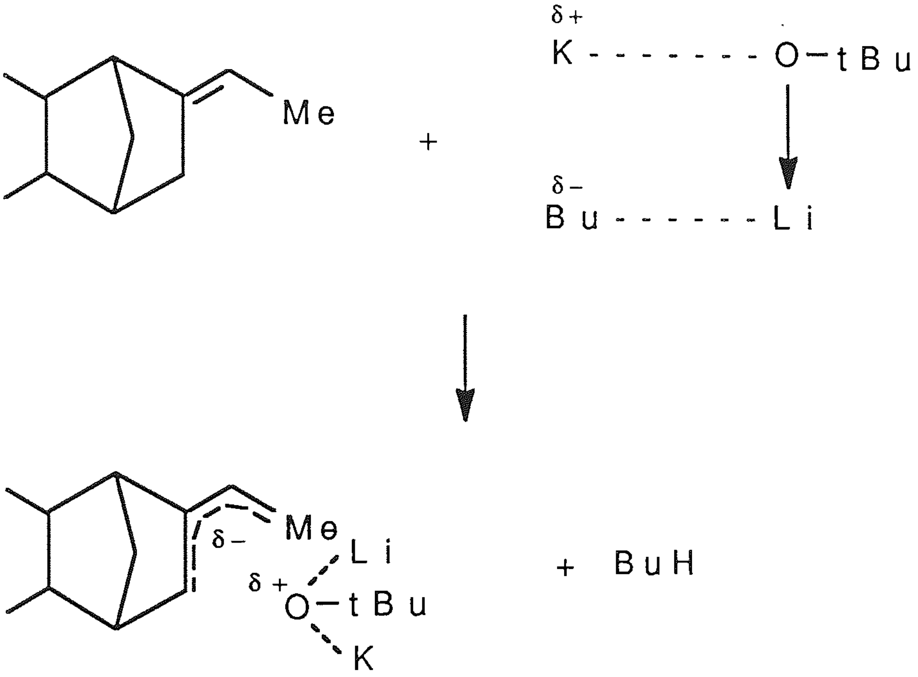


(C)

For example, the terpolymer produced from ethylidene norbornene termonomer may be represented as

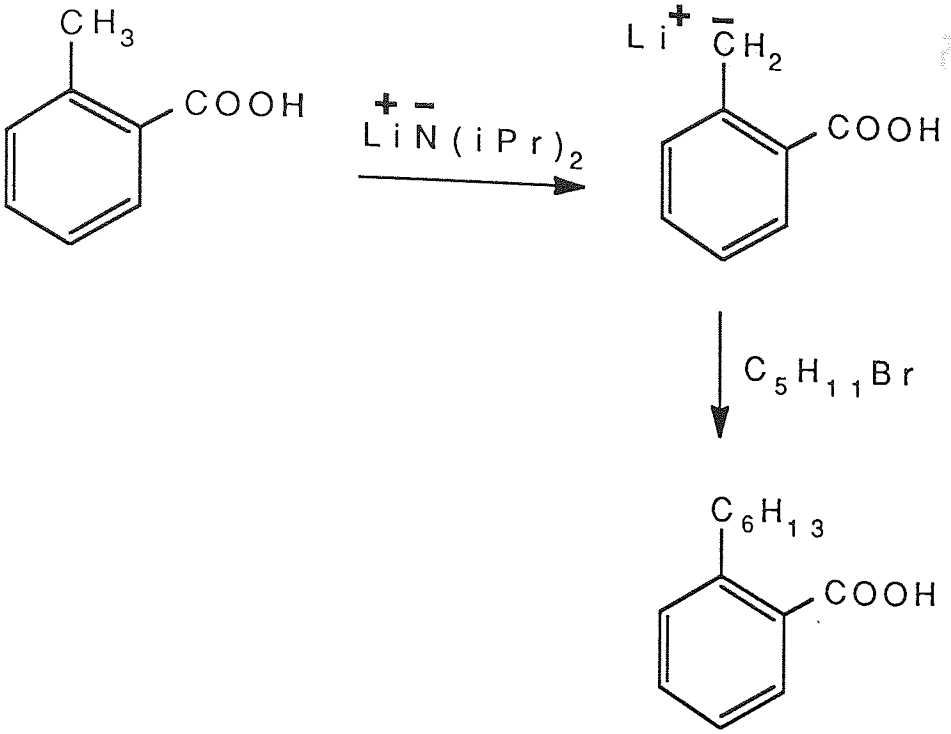


Reaction of the terpolymer with $BuLi/KBu^{t}O$ complex produces a macromolecular metal allyl i.e.



4.2.1.2. Lithiation by lithium amides

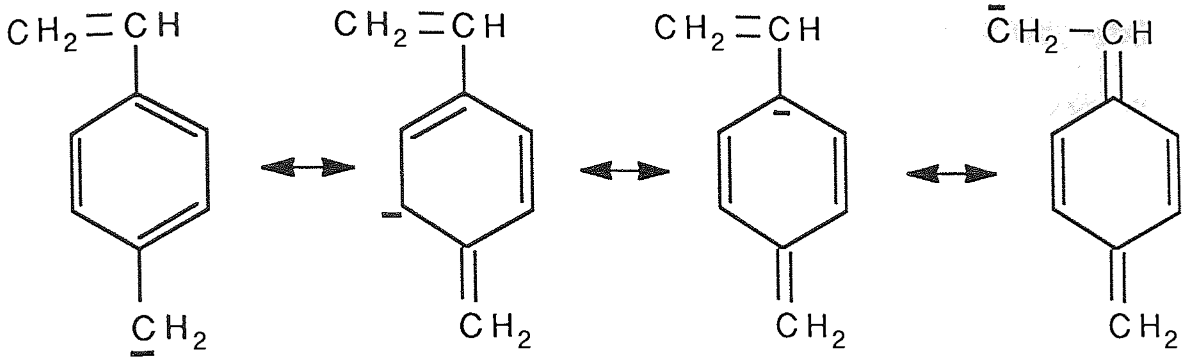
It has long been known that lithium diisopropylamide is a useful reagent for the metallation of organic compounds. For example, the reaction of lithium diisopropylamide with o-toluic acid was reported[76]. The metallation occurred preferentially at the methyl group and reaction of the intermediate with an alkyl halide afforded a route to other long chain substituted benzoic acids. Thus:



Lithium diisopropylamide is a sufficiently strong base to abstract a proton from the methyl group to form a highly delocalised carbanionic intermediate which associates to some degree with diisopropylamine.

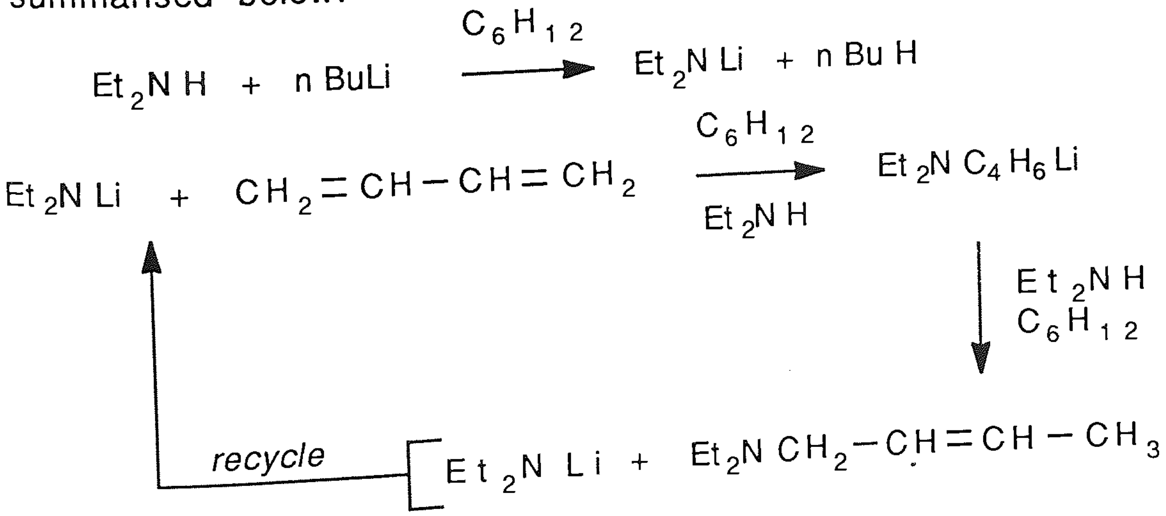
Lithium dialkylamides are produced by the reaction of butyllithium with the appropriate amine which must possess an N-H bond.

The lithium amides can, under certain conditions, add to a carbon-carbon double bond if the bond is part of an extended conjugated system. This aspect of the reactivity of lithium amides will be discussed later. However, because lithium amides are strong bases they can abstract a proton from another molecule, such as 4-methylstyrene. The reaction of lithium diisopropylamide with 4-methylstyrene leads to metallation of the monomer [77, 78] because the anion produced may be stabilised by delocalisation of the negative charge over not only the benzene ring but also the carbon-carbon double bond of the vinyl group.



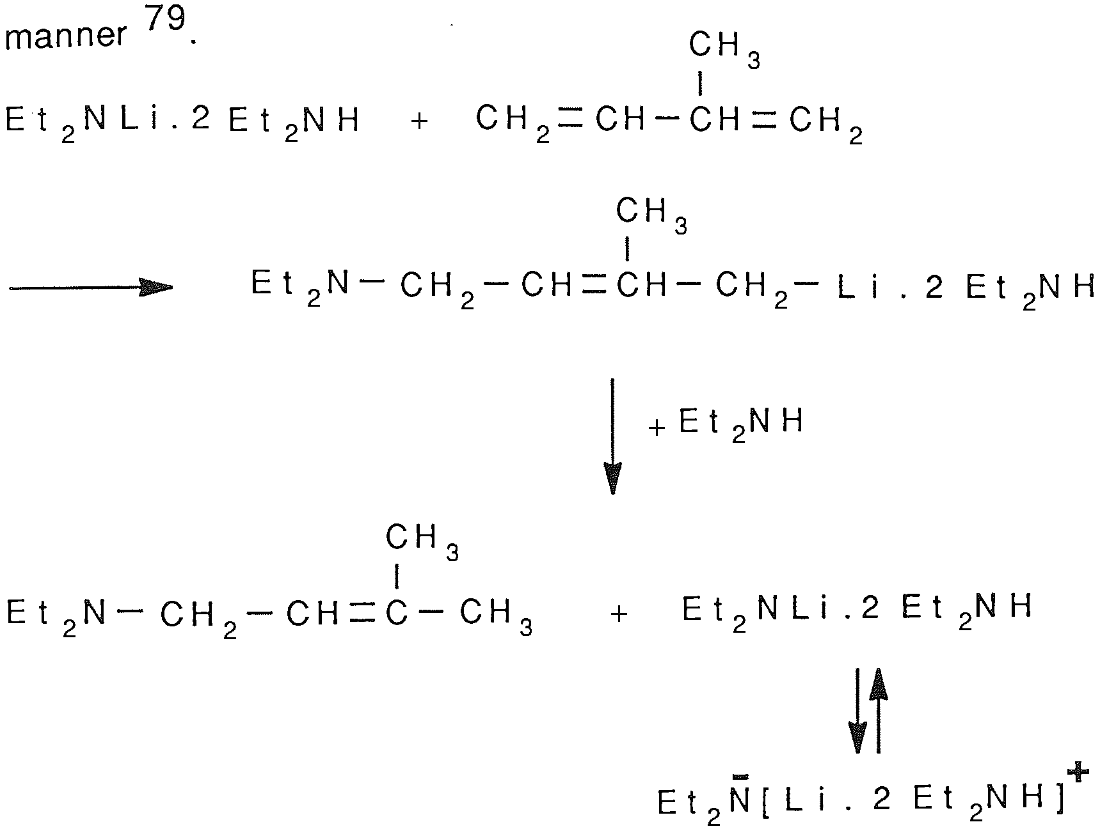
Having generated a charged species with the negative charge delocalised over the carbon-carbon double bond, this species is resistant to further anionic attack and initiation. This type of metallated monomer can then be used as an initiator for the polymerisation of styrene [77] or reacted with a substrate such as chlorotrimethylsilane to form the trimethylsilyl derivative[78].

Metallation reactions are in competition with other reactions that are feasible involving lithium dialkylamides, particularly addition to a carbon-carbon double bond that is part of a conjugated system. Addition reactions of this type are epitomised by the reaction of lithium diethylamide (Et_2NLi) with buta-1,3-diene in the presence of diethylamine (Et_2NH) to produce 1-diethylamino-cis-butene-2. [79, 80]. The reaction is summarised below:



It was found that no addition reaction occurred in the absence of free amine (NH) and it was confirmed by spectroscopic and kinetic studies that a complex formed from Et_2NLi and Et_2NH in a one to two mole ratio was responsible for the stereospecific addition reaction.

The reaction was also carried out using isoprene in place of butadiene and this reaction is thought to proceed in a similar manner[79].



$$Et_2NLi.2Et_2NH + CH_2{=}CH{-}\overset{CH_3}{\overset{|}{CH}}{=}CH_2$$

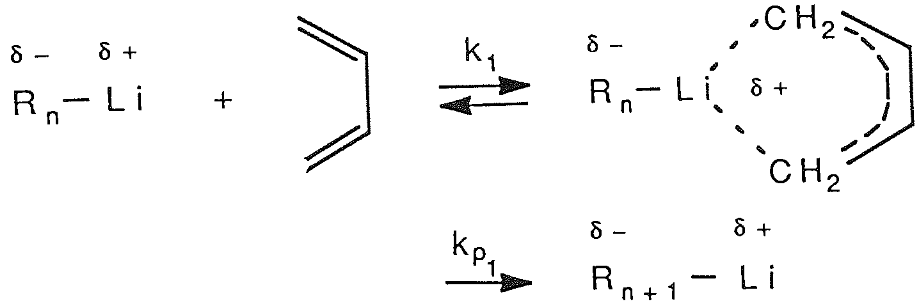
$$\longrightarrow Et_2N{-}CH_2{-}CH{=}\overset{CH_3}{\overset{|}{CH}}{-}CH_2{-}Li.2Et_2NH$$

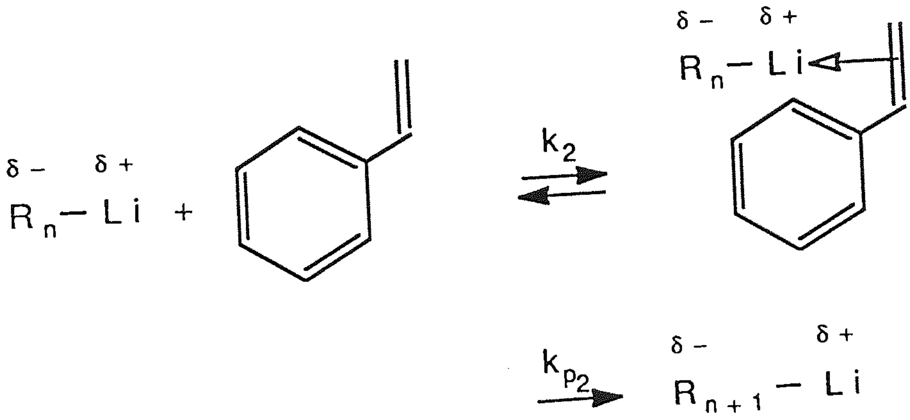
$$\Big\downarrow +Et_2NH$$

$$Et_2N{-}CH_2{-}CH{=}\overset{CH_3}{\overset{|}{C}}{-}CH_3 + Et_2NLi.2Et_2NH \rightleftharpoons Et_2\bar{N}[Li.2Et_2NH]^{+}$$

In order to investigate the character of the amide/amine complex, the reaction of this complex with para substituted styryl derivatives has been investigated[81]. The para substituted styryl derivatives used included p-methylstyrene and p-methoxystyrene. Studies of rate constants of these reactions produced results which are in good agreement with those reported for an anionic reaction system. This provides strong evidence for the polar nature of the amine/amide complex.

The reactivity of lithium diethylamide was also compared with that of alkyllithium by examining the reactivity of styrene toward the lithium amide/amine complex in the presence of butadiene. It is well known that in a styrene - butadiene copolymerisation initiated by alkyllithium in hydrocarbon media, the presence of the diene monomer pronouncedly suppresses the reactivity of styrene although the rate of homopolymerisation of styrene is greater than that of butadiene under similar conditions. It may be postulated therefore that:

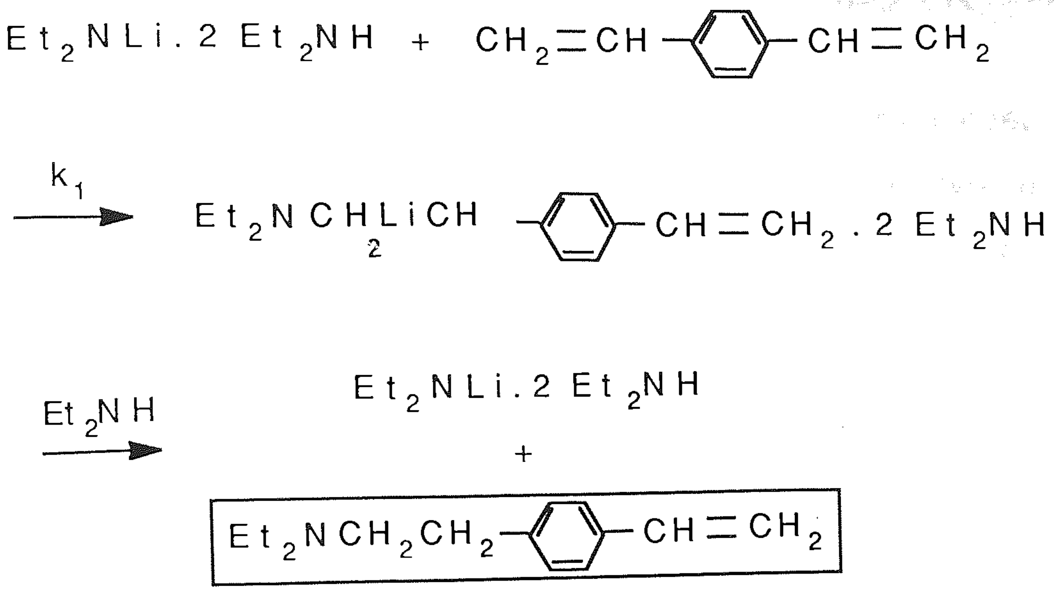




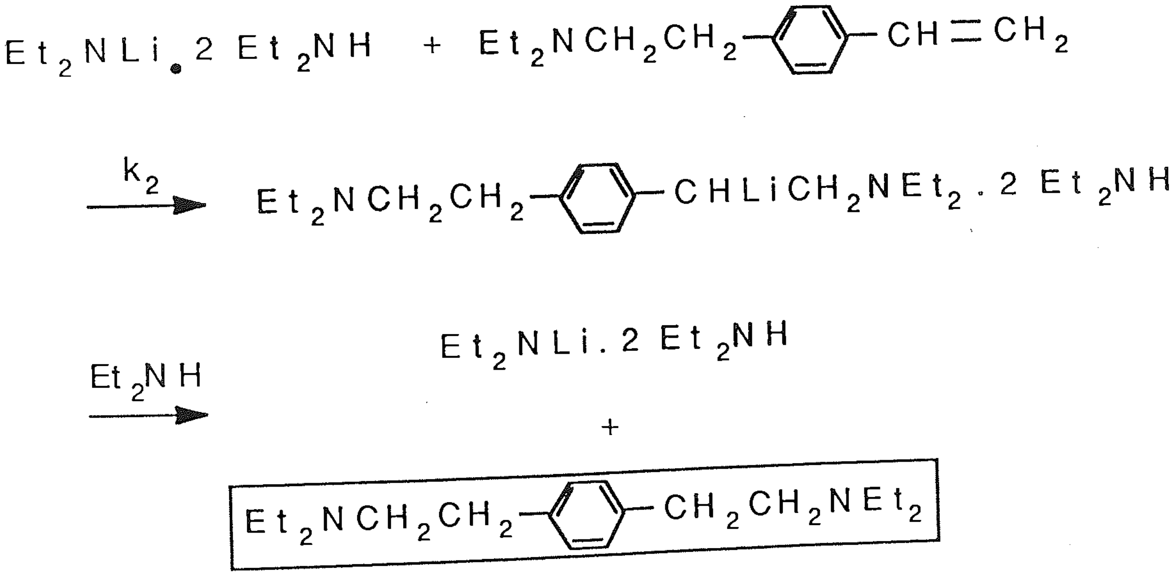
Buta-1,3-diene would be expected to be a monomer with greater coordinating ability ($K_1 > K_2$) whereas the rate constant of propagation of the styrene complex, in which the electron density of the carbon-carbon double bond would be expected to be less than the corresponding buta-1,3-diene complex, would be greater than the rate constant for propagation of the buta-1,3,-diene complex. The microstructure of the butadiene units of the copolymer prepared in the above mentioned copolymerisation system is predominantly the 1,4 structure.

On the other hand when the reactivity of styrene is increased by the addition of a Lewis base in the copolymerisation system the amount of 1,2 structure in the butadiene units is also increased. However, in the lithium diethylamide system the presence of butadiene had no effect on the reactivity of styrene in comparison with the reaction of alkyllithium and the rate constants for the addition of lithium diethylamide to the two monomers in this system were almost of the same order of magnitude. Furthermore, the 1,4 cis structure formation in butadiene units was still retained even under reaction conditions which resulted in comparable monomer reactivities. Thus such results suggest that the mechanism of the stereospecific addition reaction of the lithium diethylamide complex to butadiene is different to the usual stereospecific addition of alkyllithium in hydrocarbon solvents [81].

Studies have also been made of the addition reaction of lithium amides to 1,4 divinylbenzene (DVB) [82]. The addition reaction was found to proceed stepwise as follows



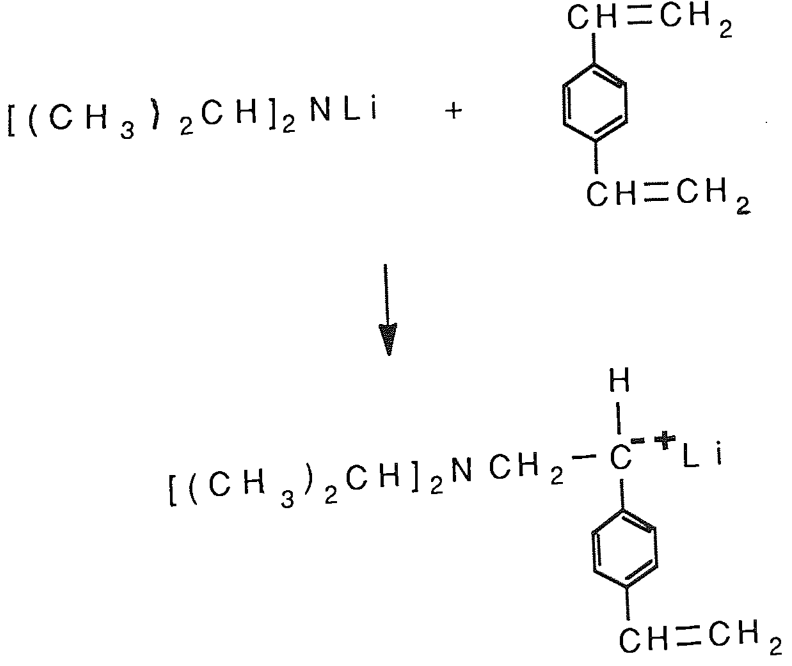
(A)



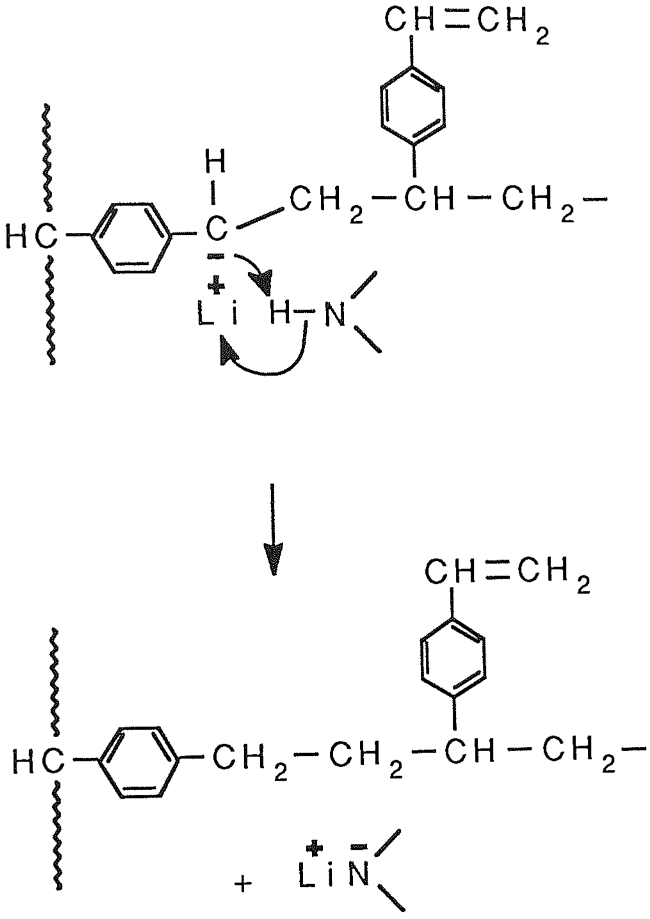
(B)

Product (A) was isolated in good yield when the reaction time was short. It took more than forty hours at 50^{o}C to produce product (B) from the amide/amine complex and product (A). Addition reactions of diethylamine onto 1,4-divinylbenzene were examined to find a synthetic route to a group of new monomers possessing dialkylamino substituents which have potential applications as starting materials for biomedical polymers such as ionic polymer complexes, polycations and others[82].

Thus lithium diethylamide in the presence of diethylamine does not induce the polymerisation of a conjugated diene or styrene but produces addition products as seen above. However, the reactivity of lithium alkylamide in this type of addition reaction was found to be dependent on the structure of the alkylamino group. For instance, lithium diisopropylamide exhibits a much lower reactivity compared to that of diethylamide or other alkylamides such as dipropylamide, dibutylamide of diisobutylamide[80, 83]. In actual fact no reaction takes place between lithium diisopropylamide and a diene or styrene. However, lithium diisopropylamide does induce polymerisation of 1,4 and/or 1,3 divinylbenzene (DVB) in the presence of diisopropylamine. Initiation was found to take place through an addition reaction of the alkylamino group to a DVB molecule as shown below:



It was found by NMR studies that the vinyl groups in poly(1,4 DVB) had low reactivity towards initiation by lithium diisopropylamide; lithium diisopropylamide did not undergo an addition reaction to the pendant vinyl group and branching reactions were considered to take place between a growing anion and poly(DVB). Soluble poly(DVB) was produced only in an excess of free amine probably due to the following reaction:

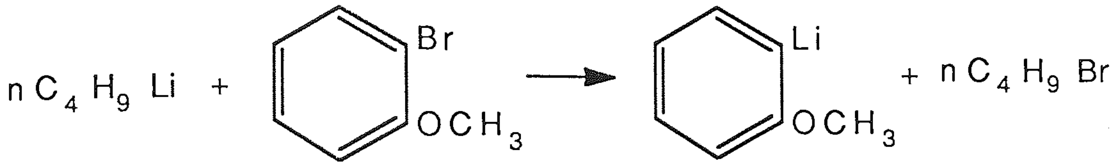


This may be the primary reason why any further crosslinking was excluded. [83]

4.2.2. Lithium - halogen interconversion

Organolithium compounds react with both alkyl and aryl halides to form organolithium intermediates which are used widely in the synthesis of carbon compounds.

The reaction of an organic halide with an organolithium compound in which the metal and halogen atoms exchange places is known as the halogen - metal interconversion reaction [84]. This interconversion was discovered by Gilman [58] who found that o-bromoanisole reacted with n butyllithium to yield o-anisyllithium and n butylbromide



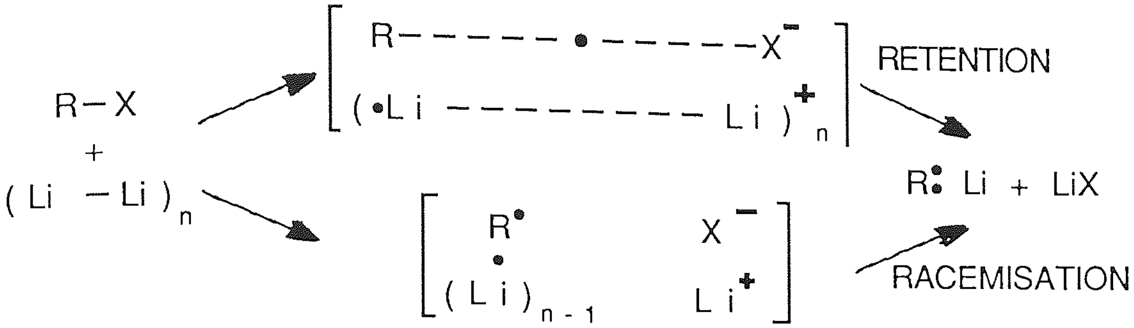
Simple reagents such as phenyllithium and n butyllithium are easily prepared by the reaction of an organic halide and metallic lithium

$$CH_3CH_2CH_2CH_2Br + 2\,Li \longrightarrow CH_3CH_2CH_2CH_2Li + LiBr$$

However, some organic halides do not react satisfactorily with metallic lithium to form RLi compounds. However, the desired organolithium compounds can often be obtained by halogen - metal interconversion reactions.

4.2.2.1. Reaction mechanisms

Several proposals have been put forward for the reaction of an organic halide with lithium metal. The fact that by-products include hydrocarbons derived from coupling and alkenes and alkanes corresponding to the alkyl halides suggests radicals may be involved. However, some vinylic halides give organolithium compounds with retention of configuration. Therefore, the type of mechanism which is felt to be most likely is one involving a one electron transfer to the alkyl halide at the metal surface as the first step. This mechanism may be represented as follows, showing possible stereochemical pathways [85, 86].



Mechanistically the metal - halogen interconversion reaction is more intriguing. A number of generalisations may be made which may be relevant to the mechanism of the reaction. These are summarised as follows:

(i) the reaction is reversible [59, 87].

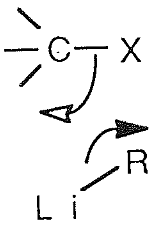
(ii) the lithium becomes preferentially attached to the organic group best able to stabilise a negative charge [84, 88]; alkyllithium compounds with the exception of methyllithium are more reactive than aryllithium compounds due to the fact that the carbanion in alkyl compounds is not stabilised by the intramolecular effects, due to resonance and polarizability, which cause, to some extent, the stabilization of the carbanion in aryl compounds [59].

(iii) the reaction takes place more rapidly with iodides and bromides and less readily with chlorides [84].

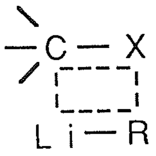
(iv) the reaction is faster in ethers than in hydrocarbon solvents [84, 89].

The kinetics of the reaction of aryllithium compounds with aryl halides have also been studied by product analysis and the reaction was shown to follow second kinetics (first order in each component) [89].

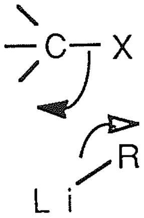
In view of all of these observations the metal - halogen interconversion is generally considered as polar. Some possible representations for its mechanism are as follows:



(i)



(ii)



(iii)

These diagrams represent variations on one theme - a four centre transition state. In (i) the dominating process is nucleophilic attack by the organolithium compound on the halogen [59, 84], (ii) represents a stepwise process with a true four centre transition state and in (iii) the dominating process is electrophilic attack on the carbon atom by the lithium atom.

The fact that often reaction products also include coupling and disproportionation species leads to the assumption that the reaction may however involve some degree of homolytic fission. It is well established that free radicals are formed during the reaction of alkyllithium compounds with alkyl halides [90] but their formation has generally been associated with Wurtz-type coupling reactions. NMR studies have further furnished strong evidence for a homolytic component in the metal - halogen interconversion reaction; NMR studies of the reaction of n-butyllithium with butylbromide gave evidence that butane was produced by the disproportionation of a free radical intermediate [91]. However, a completely free radical process does not accord with observations of partial or complete retention of configuration in certain metal halogen interconversion reactions [92]. Nevertheless, a route represented by

$$RX + R'M \rightleftharpoons [\dot{R}, X, M, R'^{\bullet}] \rightleftharpoons RM + R'X$$

must be taken into consideration; [55(c)] the bracketed term represents some kind of intermediate involving unpaired electrons which give rise to the magnetic resonance phenomena and also coupling and disproportionation products.

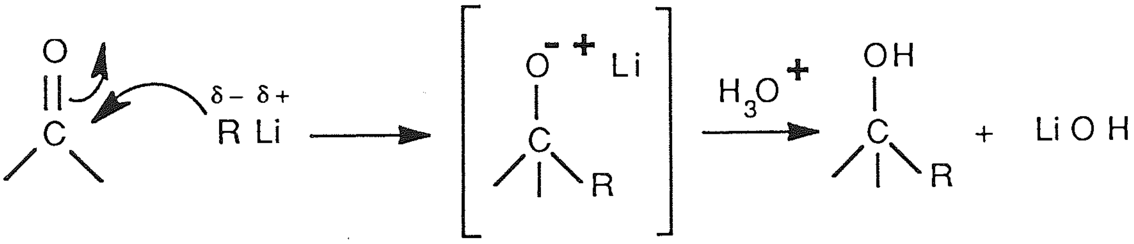
4.2.3. Reactions of organolithium derivatives

Due to the polar nature of the carbon lithium bond organolithium compounds are used greatly in synthesis. In view of the many reactions possible with lithium alkyls and aryls metallation is potentially a very versatile method of polymer modification. Having metallated a polymer it is possible to introduce a wide variety of functional groups into the polymer or to initiate the graft polymerisation of anionically polymerisable monomers at the metallation sites.

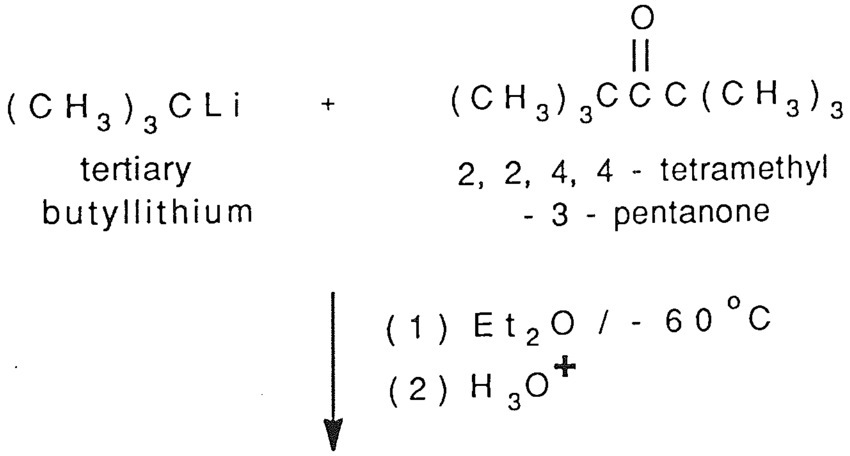
Use is made of the reactivity of organolithium compounds in producing polymers with functional end groups. For example, divinybenzene or a mixture of divinylbenzene with monovinyl aromatic compounds such as styrene is reacted with butyllithium. The polymeric polyfunctional organolithium compounds thus obtained are then reacted with low molecular weight compounds such as carbon dioxide [93].

4.2.3.1. Reaction with carbonyl compounds

Organolithium derivatives are often reacted with carbonyl compounds to introduce functional groups into molecules. The carbon-lithium bond is strongly polarised and is approximately 43% ionic in character [37, 39]. Thus the carbon atom is both nucleophilic and strongly basic as was seen previously in metallation reactions involving alkyllithium derivatives. Organolithium derivatives therefore can behave as if they were carbonions R^- and they undergo nucleophilic addition reactions with carbonyl compounds. Nucleophilic addition to the carbonyl group, followed by hydrolysis by aqueous acid [37, 39, 56, 57] generates an alcohol



An example of this type of reaction is that of a ketone with an alkyllithium derivative [37].


$(CH_3)_3CLi + (CH_3)_3CC(=O)C(CH_3)_3 \xrightarrow[(2)\ H_3O^+]{(1)\ Et_2O\ /\ -60\,^{\circ}C} [(CH_3)_3C]_3COH$

tertiary butyllithium

2, 2, 4, 4 - tetramethyl - 3 - pentanone

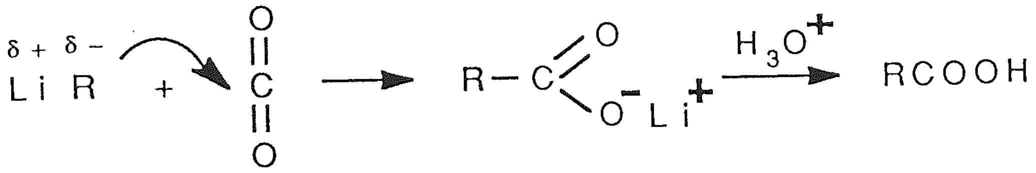
$[(CH_3)_3C]_3COH$

3 - t butyl - 2, 2, 4, 4 - tetramethyl - 3 - pentanol

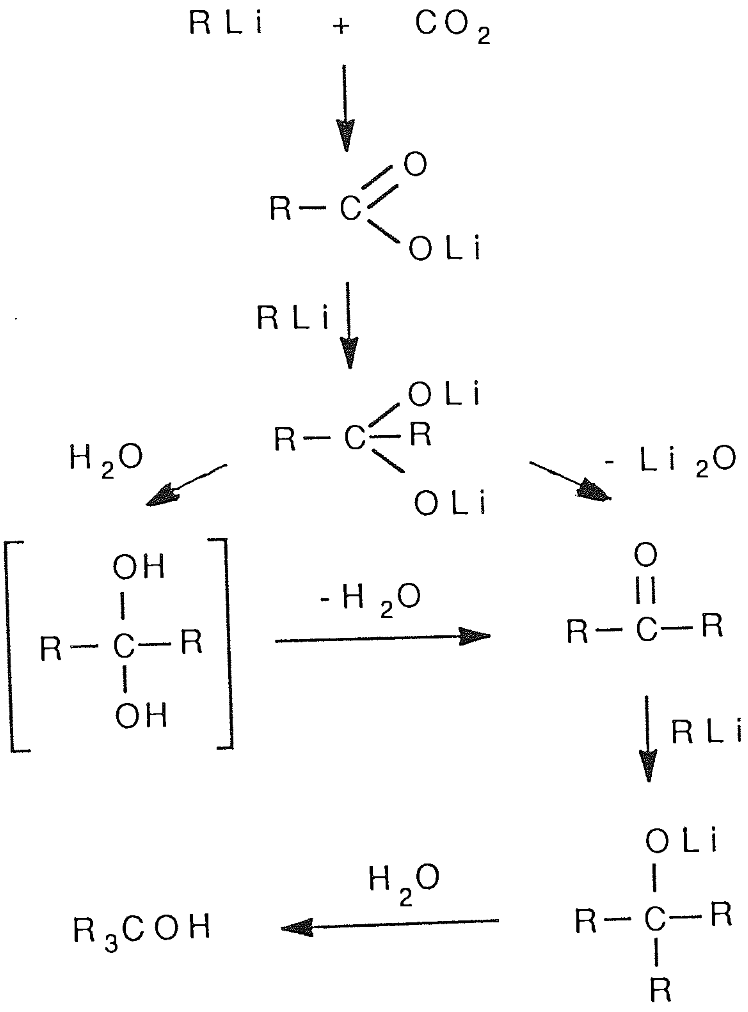
Lithium reagents are preferred to Grignards in the above addition reaction since lithium compounds are more reactive, to hindered carbonyl groups is accomplished and they are less susceptible to coupling.

4.2.3.1.1. Reaction with carbon dioxide

Carbon dioxide has the structural characteristics of the carbonyl group and readily reacts with organolithium derivatives to form carboxylic acid salts which may be acidified to form the corresponding acid i.e.



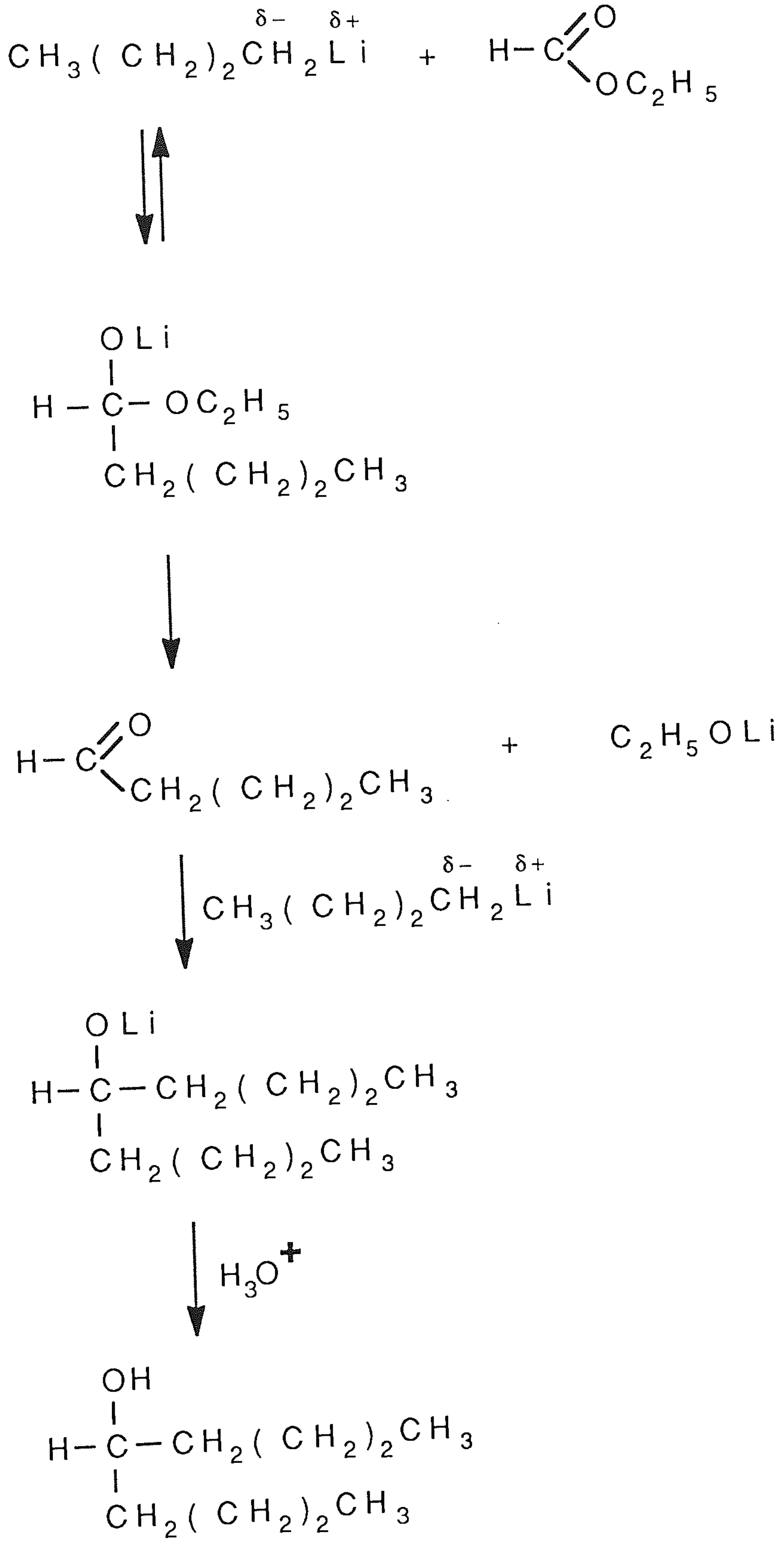
It is normally essential to ensure that an excess of carbon dioxide is present throughout the reaction otherwise secondary reactions of the type illustrated below may occur [55(d)].



4.2.3.1.2. Reaction with esters

The "normal" product of the reaction of an ester with an organolithium compound is an alcohol. However, it is sometimes possible to obtain ketones from these reactions but it is necessary to avoid an excess of the organolithium compound and careful attention to experimental detail is required. However, should a sterically hindered ketone be formed, addition of alkyllithium to this is only slow.

An example of the reaction between an ester and an alkyllithium compound is illustrated by the reaction of n-butyllithium to ethyl formate resulting in the formation of nonanol.



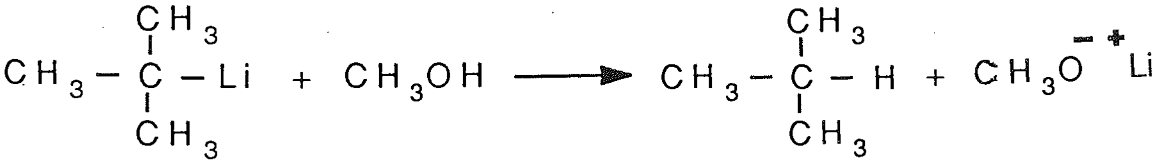
In the case of ethyl formate under appropriate conditions it should be possible to form the aldehyde rather than the secondary alcohol. Reactions of this type have been reported[55(e)].

4.2.3.2. Side reactions

The electronegativity (ε) of lithium is of the order of 1.0 and since metal alkyls of such metals ($\varepsilon < 1.7$) readily hydrolyse to the hydrocarbon and metal hydroxide, lithium alkyls are susceptible to reaction with traces of impurities.

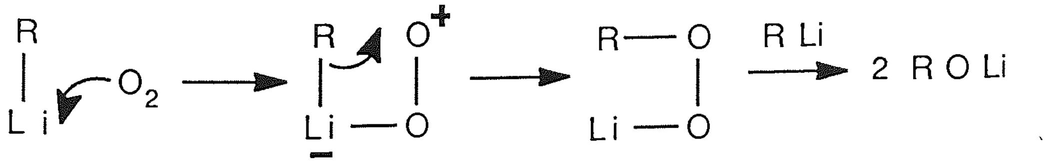
$$CH_3Li + H_2O \longrightarrow CH_4 + LiOH$$

The alkyllithiums react similarly with other hydroxylic compounds such as alcohols and carboxylic acids



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Li + CH_3OH \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-H + CH_3\overset{-}{O}\,\overset{+}{Li}$$

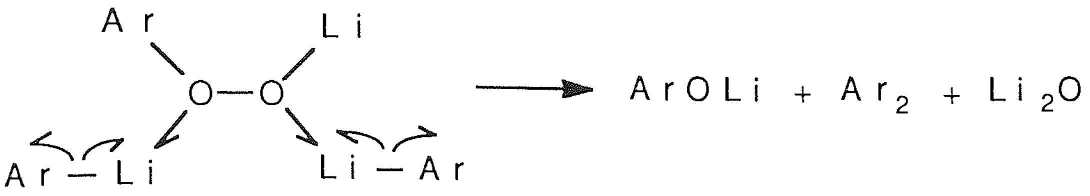
Traces of oxygen are another reactive impurity. Some possibilities exist for the autoxidation of organolithium compounds, as shown below:



(i)

$$ROOLi \longrightarrow R^{\bullet} + LiO_2 \xrightarrow{O_2} ROO^{\bullet} \xrightarrow{R\,Li} ROOLi + R^{\bullet} \qquad (ii)$$

Route (i) represents a polar mechanism and route (ii) a propagation step of a radical chain mechanism. The formation of coupling products and products derived from attack on the solvent is certainly consistent with a radical process. However, biaryls could also arise during the reaction of the peroxide with the organolithium compound 55(f).



Because of the reactivity of lithium alkyls with water and oxygen it is essential to carry out lithiation reactions in the absence of these compounds, i.e. under dry, anaerobic conditions.

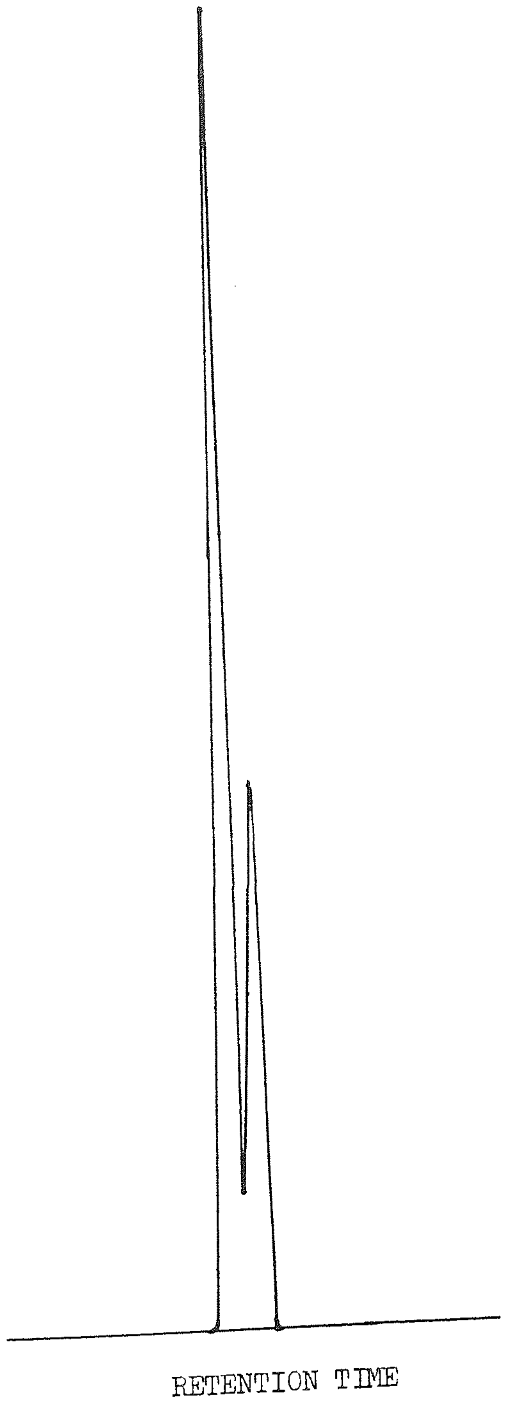


Figure 4.9

4.2.4. Experimental results

4.2.4.1. Introduction

Reports occur in the literature of the successful lithiation of reagents such as toluene and poly(p-methylstyrene) by a BuLi/TMEDA complex in both polar solvents such as THF and non polar solvents such as heptane, and accounts appear of other complexing agents such as K Bu^tO increasing the reactivity of BuLi in a similar manner to TMEDA. It seemed reasonable, therefore, to attempt the lithiation of poly(vinyltoluene) (PVT) in both polar and non polar solvents using BuLi complexed to either TMEDA or KBu^tO. Also reported in the literature was that carboxylation of lithiated poly(p-methylstyrene) resulted in the formation of the carboxylic acid derivative. Consequently it seemed logical to add carbon dioxide to lithiated PVT in order to produce the acid derivative. However, since lithiated species are known to react readily with all types of carbonyl compounds it seemed feasible to also attempt the synthesis of an aldehyde by adding ethyl formate to lithiated PVT.

4.2.4.2. Preparation of poly(vinyltoluene) (PVT)

4.2.4.2.1. Analysis of vinyltoluene monomer

The monomer was analysed by GLC, FT IR, and NMR.

4.2.4.2.1.1. GLC analysis

The GLC analysis shown in figure 4.9 confirms the purity of the monomer sample. The chromatogram shows only two peaks due

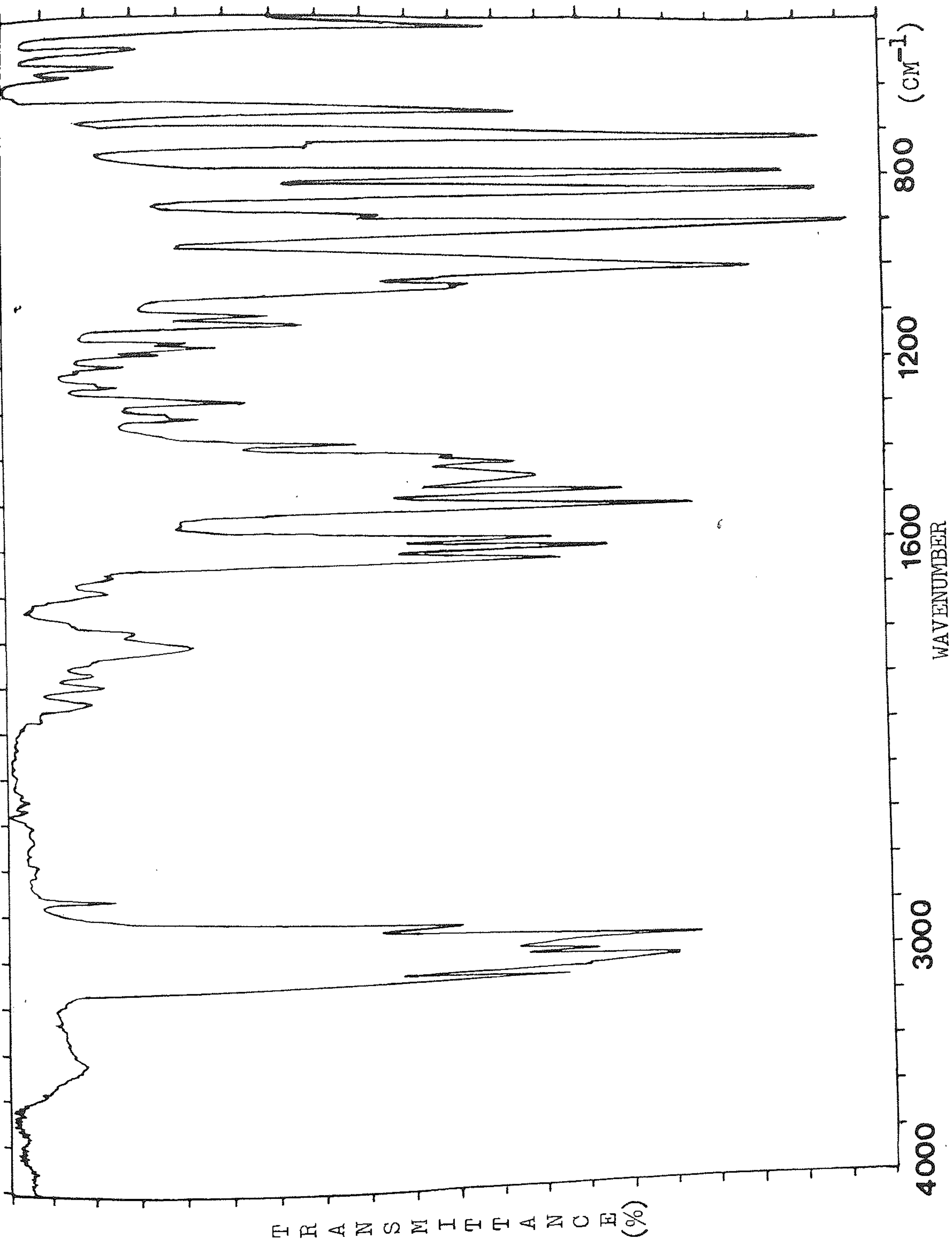


Figure 4.10

to the meta and para isomers. The relative abundance of these isomeric forms can be estimated by measurement of peak areas; the respective peak areas are 12.7cm^2 and 29.9cm^2 giving a ratio of 2.3 : 1 and corresponding percentages of 29.8 para and 70.1 meta as the manufacturers quote a value of 60% of the meta form to 40% of the para form.

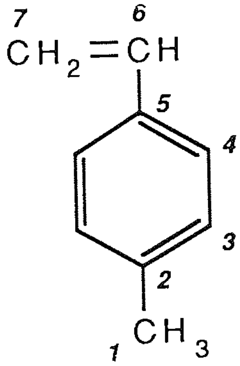
4.2.4.2.1.2. <u>IR analysis</u>

The monomer sample was analysed by IR as a thin liquid film between sodium chloride plates and the spectrum is shown in figure 4.10.

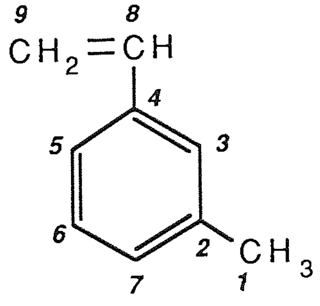
4.2.4.2.1.3. <u>NMR analysis</u>

The monomer was analysed by NMR as a solution in $CDCl_3$ solvent and the spectrum obtained is shown in figure 4.11. ^{13}C NMR was used to detect the number and type of non equivalent carbon atoms in the sample thus giving information on the structure of the monomer.

The monomer may be written as follows:



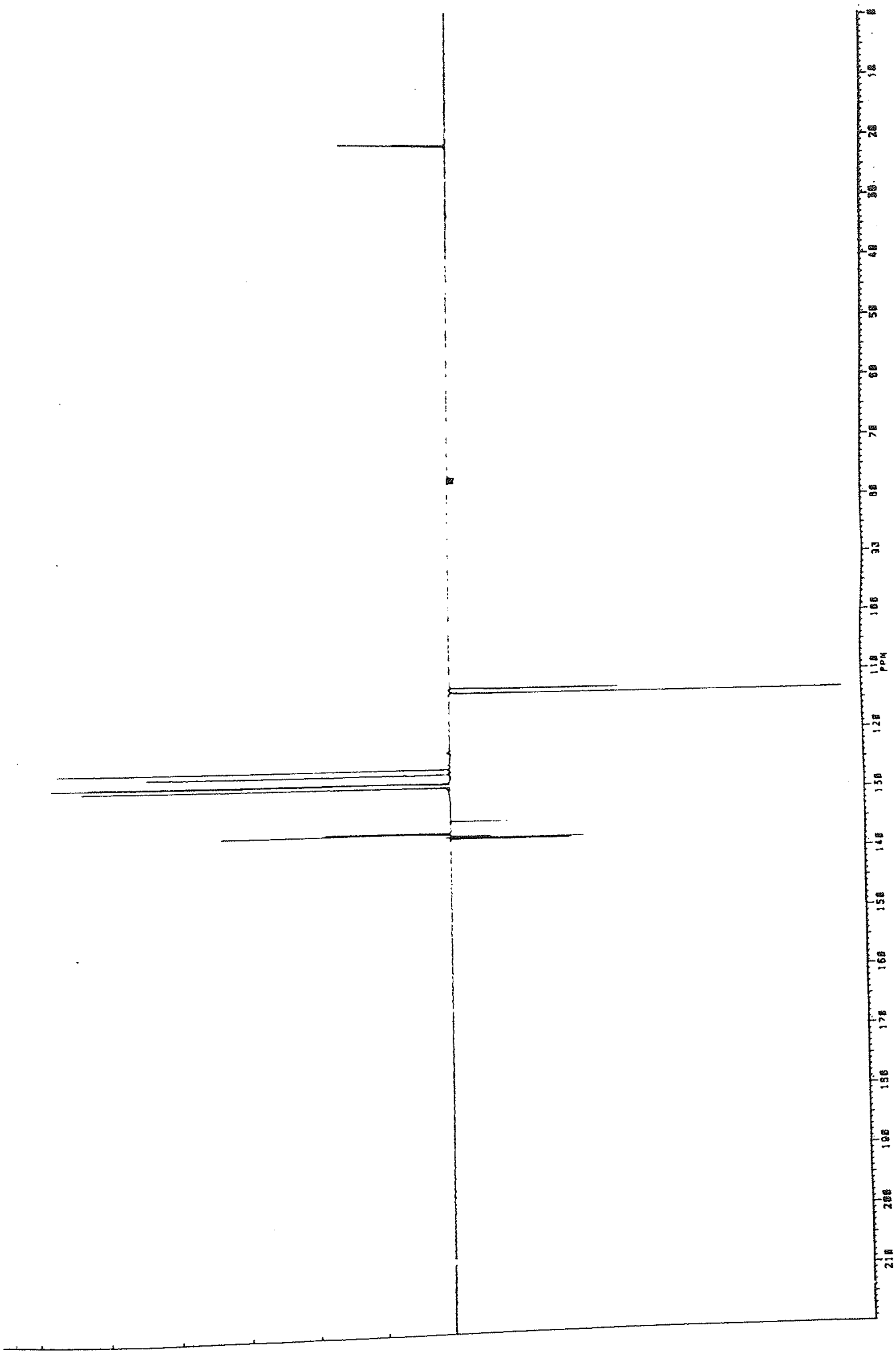
para isomer



meta isomer

The non-equivalent carbon atoms are numbered in each isomer.

For the para and meta isomers both the expected and the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90
100
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PPM
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160
170
180
190
200
210

Figure 4.11

obtained chemical shift values (δ) for each non equivalent carbon atom are shown in tables (G) and (H) in appendix 1.

On analysis of the spectrum it is seen that two different chemical shifts were obtained for the methyl carbon atom when only one was expected. This can be explained by the fact that the monomer is a mixture of isomers. For a CH_3 carbon attached to a benzene ring one would expect a chemical shift of 20 - 21 δ, but the NMR spectrum showed two absorbances at 20.87δ and 21.05δ; one possible explanation is that the CH_3 carbon is in a slightly different environment in the two isomers. The same principle can be applied to the four different absorbances obtained for the benzene ring carbon atoms at around 128δ.

4.2.4.2.2. Polymerisation of vinyltoluene

Vinyltoluene was polymerised free radically, using benzoyl peroxide as initiator, by the method described in section 2.7.1.3. A reaction mixture of 25g (0.212mol) of vinyltoluene and 0.512g (0.00212mol) of benzoyl peroxide was used and added to 25ml of toluene. Polymerisation was carried out at 60°C for 18 hours. The polymer produced was precipitated by the pouring the reaction mixture into an excess of methanol. The polymer was then dried under vacuum and purified by reprecipitating into a stirred methanol sample from a solution in THF. The resulting fine white preciptate was dried and weighed. The yield of polymer was 19.5g.

4.2.4.2.3. Analysis of poly(vinyltoluene)

The polymer sample was analysed by FT IR, NMR and GPC.

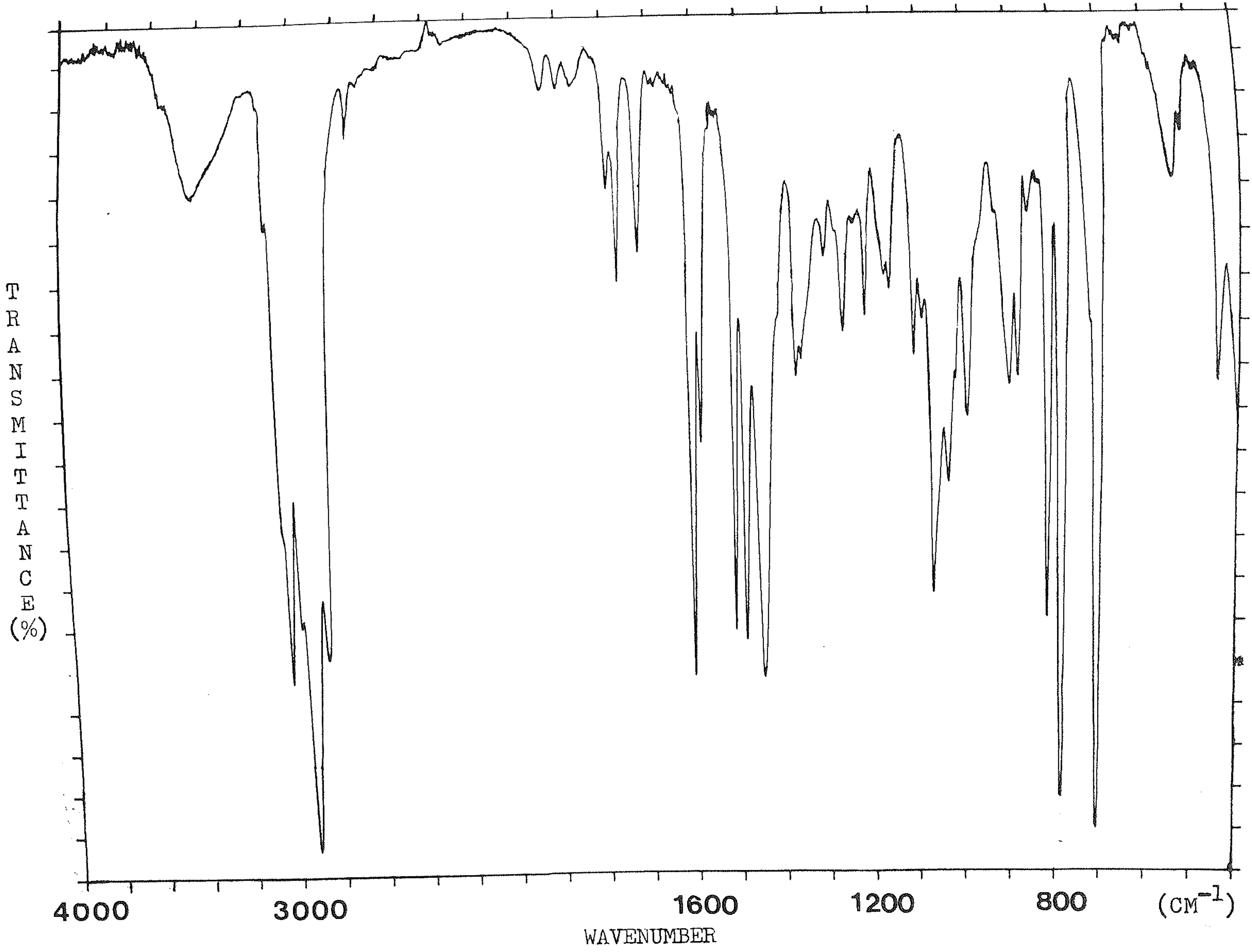


Figure 4.12

4.2.4.2.3.1. IR analysis

The polymer sample was analysed by IR as a film on sodium chloride plates by evaporation of a solution of the polymer in THF. The spectrum is shown in figure 4.12.

A comparison of the IR spectra of the monomer and polymer shows the expected changes in absorbance:

(i) the disappearance of absorbances at 1418cm^{-1}, 1630cm^{-1}, and 3088cm^{-1}, characteristic of alkene groups,

(ii) a change in the absorbances between 900 and 1000cm^{-1} due to the presence of vinyl groups in the monomer

(and)

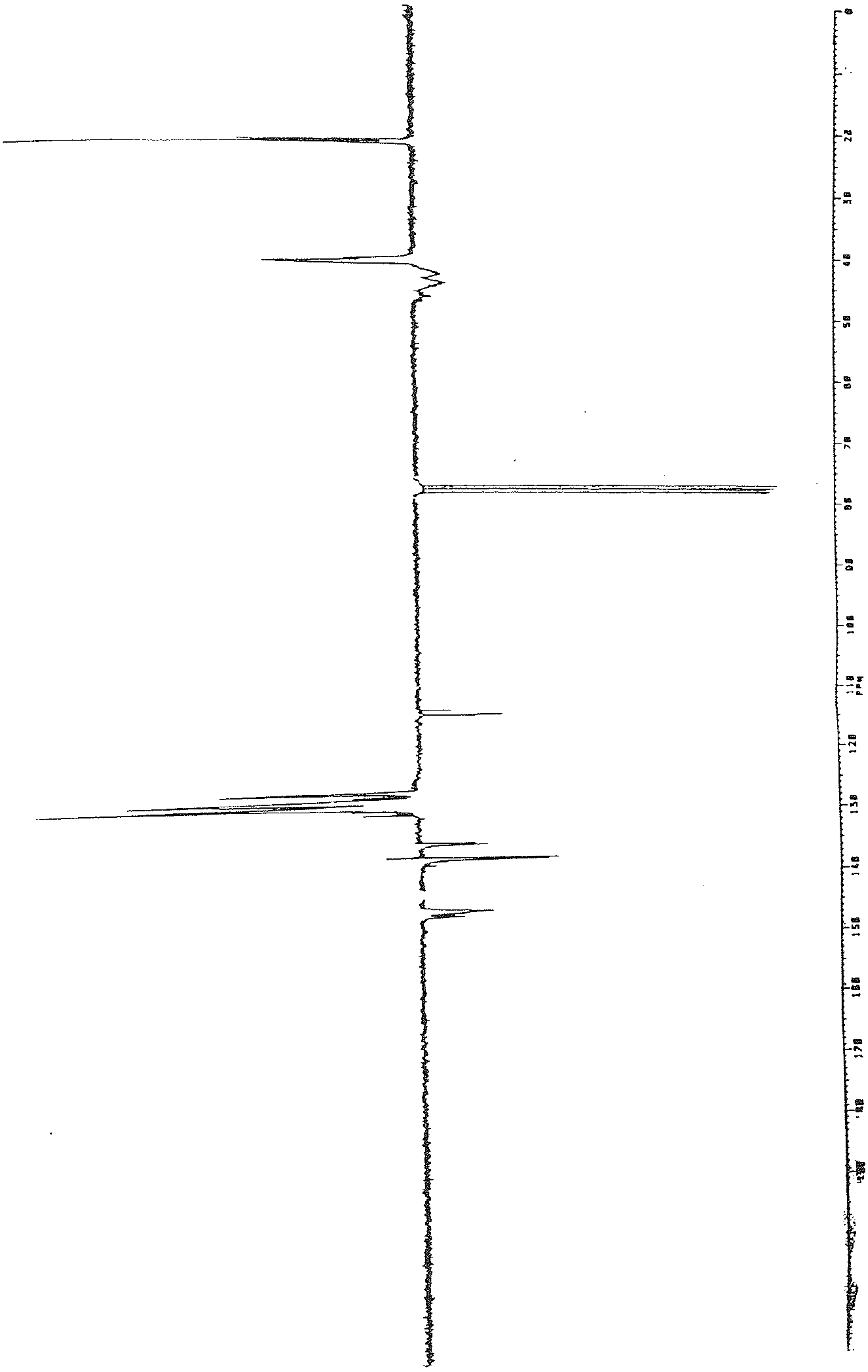
(iii) an increase in the intensity of absorbances in the polymer (1450 and 2855cm^{-1}) over that of the monomer (2922cm^{-1}) characteristic of the saturated - (CH - CH_2) - unit.

Thus all the evidence points towards the disappearance of the CH = CH_2 group and formation of the - CH - CH_2 - group as one would expect in a successful addition polymersation.

4.2.4.2.3.2. NMR analysis

The polymer was analysed by NMR as a solution in $CDCl_3$ solvent. The spectrum is shown in figure 4.13.

^{13}C NMR was used to detect the number and type of non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PPM
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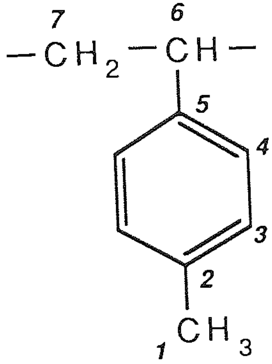
160
170
180
190

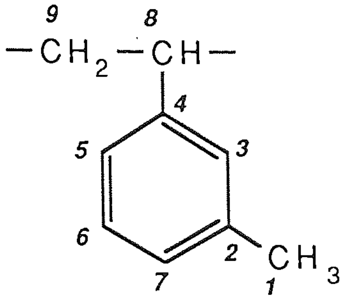
Figure 4.13

equivalent carbon atoms in the sample, thus giving information on the structure of the polymer.

The polymer may be written as follows:



para isomer



meta isomer

The non equivalent carbon atoms are numbered in each of the isomeric forms.

For the para and meta isomers both the expected and the obtained chemical shift values (δ) for each non equivalent carbon atom are shown in tables (I) and (J) in appendix 1.

When the NMR spectrum of the polymer is compared with that of the monomer, this shows the appearance of chemical shifts due to CH and CH_2 groups in an alkane chain (polymer backbone) environment at 40 - 46 δ and those due to a carbon atom of a benzene ring attached to an alkane chain at 141 - 149 δ in the spectrum of the polymer. In addition, there is a reduction in intensity of chemical shifts at 112 and 113 δ (due to CH_2 of the vinyl group) and at 136 δ (due to the CH group of the vinyl group) in the polymer.

4.2.4.2.3.3. GPC analysis

PVT was analysed by GPC as a 2% solution in THF. The

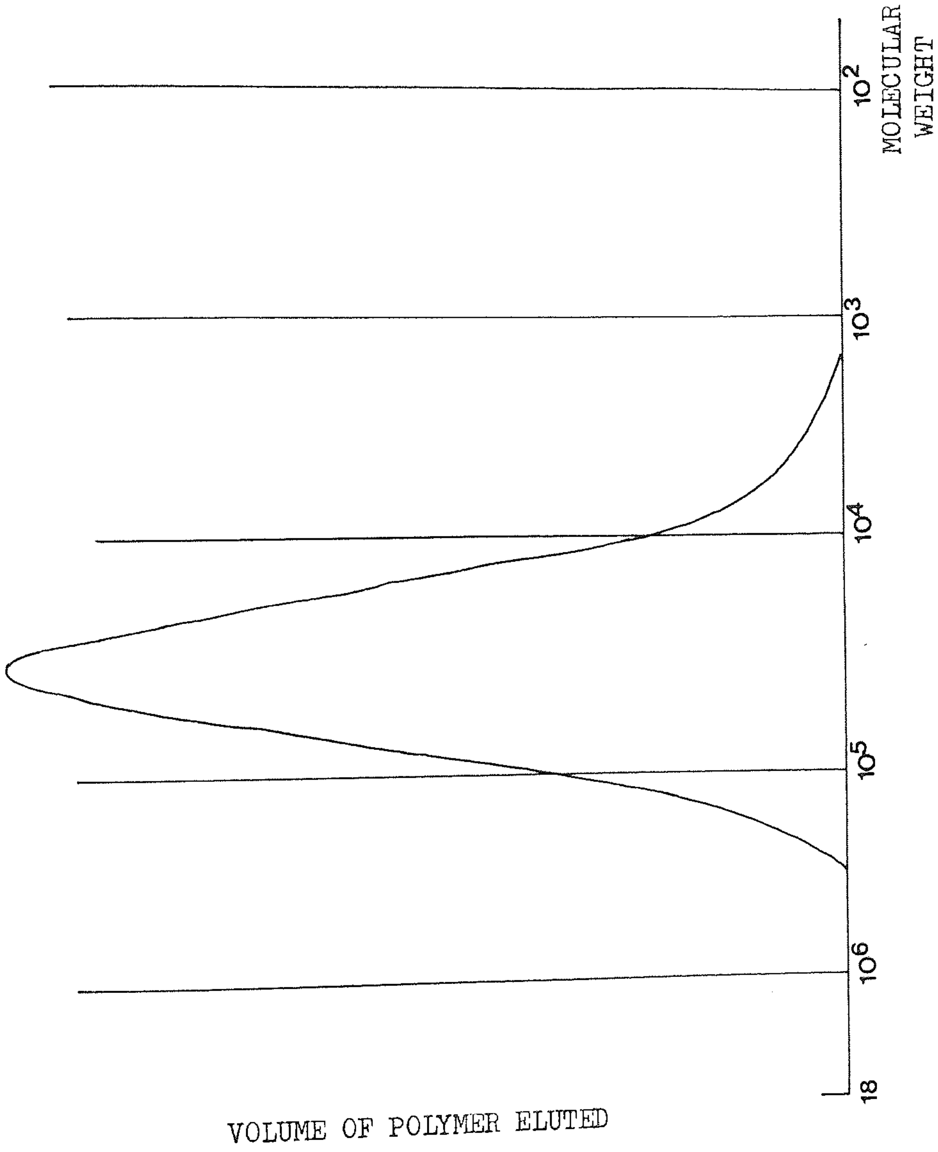

10^2
10^3
10^4
10^5
10^6
18
MOLECULAR WEIGHT
VOLUME OF POLYMER ELUTED

Figure 4.14

chromatogram is shown in figure 4.14. The polymer made by the above procedure had a weight average molecular weight (M_w) of 34200 and a number average molecular weight (M_n) of 16200 with a polydisperity ($\bar{M}_w/\bar{M}_n$) of 2.1, most likely due to the occurrence of chain transfer.

4.2.4.3. Functionalisation of poly(vinyltoluene)

4.2.4.3.1. Lithiation and carboxylation

Poly(vinyltoluene) was metallated as described in section 2.8.2.2. In a typical metallation reaction 1g (0.008mol) of PVT was dissolved in 20ml of THF. The lithiating agent, BuLi, was activated by KBu^tO; a suspension made by using 1.79g (0.016mol) of KBu^tO, 30ml of THF and 10.67ml (0.016mol) of BuLi solution was added to the reaction flask to give a 2:1 molar ratio of BuLi to monomer units. The metallation reaction was carried out at 50^oC in a constant temperature water bath for seven hours.

When metallation was complete the flask containing the metallated polymer solution was returned to the vacuum line and $1.3dm^3$ (0.058mol) of CO_2 gas was admitted to the flask. The dark red solution immediately decolourised and the solution gelled. When the reaction was complete the gel was broken down by the addition of 20ml of IM hydrochloric acid and then poured into an excess of water to precipitate the polymer product. The polymer was dried under vacuum and purified by dissolution in THF and reprecipitation into water.

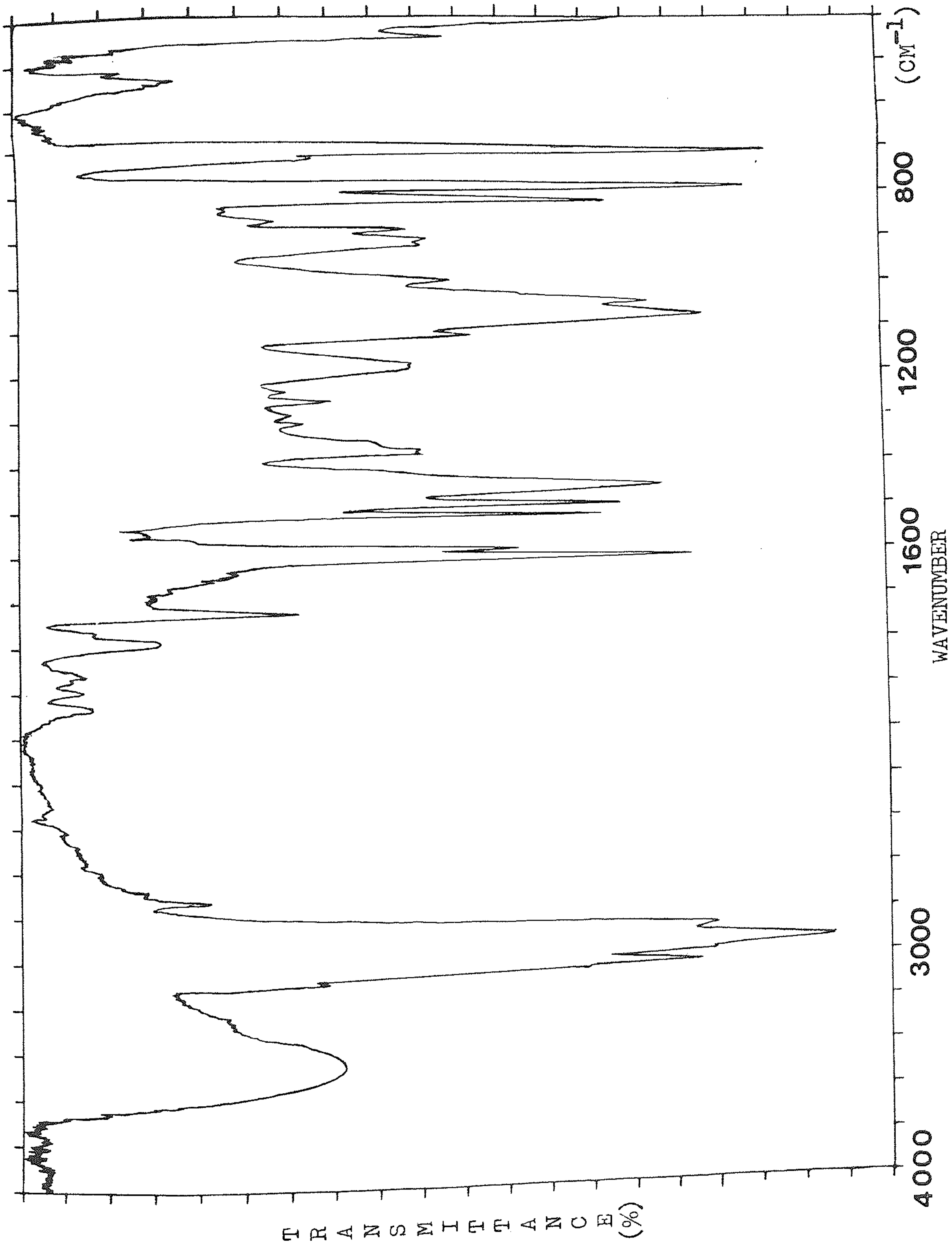


Figure 4.15

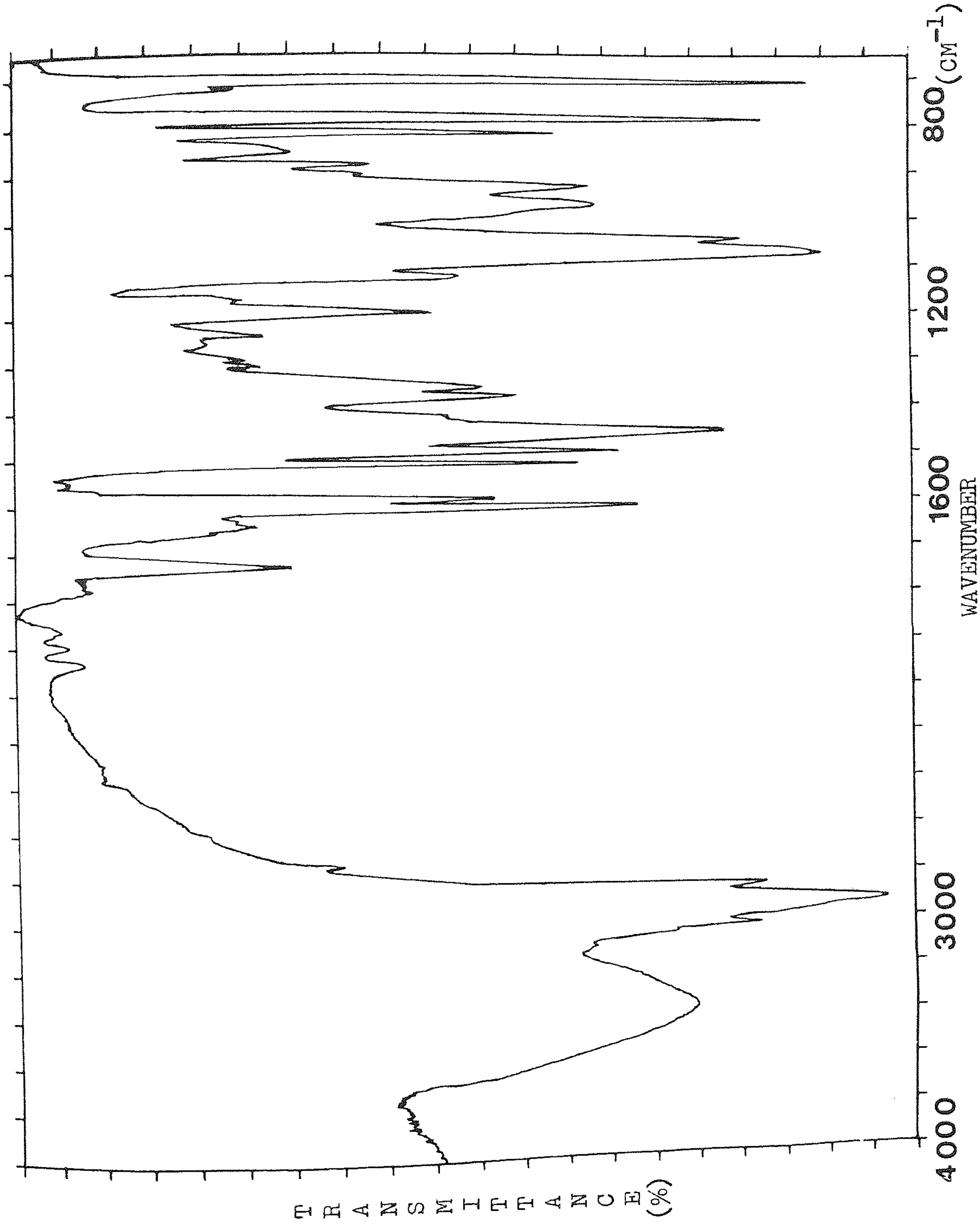


Figure 4.16

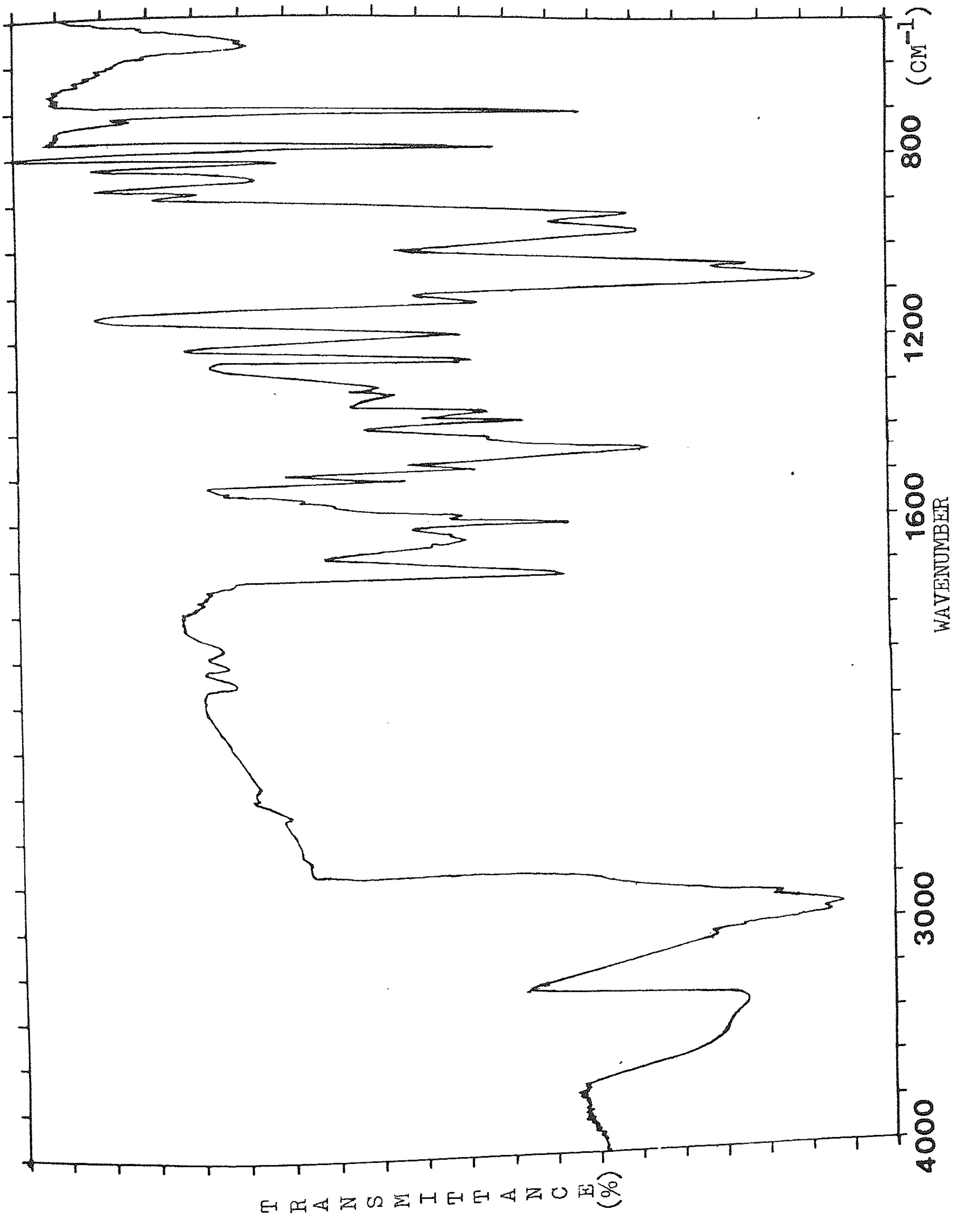


Figure 4.17

4.2.4.3.1.1. Analysis of the product

The polymer product was analysed by FT IR and NMR.

IR analysis

The spectrum of the product obtained after seven hours reaction time is shown in figure 4.17. The sample was analysed as a film by evaporation of a solution of the polymer in THF.

On comparison of the spectrum of the product with that of PVT some interesting changes can be observed. There is the appearance of absorbances characteristic of the carboxylate anion at 1354cm^{-1}, 1373cm^{-1} and 1637cm^{-1} and of the carboxylic acid group at 1192cm^{-1}, 1239cm^{-1}and 1728cm^{-1}.

Thus all the evidence points to the fact that lithiation and carboxylation led to the formation of the carboxylic acid derivative. In addition, however, the carboxylate anion was formed when the reaction did not go to completion.

Unfortunately it is very difficult to postulate at which site lithiation occurred due to the fact that any change in the intensity of the absorbance due to the CH_3 group is masked by absorbances due to the carboxylate anion between 1300cm^{-1} and 1400cm^{-1}.

Effect of reaction time on the degree of lithiation and carboxylation by infrared analysis

10ml samples were removed from the reaction vessel and carboxylated after one hour and four hours' reaction time. The remaining 30ml of the reaction mixture was carboxylated after seven hours' reaction time. The respective carboxylated products were analysed by IR as polymer films by evaporation of THF solution. The spectra are shown in figures (4.15) (4.16) and (4.17).

Thus the degree of reaction after one hour, four hours and seven hours respectively can be estimated by comparison of the absorbance at 1728cm^{-1} with that of the benzene ring which remains constant in all cases at 1606cm^{-1}. The results of this type of comparison are shown in table 4.1

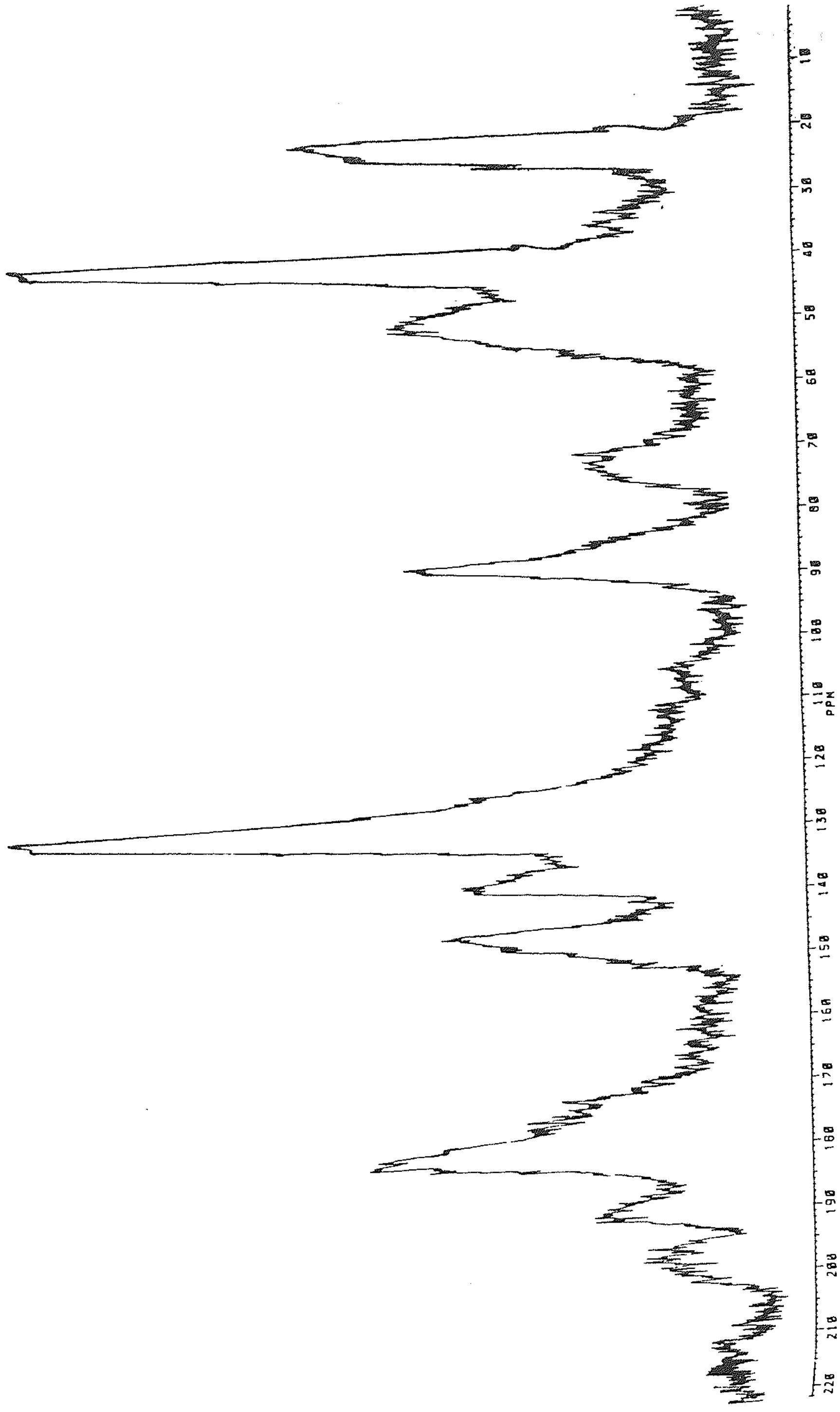
Table 4.1

Reaction time (hours)	$\frac{\text{Absorbance } 1728\text{cm}^{-1}}{\text{Absorbance } 1606\text{cm}^{-1}}$
1	$^{1}/_{4}$
4	$^{1}/_{3.2}$
7	$^{1}/_{1.8}$

Thus it is seen that there is an increase in the degree of lithiation and carboxylation with reaction time.

NMR analysis

In preparing a sample for NMR analysis samples were not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100
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PPM
120
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140
150
160
170
180
190
200
210
220

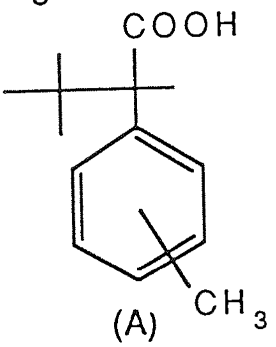
Figure 4.18

removed from the reaction flask after one hour and four hours' reaction time.

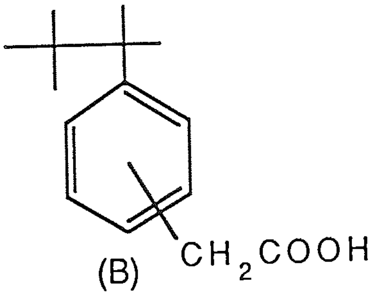
The polymer product was analysed by NMR in the solid state. The spectrum obtained is shown in figure 4.18

^{13}C NMR was used to detect the number and type of non equivalent carbon atoms in the sample, thus giving information on the structure of the polymer product.

If it is assumed that metallation can occur either on the backbone of the chain or at the methyl group pendant to the benzene ring i.e



(A)



(B)

Estimates can be made of the expected chemical shifts to be obtained in these cases. These chemical shifts are shown in tables (K), (L), (M), (N) in appendix 1.

A comparison of the NMR spectrum of the carboxylated product with that of PVT shows the appearance of the chemical shift due to the carbon of a carboxylic acid group or a carboxylate anion at 181δ.

The presence of a chemical shift at 24δ which is due to a CH_3 group attached to a benzene ring provides evidence in favour of reaction occurring along the polymer backbone giving product (A). The fact that this chemical shift may be due to unreacted

PVT must also be considered. However, the chemical shift of the CH_3 group in the product is different from that in PVT which would seem to suggest that it is not due to unreacted PVT but a pendant methyl group in a product carboxylated along the polymer backbone. Reaction at the backbone site is further supported by the chemical shift at 42δ which could be due to the carbon on the polymer backbone where carboxylation can occur or that at 53δ which could be accounted for by the CH_2 group adjacent to the backbone reaction site.

However, it is impossible to disregard reaction at the pendant methyl group since the chemical shift at 53δ is possibly that of a backbone CH_2 group in the β position to the benzene ring of a product carboxylated at the pendant methyl group. In addition the chemical shift at 42δ could be due to a CH_2 group attached to both a carboxylic acid group and a benzene ring.

In conclusion, it is impossible to ascertain the exact positon at which lithiation and subsequent carboxylation occurred and in fact a mixture of products may have been formed.

4.2.4.3.2. Lithiation and reaction with esters

In a typical metallation reaction 1g (0.008mol) of PVT was dissolved in 10ml of cyclohexane. The lithiating agent, butyllithium, was activated by complexing with TMEDA; a solution of 10.67ml (0.016mol) of BuLi, 2.4ml (0.016mol) of TMEDA and 40ml of cyclohexane was added to the reaction flask. The reaction was carried out at $60^{\circ}C$ for six hours.

On termination of the lithiation reaction the reaction flask was

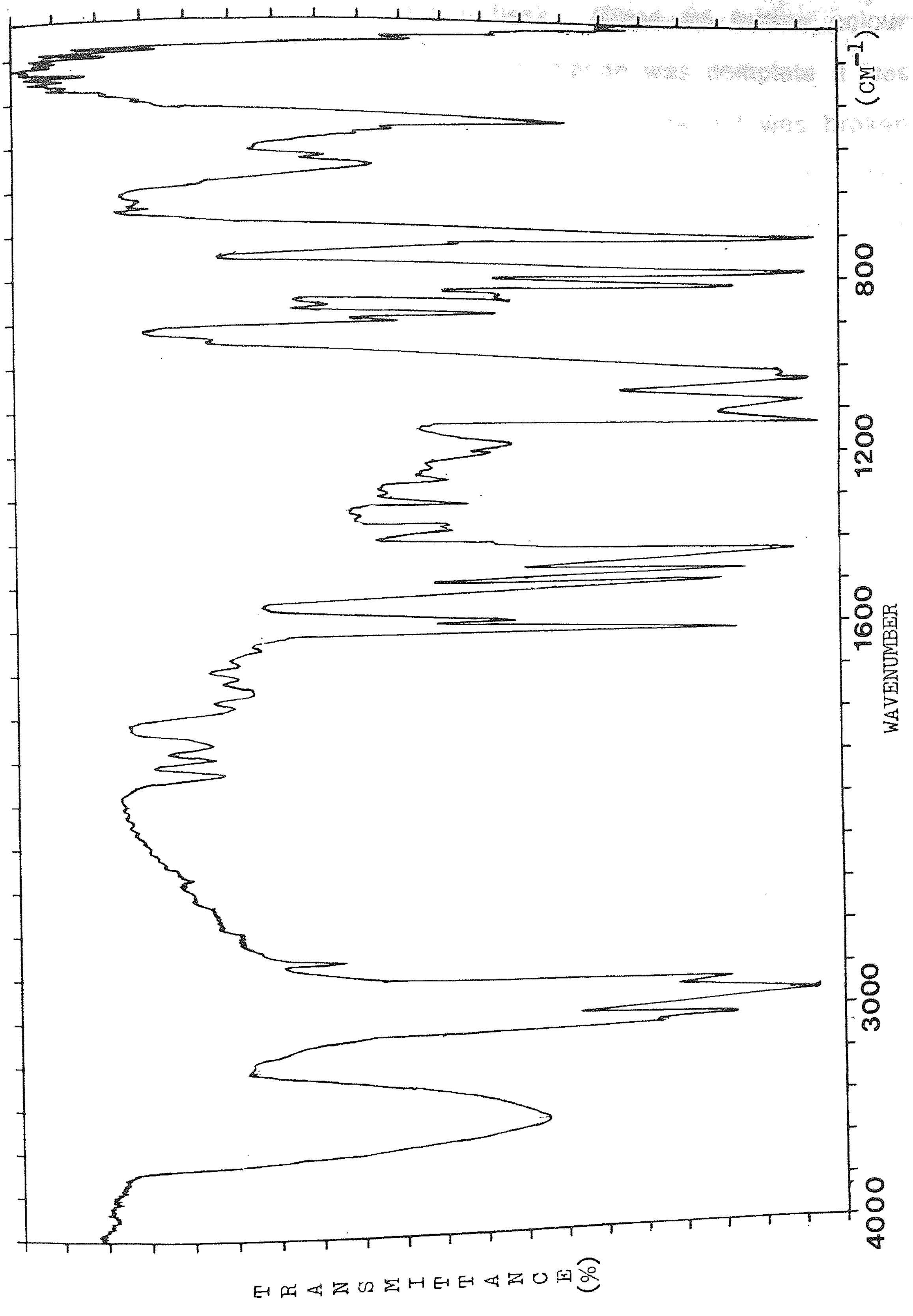


Figure 4.19

returned to the vacuum line and ethyl formate was allowed to distil slowly into the reaction flask. When no further colour changes were observed and gel formation was complete it was assumed that the reaction was finished. The gel was broken down by the addition of 30ml of 1M hydrochloric acid. The thick viscous organic layer was separated and poured into methanol. The resulting polymer was dried under vacuum. Purification of the polymer product was difficult since once precipitated the polymer showed only limited solubility in most common organic solvents such as THF.

4.2.4.3.2.1. Analysis of the product

The polymer product was analysed by FT IR, and GPC.

IR analysis

The polymer was analysed by IR as a KBr disc. The spectrum obtained is shown in figure 4.19.

On comparison of the spectrum of the product with that of PVT some interesting changes can be observed, notably the appearance of absorbances due to a secondary alcohol group at 1078cm^{-1}, 1133cm^{-1} and at 3469cm^{-1}.

Furthermore, a second band appears at 843cm^{-1} in the absorbance region associated with para-disubstituted benzene rings. This could possibly be explained by the fact that a second benzene ring was attached at the para position in the product.

In addition, there is a sharp decrease in intensity of the

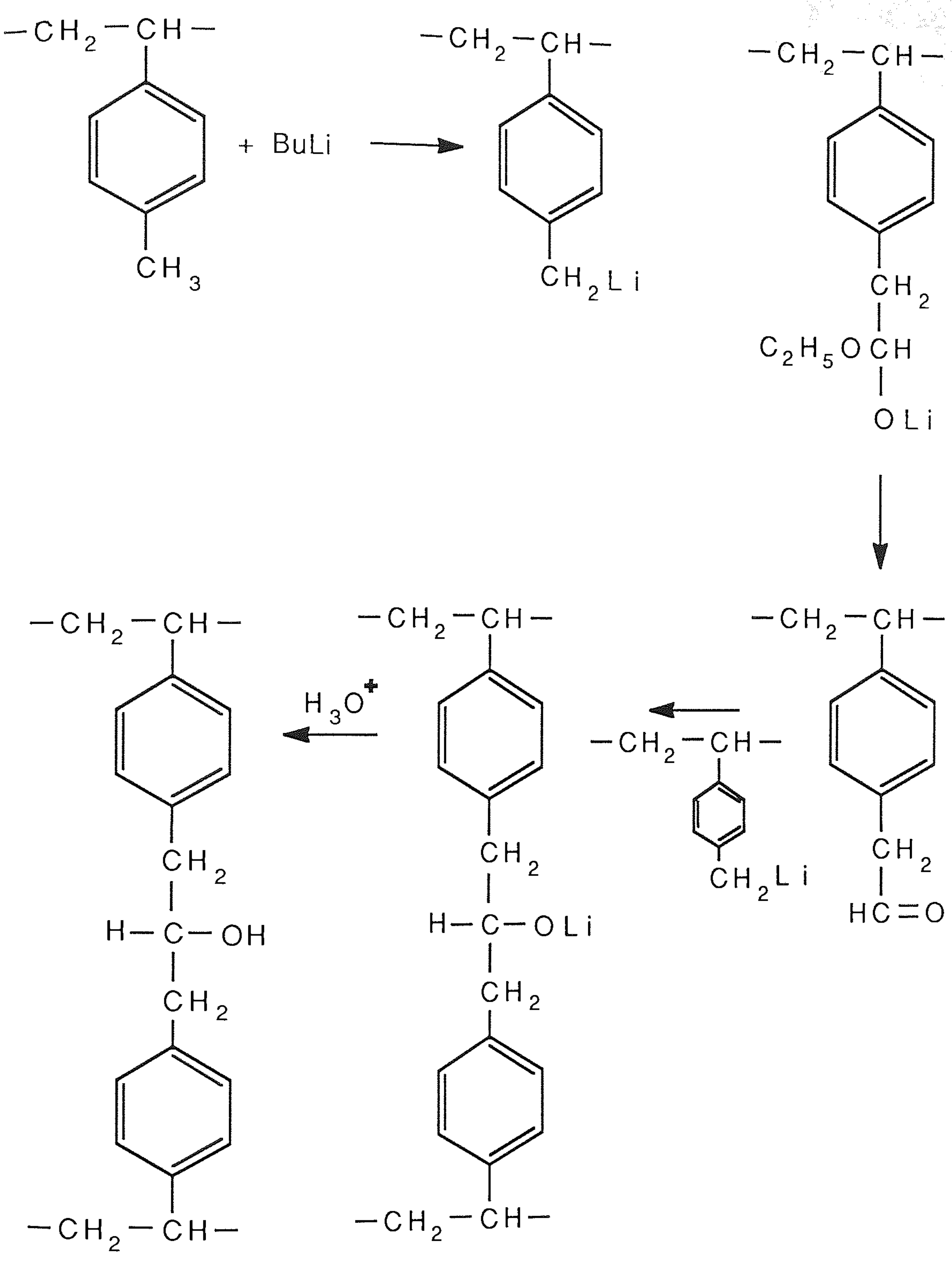


Figure 4.20

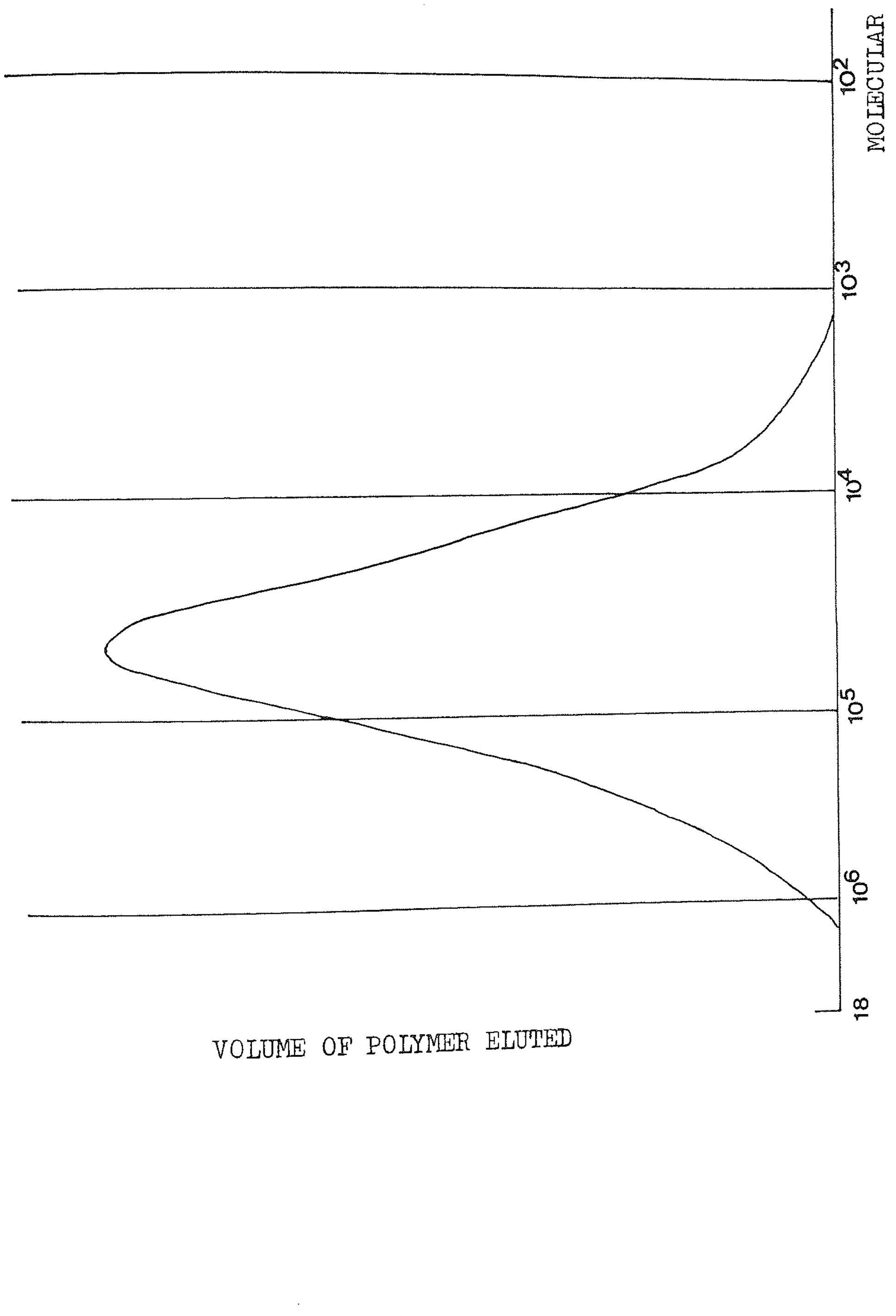

MOLECULAR WEIGHT
10^2
10^3
10^4
10^5
10^6
18
VOLUME OF POLYMER ELUTED

Figure 4.21

absorbance due to the CH_3 group at $1376cm^{-1}$.

Thus all the evidence points towards the formation of a secondary alcohol at the pendant methyl group. The proposed reaction scheme for the para isomer is shown in figure 4.20.

GPC analysis

The product was analysed as a 2% solution in THF. The chromatogram is shown in figure 4.21. The weight average molecular weight ($\overline{M}_w$) of the product was 65400 compared to that of PVT which was 34200. There was also an increase in the number average molecular weight ($\overline{M}_n$) from 16200 for PVT to 21400. Thus there was an increase in the amount of higher molecular weight polymer which was seen by the initial elution volume of the product compared to that of PVT. Furthermore there was an increase in the polydispersity from 2.1 for PVT to 3.1 for the product which shows that there was increased branching in the polymer chains of the product.

All the evidence points towards the formation of a secondary alcohol thus causing crosslinking between polymer chains.

4.2.4.4. Functionalisation of vinyltoluene

Since it was difficult to control both the site of reaction and the degree of reaction during attempts to functionalise PVT the approach of functionalisation of the monomer and subsequent polymerisation was adopted. It was seen in the literature reviewed previously that the methyl group of 4-methylstyrene was successfully lithiated by lithium diispropylamide whilst

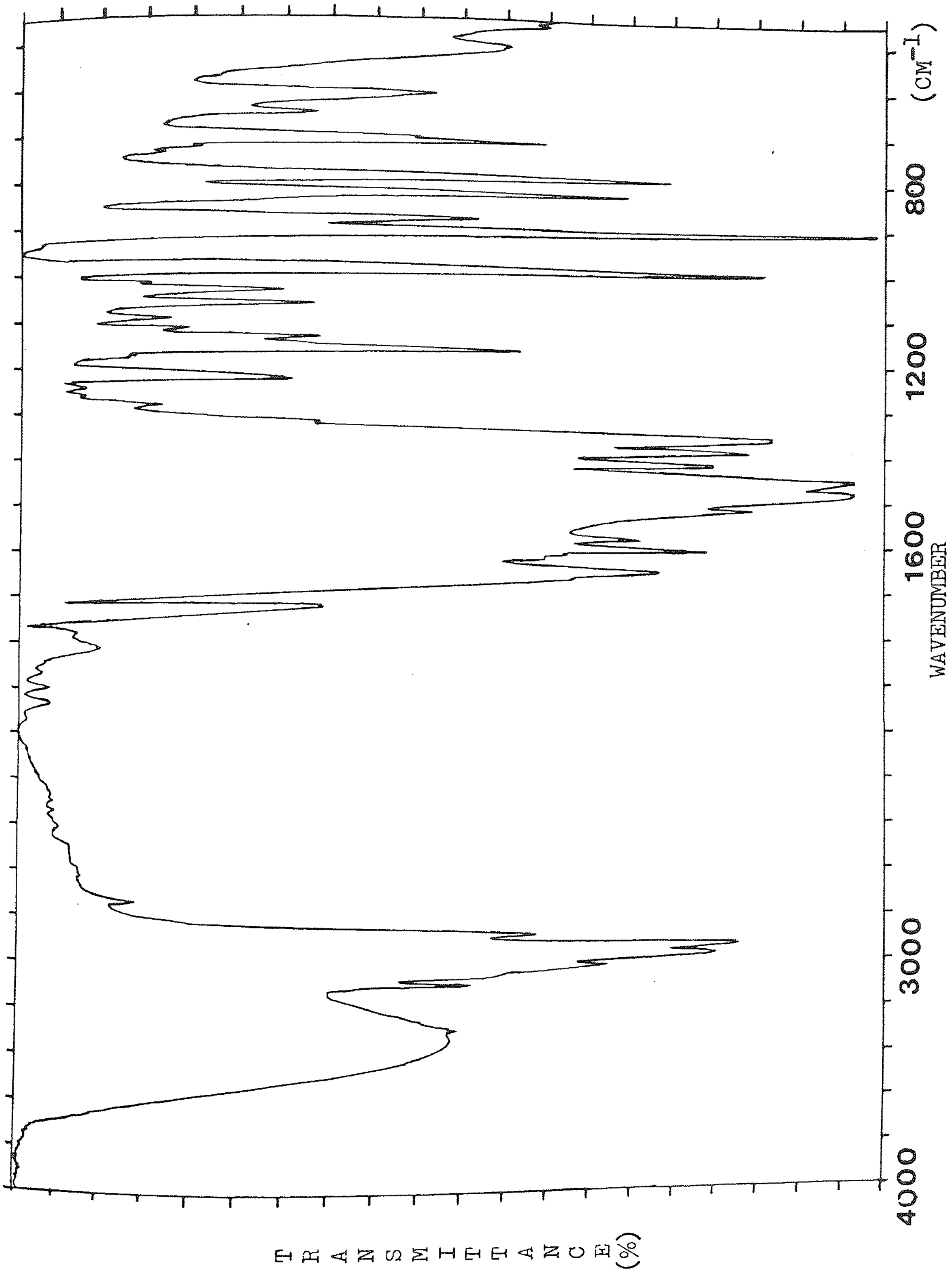


Figure 4.22

the vinyl group remained unchanged. Thus it seemed logical to adopt this method in carrying out the lithiation of vinyltoluene.

4.2.4.4.1. Lithiation and carboxylation

A typical reaction system for the metallation of vinyltoluene consisted of 14ml(0.1mol) of diisopropylamine, 33.2ml (0.05mol) of butyllithium in 35ml of THF and 6.6ml (0.05mol) of vinyltoluene. The reaction was carried out as described in section 2.6.2.1.

When metallation was judged to be complete the reaction vessel was returned to the vacuum line. The line was filled with CO_2 (0.058mol) and CO_2 was admitted to the metallated solution to carboxylate the monomer.

On completion of carboxylation the reaction mixture was degassed and 25ml of 1M hydrochloric acid were added. The organic layer was separated and any residual solvent was removed from the reaction flask by distillation under vacuum.

4.2.4.4.1.1. Analysis of carboxylated vinyltoluene

IR analysis

A 0.5ml sample was removed from the reaction flask and analysed by FT IR as a thin liquid film between sodium chloride plates. The spectrum is shown in figure 4.22.

On comparison of the spectrum of the functionalised monomer with that of vinyltoluene some interesting changes can be observed. Firstly there is the appearance of absorbances characteristic of the carboxylic acid group at 1163cm^{-1}, 1229cm^{-1} and 1722cm^{-1}. It is very difficult, however, to ascertain whether there was also some carboxylate anion formation as peaks characteristic of this group may be masked in the region 1300 - 1400 cm^{-1} by absorbances due to a $(CH_3)_2CH$ group and at 1649cm^{-1} by absorbances due to either the vinyl group or an amide group.

However, it can be seen that the functionalised monomer has not poymerised due to other absorbances at 908cm^{-1}, 996cm^{-1} and 3087cm^{-1} which are present in the unreacted monomer and are due to the vinyl group.

The presence of diisopropylamine is also detected due to absorbances at 1359cm^{-1} and 1385cm^{-1} which could be due to the $(CH_3)_2CH$ group, and the absorbance at 3296cm^{-1} which is due to the NH group, although shaking with hydrochloric acid would be expected to remove any excess diisopropylamine present.

Thus all the evidence points towards the formation of the carboxylic acid derivative. The presence of diisopropylamine can be accounted for by either its formation as a by-product during the metallation reaction or the presence of an excess of the reactant. The evidence is also indicative of the fact that the vinyl group remained intact during the course of reaction and did not undergo polymerisation. However, since both vinyl-toluene and the carboxylated product show absorbances due to the presence of the conjugated vinyl group at 901 - 903 cm^{-1} together with the absorbance at 1603cm^{-1}due to the benzene

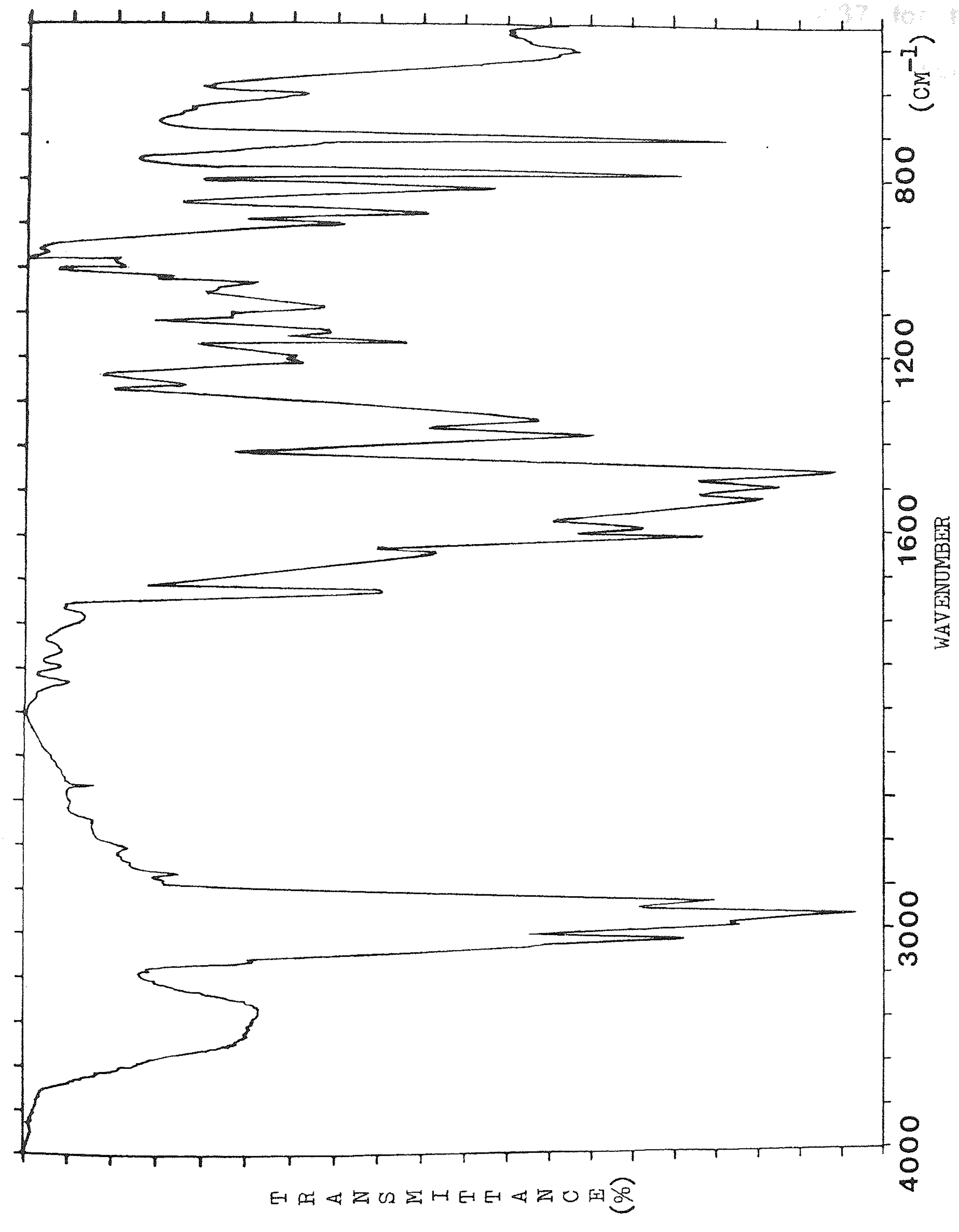


Figure 4.23

ring a comparison can be made of the ratio $\text{Absorbance}_{901-903\text{cm}^{-1}}/\text{Absorbance}_{1603\text{cm}^{-1}}$ for both compounds. The results of this comparison show that there is a slight reduction from 2.98 for the reactant to 2.37 for the carboxylated monomer. This may be brought about by some polymerisation or could be due to the inherent inaccuracy of the infrared technique when applied to such estimations.

4.2.4.5. Polymerisation of carboxylated vinyltoluene

The carboxylated monomer, vinylphenylacetic acid was polymerised according to the procedure described in section 2.7.1.4. 0.12g (0.0005mol) of benzoyl peroxide dissolved in 25ml of toluene was added to the product of the carboxylation procedure described above. The polymerisation reaction was carried out at 60°C for 18 hours. When the reaction was complete the contents of the reaction vessel were added to an excess of methanol. The precipitated polymer was then dried under vacuum. Purification of the polymer was difficult as once precipitated it showed limited solubility in common organic solvents such as THF and chloroform. The yield of polymer was 3.25g.

4.2.4.5.1. Analysis of the product

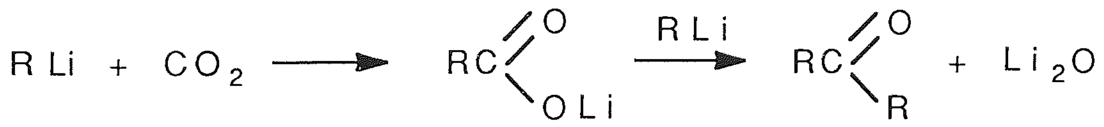
The polymer product was analysed by FT IR, NMR and GPC.

IR analysis

The polymer product was analysed by IR as a KBr disc and the spectrum is shown in figure 4.23.

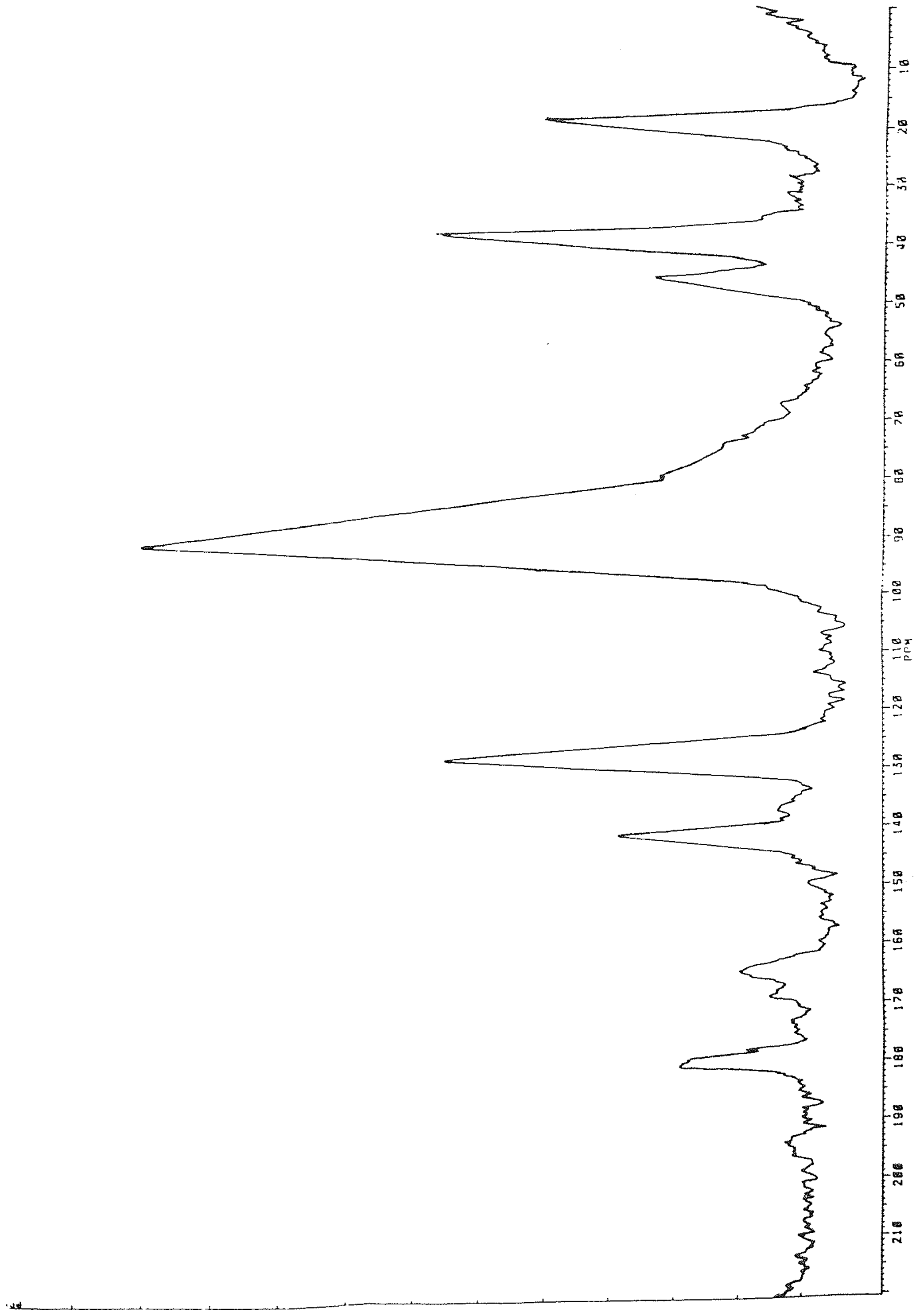
Comparison of the IR spectra of the monomer and the polymer show some inconsistencies that would suggest that the reactions involved are not as simple as first thought. The disappearance of the absorbance in the monomer at $1417cm^{-1}$ on polymerisation and the expected reduction in intensity of the peaks between 900 and $1000cm^{-1}$ are indicative of addition polymerisation taking place. The polymer also shows the absorbance expected of a carboxylic acid at $1732cm^{-1}$ but the peak at $1647cm^{-1}$ in the polymer is not readily explained. A peak occurs in this region in the monomer and this is normally associated with a vinyl group, but amides and carboxylate anions also absorb near this frequency. Further inspection of the infrared shows the existence of peaks between 1300 and $1400cm^{-1}$, characteristic of the ispropyl group, but no absorbance at $3296cm^{-1}$ due to the NH of an amine. It is possible therfore that the product contained not only carboxylic acid groups but N,N-dialkyl substituted amide groups also.

To explain this possibility one can refer to the reaction of carbon dioxide with an excess of alkyllithium reagents[55(d)]. In this case the initially formed lithium salt reacts with the alkyllithium present in the system. Thus:



Furthermore, reactions of esters such as ethyl benzoate with reagents such as lithium diisopropylamide to produce N,N-dibenzylbenzamide have been reported[94].

It seems reasonable to suggest that the lithiated vinyltoluene will react with carbon dioxide as expected and the product is


10
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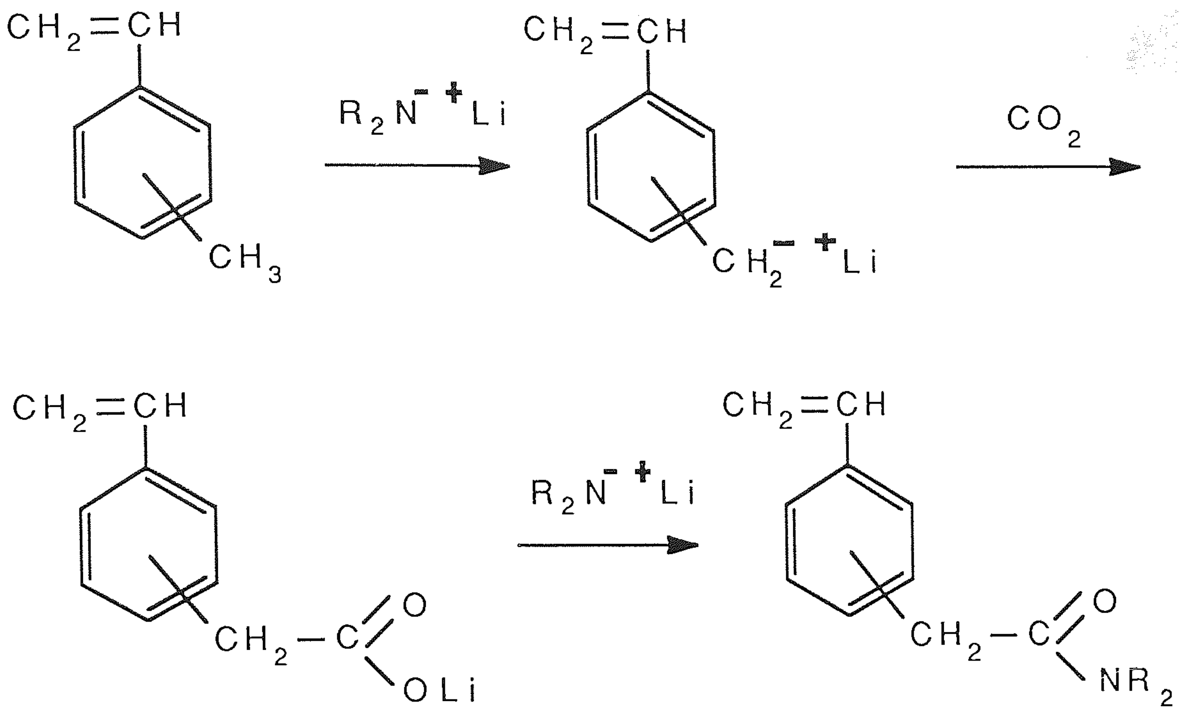
190
200
210

Figure 4.24

then attacked by unreacted lithium diisoproplylamide to form the amide

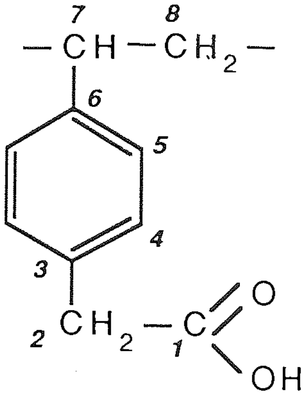


Conclusive evidence for the formation of the amide is not available from the IR analysis as although it seems likely that certain absorbances are due to the amide they could be masked by absorbances due to other groups such as the carboxylate anion or unreacted vinyltoluene. However, proof of the presence of an amide can be obtained by further analysis of the polymer sample by NMR.

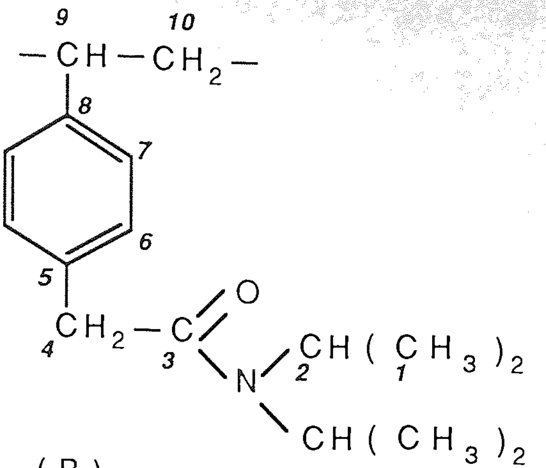
NMR analysis

The polymer product was analysed by NMR in the solid state and the spectrum obtained is shown in figure 4.24.

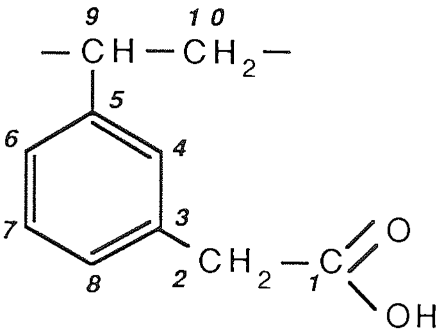
^{13}C NMR was used to detect the number and type of non equivalent carbon atoms in the sample. Assuming that some amide was formed the expected products are shown below.



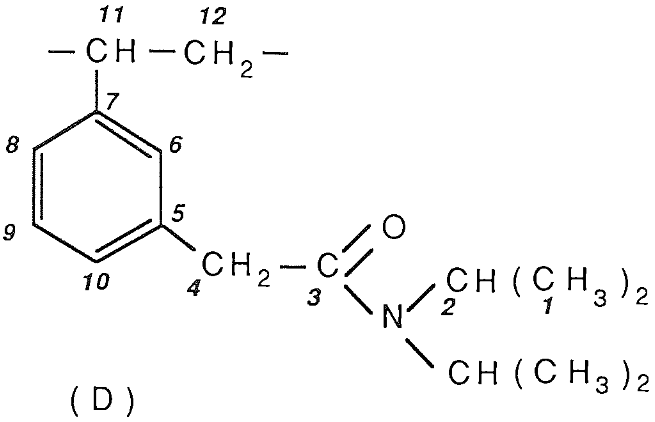
(A)



(B)



(C)



(D)

The non equivalent carbon atoms in each product are numbered. A detailed analysis of the NMR spectra of the above structures is shown in tables (O), (P), (Q), (R) in appendix. 1 It is pertinent here to extract from this data the fact that an amide is expected to show a signal between 162 and 179 ppm from TMS.

Analysis of the polymer sample confirms the presence of a peak with a chemical shift of 165 δ which is possibly due to an amide carbonyl group. In addition, there is a chemical shift at 20 δ which is possibly due to CH_3 and CH groups attached to the nitrogen atom in an amide. Nevertheless, this shift could also be accounted for by unreacted vinyltoluene since the pendant methyl group has an expected chemical shift of 21 δ. There is also some carboxylic acid presence in the polymer sample due

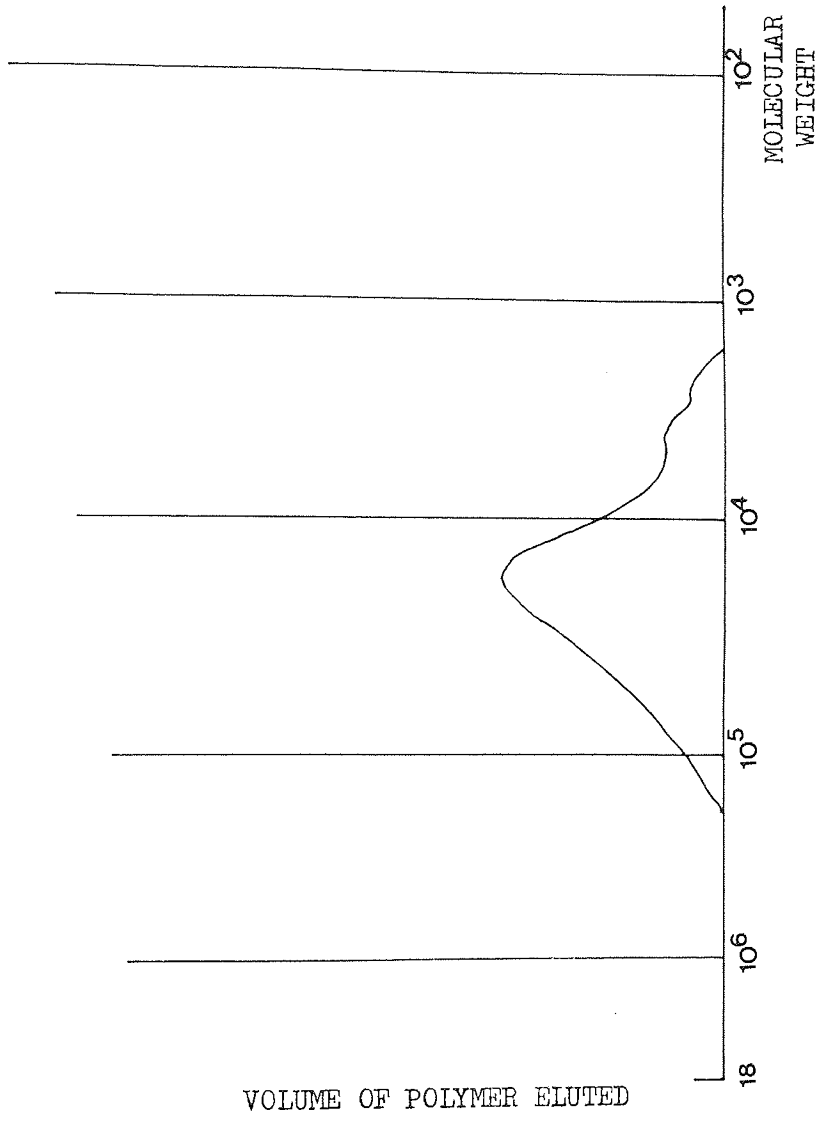

MOLECULAR WEIGHT
10^2
10^3
10^4
10^5
10^6
18
VOLUME OF POLYMER ELUTED

Figure 4.25

to the shift at 181 δ. It appears that only some of the carboxylic acid was converted to amide which correlates well with IR evidence; the IR spectrum of the polymer possessed absorbaces due to both the acid and the amide. The presence of a shift at 46 δ confirms the presence of the CH_2 group in the polymer chain. However, the shift at 39 δ could be due to either the CH group in the polymer chain or a CH_2 group attached to an amide or a carboxylic acid group.

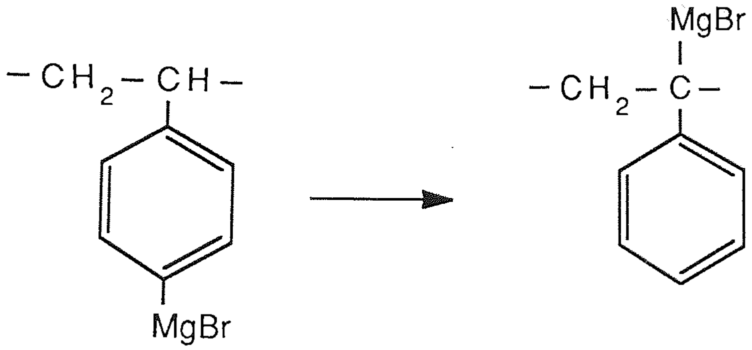
GPC analysis

The polymer sample was analysed as a 2% solution in THF. The chromatogram is shown in figure 4.25. The polymer sample had a weight average molecular weight ($\bar{M}_w$) of 16000 and a number average molecular weight of 7500 with a polydispersity of 2.1. On comparison of these molecular weight averages with those of PVT ($\bar{M}_n$ = 16200 and $\bar{M}_w$ = 34200) it is seen that they are greatly reduced in value.

4.3 Discussion and conclusions

The evidence suggests that both Grignard and lithiation reactions carried out on polymers derived from substituted styrene monomers were successful but complications occurred due to rearrangement in the case of the Grignard reactions and difficulties in controlling and ascertaining the reaction site in the case of lithiation.

The IR evidence indicates that a Grignard reagent may be formed by reaction of magnesium with the pendant bromine atom of 4-bromostyrene resulting in a decrease in the intensity of the absorbance due to the C-Br bond. However, other evidence suggests that once formed the Grignard rearranges to form a more stable species in a reaction of the following type:



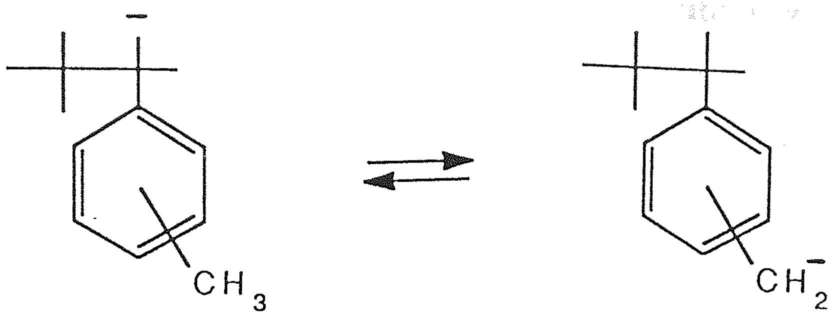
(A) (B)

The reaction is feasible as derivative (B) is more stable than derivative (A); in derivative (B) the charge on the carbon attached to the magnesium or the lone electron of any free radical character can be delocalised around the ring by the resonance effect. However, this type of delocalisation cannot occur in (A) since the charge is associated with one of the ring carbon atoms. The formation of derivative (B) may give rise to chain scission and degradation of the polymer by the sequence of reactions shown in figure 4.6. All the experimental evidence correlates well with this theory of rearrangement and degradation.

Furthermore, the rearrangement of the Grignard appears to occur before subsequent reactions with carbonyl groups and therefore the reaction products were the same irrespective of the reagent used following Grignard formation, i.e. reduced molecular weights and no functional group formation.

When poly(vinyltoluene) was functionalised via lithiation, the metallation route produced a very reactive centre on the polymer but it has to be said that it is very unlikely that each monomer unit in the chain could be reacted to produce a site for functionalisation. The reaction was further complicated by the fact that the metallation of a particular monomer unit could take place either at the backbone carbon atom or at the pendant methyl group of the monomer. Distribution between the products of carboxylation was impossible by IR analysis and extremely difficult by NMR. The assignment of the chemical shifts to ring and side chain carbon atoms was not possible with sufficient accuracy to distinguish between the various isomeric forms.

Such evidence as exists for the reaction of the metallated polymer with either CO_2 or an ester seems to be conflicting. In the case of reaction with CO_2, carboxylation of the carbon backbone appears to take place, whereas reaction with ethyl formate suggests that the site of reaction is the methyl group attached to the benzene ring. One possible explanation to account for this difference is the fact that an equilibrium might exist between these two forms or proton migration may occur.



Furthermore, reaction with ethyl formate was difficult to control; an excess of the ester was used in order to terminate the reaction at the aldehyde stage. However, it was virtually impossible to prevent reaction from going to completion and forming a secondary alcohol.

The synthesis of a functionalised polymer can be approached in two ways:

(i) the functionalisation of a simple polymer

and

(ii) the synthesis of a monomer containing a functional group and its subsequent polymerisation.

Hence functionalisation of vinyltoluene monomer was also attempted via lithiation and carboxylation. In this case, however, lithium diisopropylamide was used as a lithiating agent since butyllithium, a more powerful nucleophile, would have attacked the vinyl group and caused polymerisation. Although some carboxylic acid was produced complications arose due to further reaction of the acid with the lithiating agent resulting in amide formation. Furthermore, although free radical polymerisation of the functionalised monomer did result in some polymer product, polymerisation was not as effective as with the original monomer due to the reactivity of the carboxylic acid or amide group. Free radicals are known to react with carbonyl groups and to complicate the conventional chain reactions that lead to high molecular weight polymers. It is concluded, however, that provided problems such as these can be overcome, the route involving polymerisation of a functionalsed monomer is more likely to show promise than that involving reactions of a random nature on a polymer.

CHAPTER FIVE

PREPARATION AND CHARACTERISATION OF POLYMERS WITH PROTECTED FUNCTIONAL GROUPS

5. Preparation and characterisation of polymers with protected functional groups.

5.1. Introduction

The work described previously in chapter four has shown that although the approach involving functionalisation of a polymer is theoretically suitable, it invariably suffers from a number of practical deficiencies. Amongst these are primarily the inability to control the site at which reaction takes place and the random distribution of reaction sites along a polymer. It was concluded that the key to the production of polymers possessing functional groups was to functionalise the monomer prior to polymerisation.

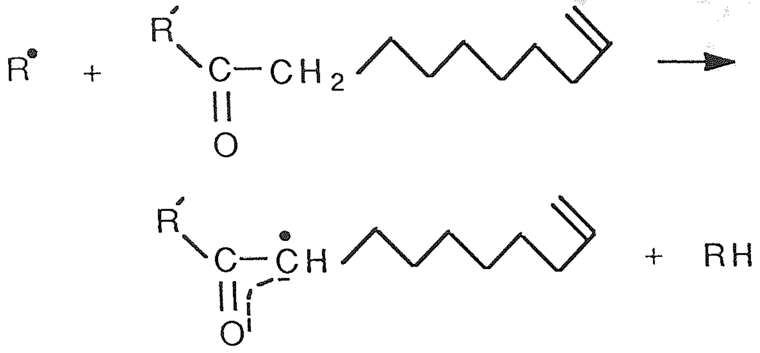
5.1.1. Anionic and free radical polymerisation of monomers with reactive functional groups.

It is often relatively simple to functionalise a monomer and purify it; analytical techniques are availabe to assess the purity of such materials. Problems have been incurred in the past when attempts have been made to polymerise these monomers because invariably the propagating centre preferentially reacts with the functional group to generate a stabilised free radical or to destroy the potentially propagating centre in anionic polymerisation.

5.1.1.1. Carbonyl groups

A useful example of the above is the polymerisation of monomers containing carbonyl groups.

5.1.1.1.1. Free radical polymerisation

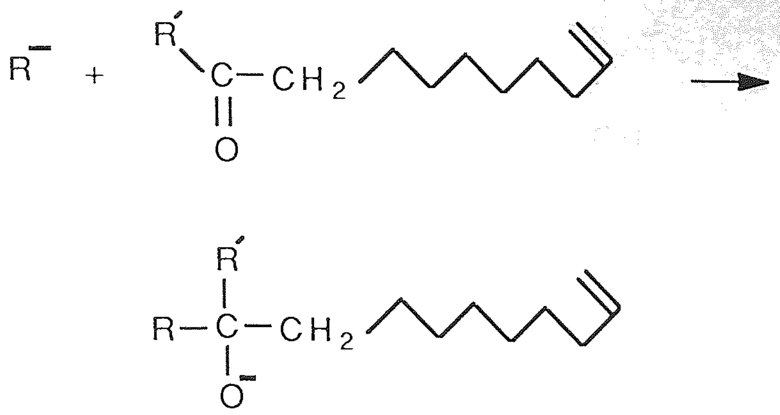


The free radical R• abstracts a hydrogen atom from the monomer resulting in a free radical that is stabilised by delocalisation over the carbonyl group.

Work has been carried out on the free radically initiated copolymerisation of styrene and 4-vinylbenzaldehyde [95]. It was observed that increasing the 4-vinylbenzaldehyde concentration decreased the solubility of the copolymer in organic solvents because crosslinking occurred at the CHO group by combination of stabilised radicals. In addition 4-vinylbenzaldehyde has been copolymerised with methyl methacrylate. It was found that the rate of free radical copolymerisation was slower than the rate of homopolymerisation of methyl methacrylate. Furthermore an increase in the initial concentration of 4-vinylbenzaldehyde decreased the molecular weight of the copolymer [96]. Both effects were ascribed to an increase in the rate of termination via degradative chain transfer.

5.1.1.1.2. Anionic polymerisation

When polymerisation or copolymerisation of such monomers has been attempted using anionic initiators, destruction of the active centre has taken place by reaction of the alkyl metal with the electrophilic carbonyl group.



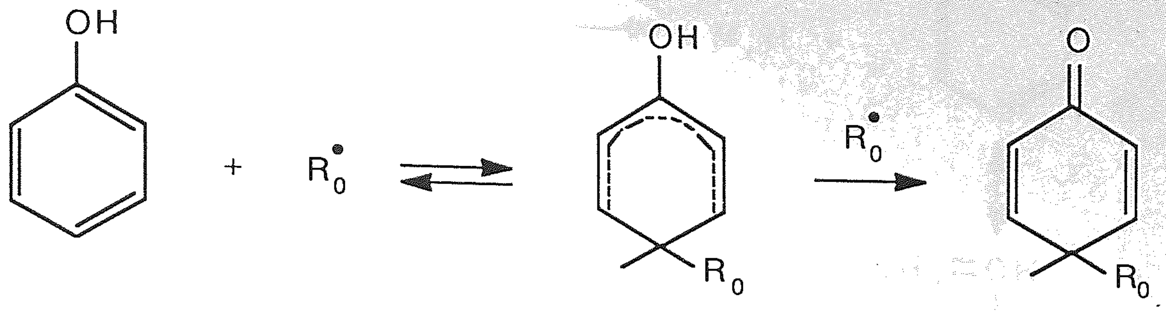
The alkoxide produced may inhibit reaction in two ways. Firstly it is not a sufficiently strong nucleophile to initiate further polymerisation and secondly it may complex with any excess alkyl metal present preventing any further intiation by the alkyl metal. The presence of lithium t-butoxide in the butyllithium initiated polymerisation of styrene is known to retard polymerisation [97, 98].

5.1.1.2. Hydroxyl groups

The hydroxyl group may occur in a monomer either as a phenol in aromatic monomers or an alcohol group in other monomers. In the case of free radical polymerisation the phenolic monomers will be discussed in detail whereas in anionic polymerisation both phenolic and alcoholic OH groups will be important.

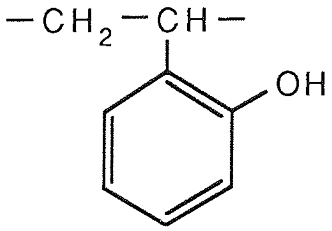
5.1.1.2.1. Free radical polymerisation

Work has been carried out on the free radical polymerisation of o-hydroxystyrene (OHS). It was found that the benzoyl peroxide initiated polymerisation of OHS resulted in very slow polymerisation. Phenol has also been shown to react with the peroxy radical ($R_O^{\bullet}$) in the following manner : [99].

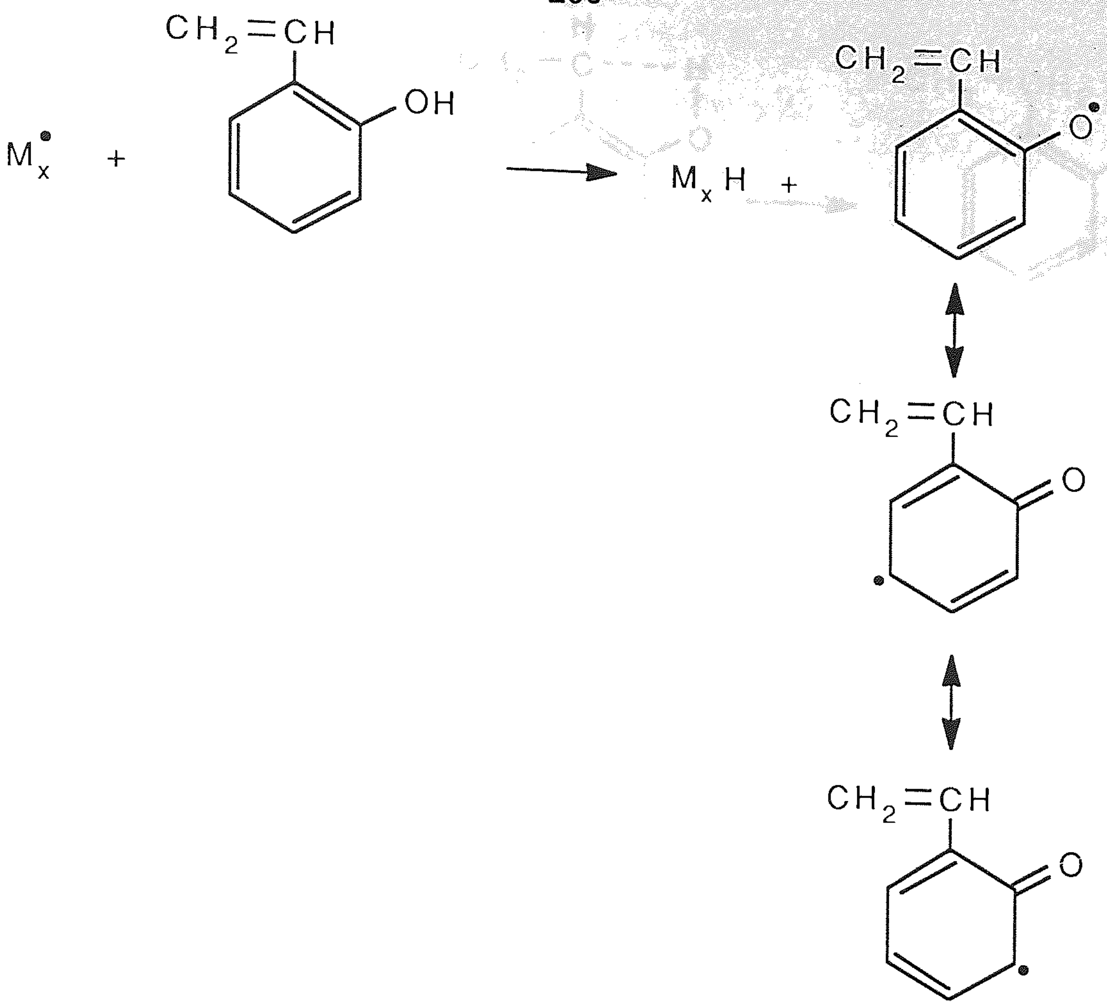


The first step of the reaction is the reversible formation of a loose molecular complex between phenol and $R_0^{\bullet}$. This complex is then destroyed by reacting with a second $R_0^{\bullet}$ radical. A similar reaction is thought to occur between benzoyl peroxy radicals and OHS thereby decreasing the initiating action of benzoyl peroxide markedly. Normal free radical vinyl addition polymerisation is virtually inhibited because the peroxy radical can add to the vinyl monomer in the above way [99].

Polymerisation of OHS has also been carried out using azobisisobutyroniltrile (AZBN) and Kato et al suggested that the polymer is produced by a normal free radical mechanism resulting in the following product.



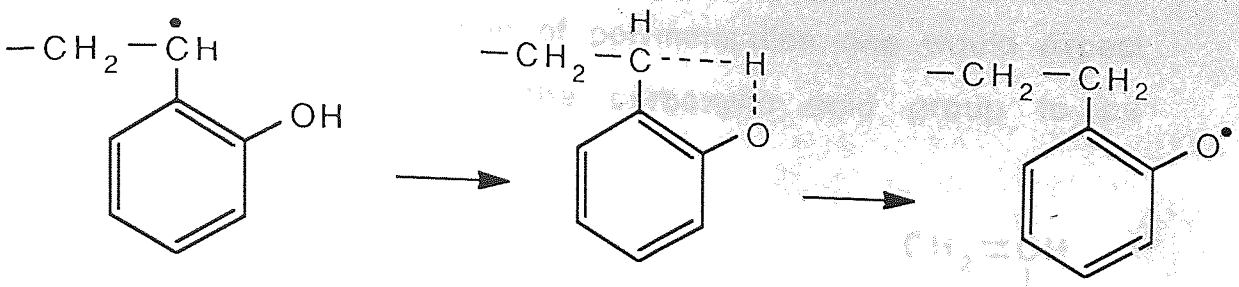
However, the molecular weights of the polymers produced were not as high as for the homopolymerisation of styrene [100]. Such results indicate that degradative chain transfer may occur. A possible chain transfer mechanism to the OHS monomer is illustrated below: [100, 101]



A growing radical $M_x^\bullet$ attacks the hydroxyl group of the monomer abstracting a hydrogen atom. The free radical thus produced should be resonance stabilised and reluctant to generate active polymer chain radicals by adding to a monomer molecule. Such radicals eventually disappear by combination with other growing radicals or with each other. In this way they behave, in effect, as inhibitors.

Termination of $M_x^\bullet$ by transfer to the phenol nucleus may also occur to a small extent.

One other way, however, in which chain transfer may take place is by the intra-molecular mechanism shown below.[101]



The radical product is again stabilised by resonance.

In contrast to the above reports Still and Whitehead investigated the AZBN initiated polymerisation of hydroxystyrene and suggested that this monomer does not polymerise through a free radical mechanism but by an ionic mechanism involving self initiation to produce a low molecular weight polymer [102].

5.1.1.2.2. Anionic polymersation

In the case of anionic polymerisation of a monomer containing an OH group, attack by the alkyl metal results in the formation of an alkoxide by hydrogen abstration [55(g)]. The presence of an alkoxide in an anionic polymerisation system has been discussed above.

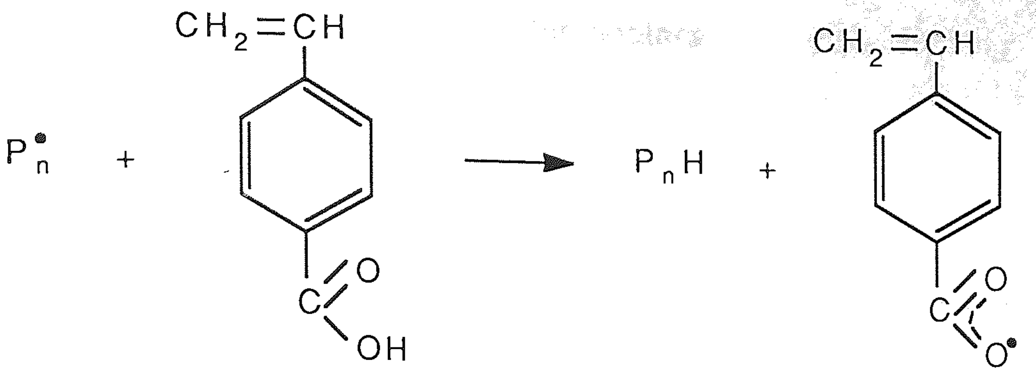
5.1.1.3. Carboxylic acid groups

5.1.1.3.1. Free radical polymerisation

Carboxylic acids such as methacrylic acid can be polymerised comparatively easily by free radical methods [103].

4-vinylbenzoic acid has been polymerised free radically. Studies have been made of the free radical copolymerisation of this monomer with acrylonitrile, styrene and acrylic acid [104].

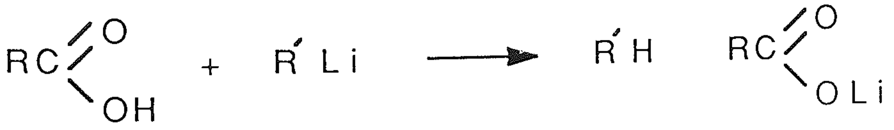
Nevertheless, in this type of polymerisation one would expect the hydrogen atom of the carboxylic acid group to be susceptible to transfer reactions.



The product is a stabilised free radical and depending on the structure of the monomer, the rate of re-initiation might be quite slow.

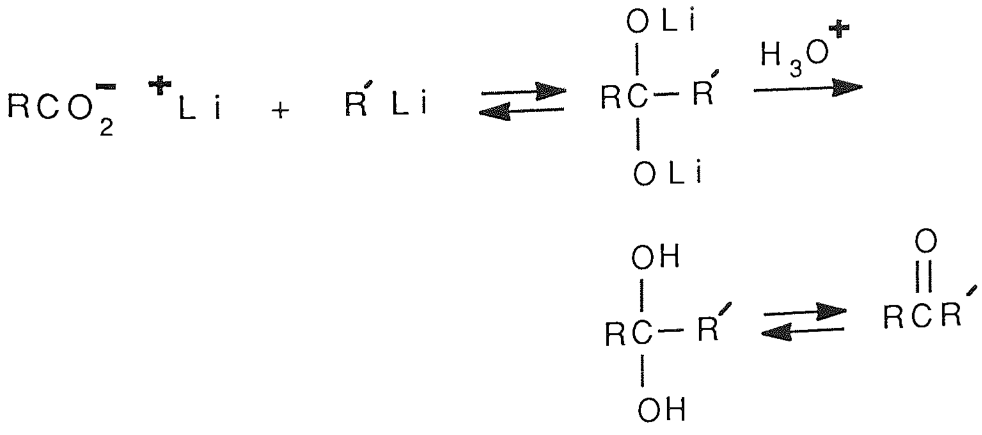
5.1.1.3.2. Anionic polymerisation

The carboxylic acid group is attacked by an anionic polymerisation initiator resulting in the formation of the carboxylate anion and the destruction of the propagating or initiating centre. The reaction is exemplified below:



$$RCOOH + R'Li \longrightarrow R'H \quad RCOOLi$$

However, when there is an excess of the organolithium reagent a ketone may be formed by further reaction between lithium carboxylate and the excess organolithium [105]



$$RCO_2^- \, ^+Li + R'Li \rightleftharpoons RC(OLi)_2-R' \xrightarrow{H_3O^+} RC(OH)_2-R' \rightleftharpoons RCOR'$$

In conclusion species involved in the initiation of anionic polymerisation react with the carboxylic acid functional group to give products which are not capable of continuing the polymerisation and thus act as terminators.

5.1.1.4. Esters

Amongst the functional groups, the ester group is an anomolous group in that it normally does not interfere with the propagating free radical chain and in selected cases does not drastically affect the propagation reaction in an anionic polymerisation.

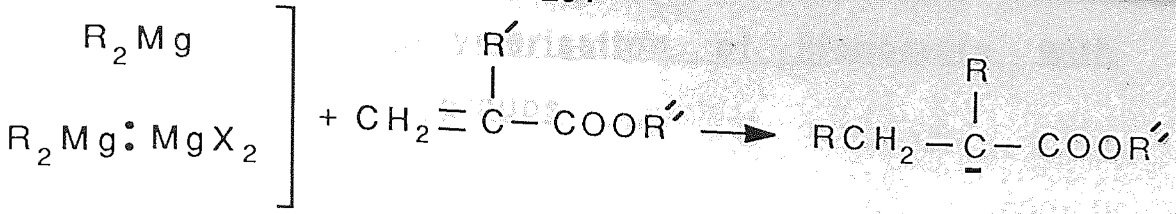
5.1.1.4.1. Free radical polymerisation

The free radically initiated polymerisation of unsaturated esters, such as methyl methacrylate, is a well documented polymerisation process and is often quoted as a typical example of a free radical polymerisation.[103]

5.1.1.4.2. Anionic polymerisation

Esters such as methyl methacrylate can be polymerised anionically using Grignard reagents [106(a)] and butyllithium[106(b)].

Studies have been made of the polymerisation of methyl methacrylate using phenylmagnesium bromide as initiator[106(a)]. In this reaction it was assumed that initiation proceeded by a 3,4 addition of the Grignard reagent to the unsaturated ester to give a carbanionic intermediate:



$$\left.\begin{matrix} R_2Mg \\ R_2Mg\colon MgX_2 \end{matrix}\right] + CH_2{=}\overset{R'}{\overset{|}{C}}{-}COOR'' \longrightarrow RCH_2{-}\overset{R}{\overset{|}{\underset{-}{C}}}{-}COOR''$$

It was also assumed that only one aryl group from the initiator became attached to the polymer chain. Tritium labelled phenylmagnesium bromide was used to initiate the polymerisation. Number average molecular weights determined by polymer radioactivity correlated well with number average molecular weights determined by osmometry. This was interpreted as indicating that consumption of the Grignard only occurred by the normal conjugate addition to the monomer and not by reaction of the organometallic with the ester group.

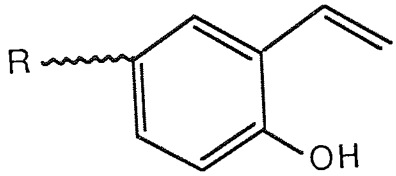
5.1.1.5. Other functional groups

In addition, work has been carried out regarding the free radical polymerisation of a monomer possessing an amine functional group. However, it was found that p-aminostyrene polymerised with great difficulty; only at 150°C was an appreciable formation of polymer observed[107]. The polymerisation of p-dimethylaminostyrene has also been investigated and it was found that this monomer polymerised more readily at 120 - 130°C than p-aminostyrene but with an increase in temperature to 150°C decomposition of the substance with evolution of volatile lower aliphatic amines was observed.

To date there have been no references cited in the literature concerning the anionic polymerisation of monomers possessing amine groups.

5.1.2. Cationic polymerisation of monomers with reactive functional groups

The free radical and anionic polymerisation of monomers containing functional groups has been discussed. However, some monomers, possessing electron donating groups, lend themselves to cationic polymerisation. For example, hydroxystyrene can be polymerised cationically using borontrifluoride etherate (BF_3OEt_2) [108]. The polymerisation of p-hydroxystyrene takes place through a normal vinyl polymerisation mechanism. However, with o- and m-hydroxystyrene, as well as the normal vinyl addition polymerisation occurring, Friedal-Craft type reactions take place between the propagating carbocation and the aromatic ring. Evidence from IR Spectroscopy is interpreted as producing structures of the following type:

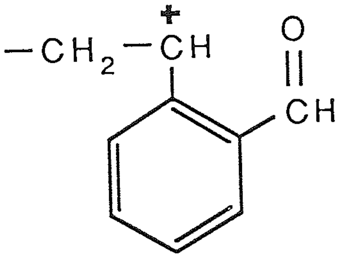


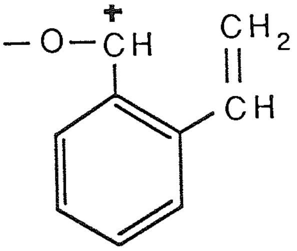
Other monomers which can be polymerised cationically are amines. However, in the case of initiation by Brønstead acids the amine group may undergo protonation i.e.

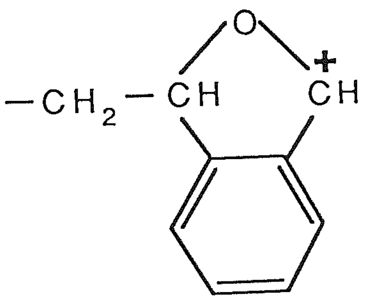
$$H^{+} + RNH_2 \longrightarrow R\overset{+}{N}H_3$$

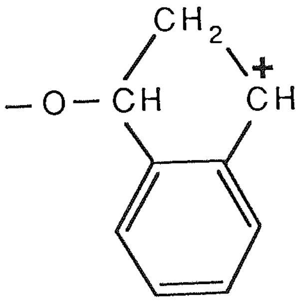
In the case of 4-vinylaniline, protonation suppresses the activation of the aromatic nucleus and thus the double bond. The reaction also serves to remove the cationic initiator species from the reaction system and reduce the rate of polymerisation.

The cationic polymerisation of 2-vinylbenzaldehyde initiated by BF_3OEt_2 has been investigated. [109]. On analysis of the polymer obtained it was found that it contained approximately 20% pendant vinyl groups and 5% aldehyde groups. It was therefore concluded that the rest of the monomer units were cyclised. On the basis of such structural data, a propagation scheme was proposed; it was thought that the neighbouring aldehyde reacted with the growing cation to form a cyclised unit and this type of intra-molecular cyclisation was competitive with inter-molecular propagation. Thus the following four structures can be conceived as the terminal carbonium ion:







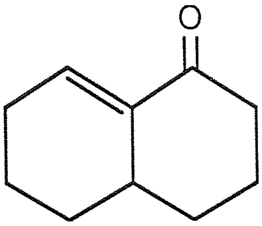


5.2 Protection of functional groups

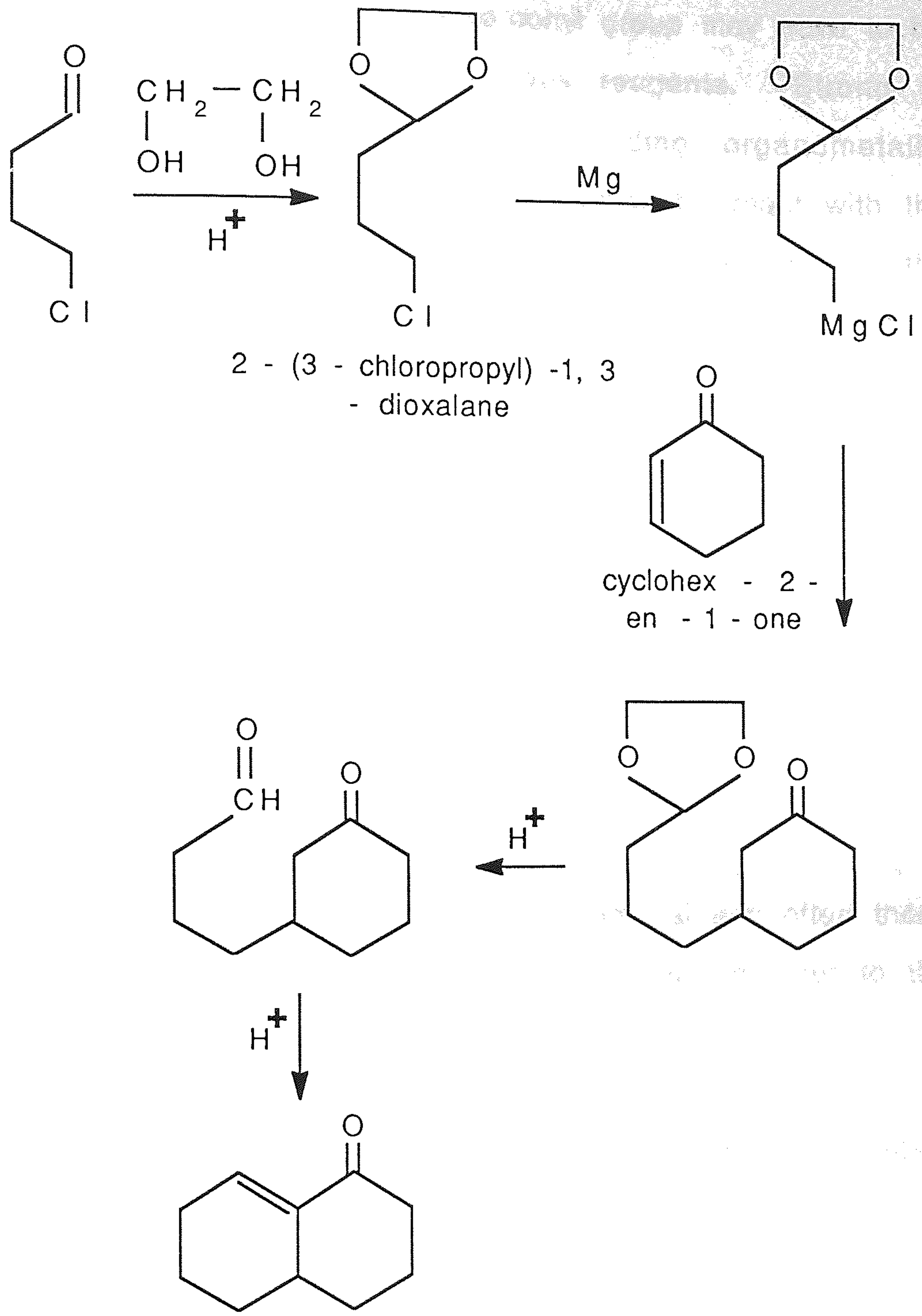
Interference of one functional group with the intended reactions of a second functional group is often encountered in organic synthesis. For example a Grignard reagent cannot be prepared from a haloalcohol owing to the incompatible presence of a carbon magnesium bond and acidic hydroxyl groups in the same molecule. In order to carry out this type of synthesis the interfering functional hydroxyl group must be protected. Protection involves three steps:

(i) formation of an inert derivative
(ii)carrying out the desired reaction
and
(iii) removal of the protecting group.

The advantage of protection of functional groups in synthesis is exemplified by the preparation of bicyclodec-[4,4,0]-8-en-1-one.



Use is made of an acetal which protects a carbonyl moiety in the following reaction scheme: [110]



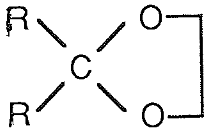
This reaction is only possible because the carbonyl group has been protected in the critical stages. There are various synthetic techniques used to protect specific functional groups and these are reviewed below.

5.2.1. Protection of a carbonyl moiety

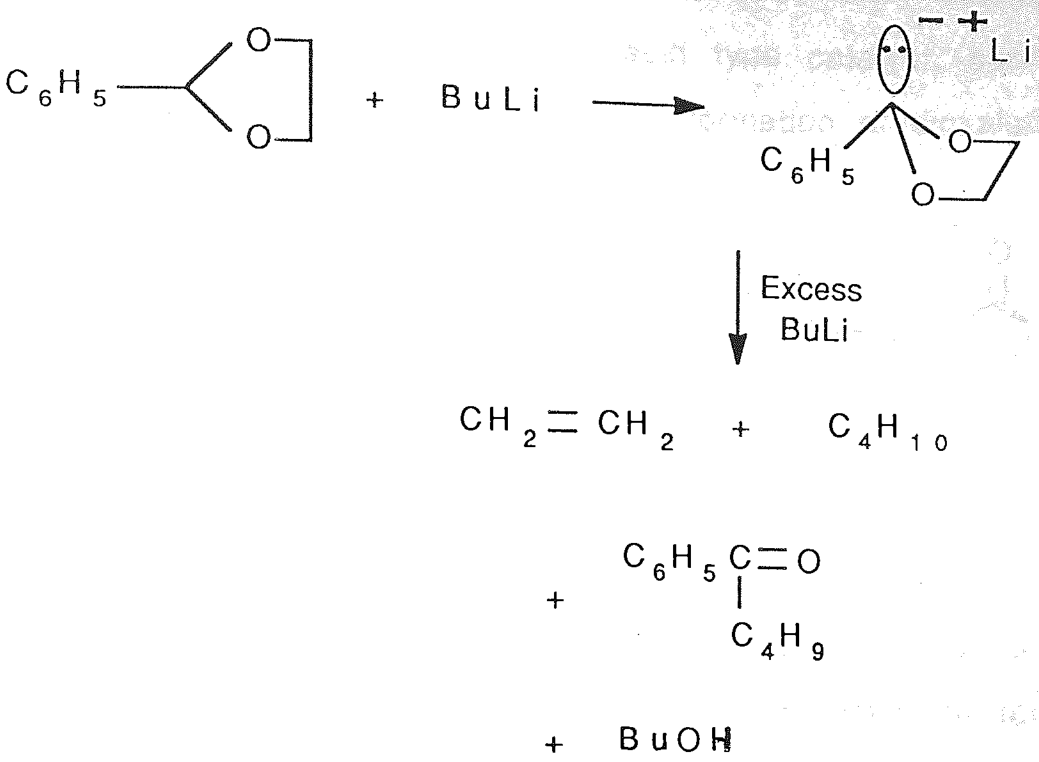
During a synthetic sequence a carbonyl group may have to be protected against attack by various reagents. Strong or moderately strong nucleophiles, including organometallic reagents, reducing agents and some oxidants, react with the carbonyl group. The most useful protecting groups are the acyclic and cyclic acetals and ketals and the acyclic and cyclic thio acetals and thio ketals. The protecting group is introduced by reacting the carbonyl compound with an alcohol, diol, thiol, or dithiol in the presence of acid. Cyclic and acyclic acetals and ketals are stable to nucleophiles, aqueous and non-aqueous bases, to hydride, neutral, and basic reduction and most oxidants. They are, however, cleaved by acid hydrolysis.

The carbonyl groups form a number of other stable derivatives such as hydrazones and oximes but they are less used owing to the greater difficulty involved in their removal and often these groups react with the nucleophile in a similar manner to the carbonyl group although more slowly.

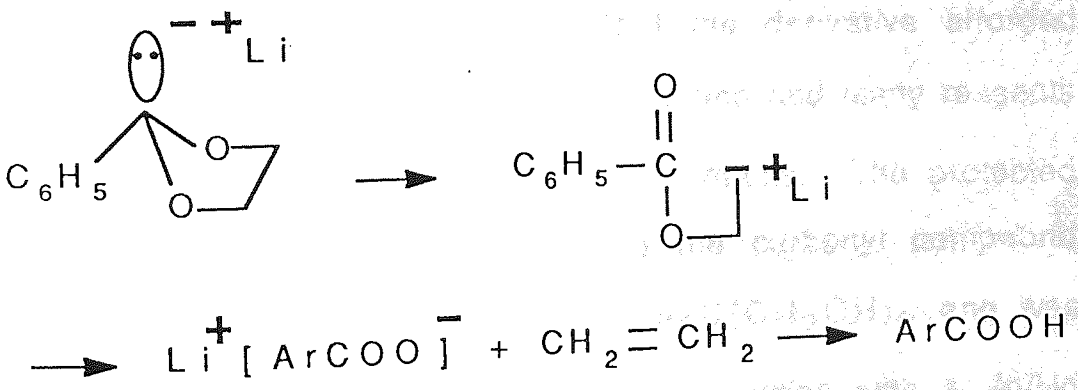
A specific example of an acetal employed as a protecting agent is 1,3,-dioxalane:



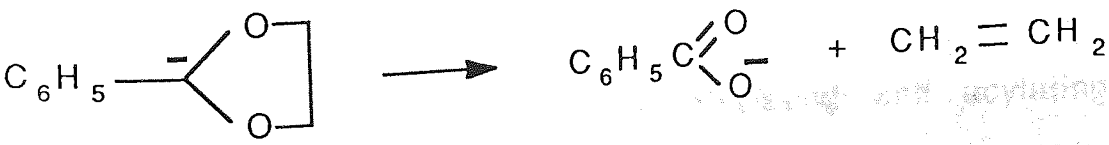
It is the most commonly encountered protecting group for aldehydes and ketones. It is stable to strong bases such as lithium diisopropylamide, potassium t-butoxide, to nucleophiles such as NH_3 and RNH_2, and to organometallic reagents[111]. However, the 1,3,-dioxalane may be cleaved when aromatic aldehydes are used. Such dioxalanes are vulnerable to attack by the removal of a labile benzylic proton [112] when reacted with a 3:1 excess of butyllithium



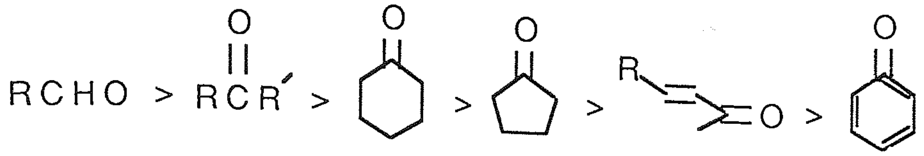
In the absence of an excess of butyllithium other products such as benzoic acid were observed i.e.



When 2-phenyl-1,3,-dioxalane is treated dropwise with phenyllithium in ether at room temperature ethylene is rapidly evolved according to the following reaction [113].



Dioxalanes are most commonly prepared by the reaction of the carbonyl group with ethylene glycol in the presence of an acidic catalyst. The water formed is removed azeotropically by a refluxing solvent immiscible with water, by slow distillation in vacuo, or by using a Lewis acid type catalyst, such as borontrifluoride [114]. The ease of formation of dioxalans is roughly in the order.



Variations in this order are experienced as a result of additional steric and electronic factors.

At the end of the reaction sequence 1,3,-dioxalane can be cleaved by acidic hydroysis. The ease of cleavage roughly parallels the ease of formation [114].

Work has also been carried out with regard to the protection of aldehydes and ketones as 5,5-dibromo-1,3-dioxane derivatives[115]. It was found that the derivative afforded protection against $NaBH_4$, peracids, diborane and many reagents with which the carbonyl group normally reacts. The protected derivative was prepared by reacting the carbonyl compound with 2,2,-dibromo-1,3-propanediol $Br_2C(CH_2OH)_2$ and was cleaved on completion of reaction by reduction with a Zn/Hg couple.

5.2.2. Protection of the hydroxyl moiety

Alcohols and phenols react with alkylating and acylating agents; they also react with other electrophiles e.g. primary and secondary alcohols may be oxidised and tertiary alcohols are susceptible to acid catalysed dehydration.

Although a large number of different protecting groups have been used for the protection of alcohols and phenols the most common examples fall into three main classes:

(a) ethers including trimethylsiloxy derivatives
(b) acetals and ketals
and
(c) esters

Generally the most useful method of protecting hydroxyl groups against reactions which proceed under acidic and neutral conditions is by formation of a carboxylate ester [114]. Acylation may be effected by treatment of the alcohol or phenol with the appropriate acid anhydride or acyl halide e.g.

$$\mathrm{ROH} + \mathrm{R'COCl} \xrightarrow{\mathrm{DMAP}} \mathrm{ROCOR'}$$

where DMAP = 4 - N N - dimethylaminopyridine

$$\mathrm{ArOH} + \mathrm{CH_3COCl} \xrightarrow[\mathrm{Bu_4N^{+}HSO_4^{-}}]{\mathrm{NaOH / dioxane}} \mathrm{ArOCOCH_3}$$

The removal of the carboxylate ester protecting group is usually brought about under basic conditions.

Another group which has been used to protect alcohols and phenols is the trimethylsilyl group. As will be seen later, this may find useful applications in anionic polymerisations. An important feature of the trimethylsilyl group is that it may both be introduced and removed under mild conditions. The most common method of formation is the reaction between the substrate and trimethylchlorosilane in the presence of pyridine[111].

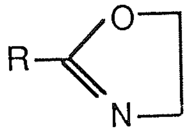
$$\mathrm{ArOH} \xrightarrow{\mathrm{Me_3SiCl\ /\ Py}} \mathrm{ArOSi(CH_3)_3}$$

The trimethylsilyl group is generally removed by heating a solution of the protected intermediate in aqueous methanol under reflux [114].

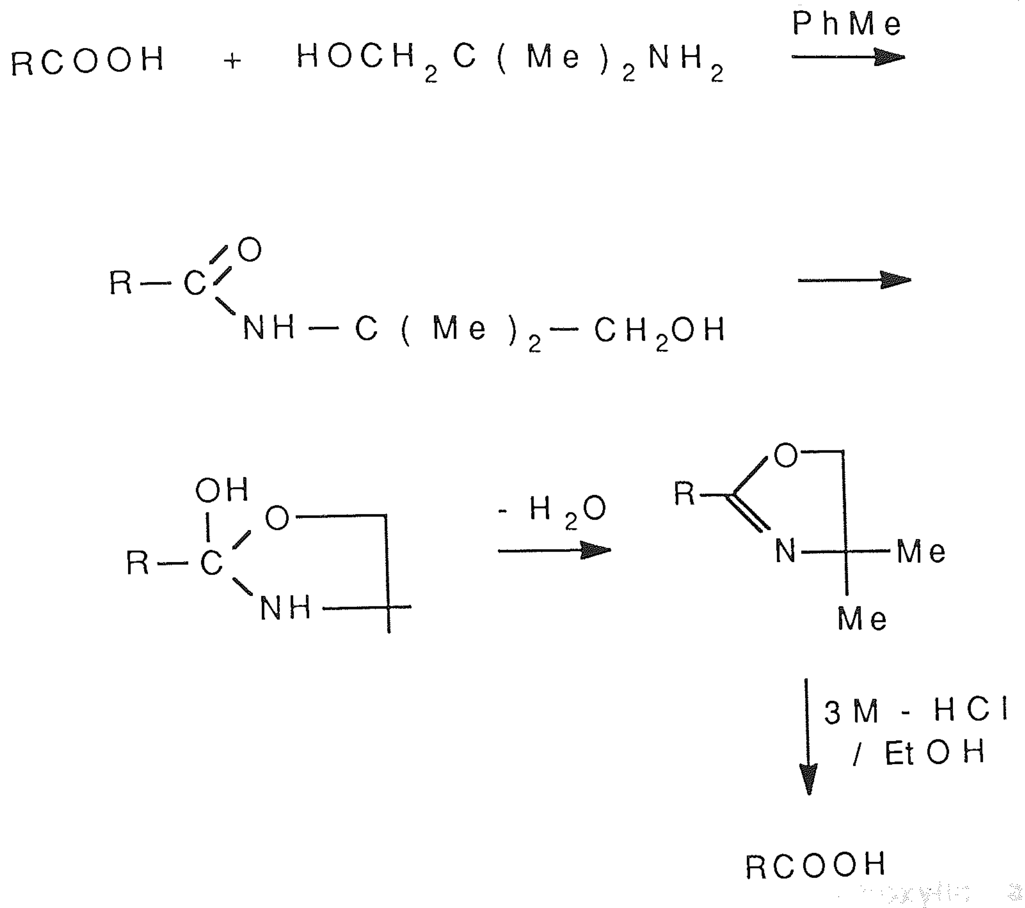
5.2.3. Protection of carboxylic acids

The carboxylic acid group is most readily blocked by the formation of an ester. There are various synthetic routes which may be employed in the formation of an ester. Some examples of these routes were reviewed in section 5.2.2.

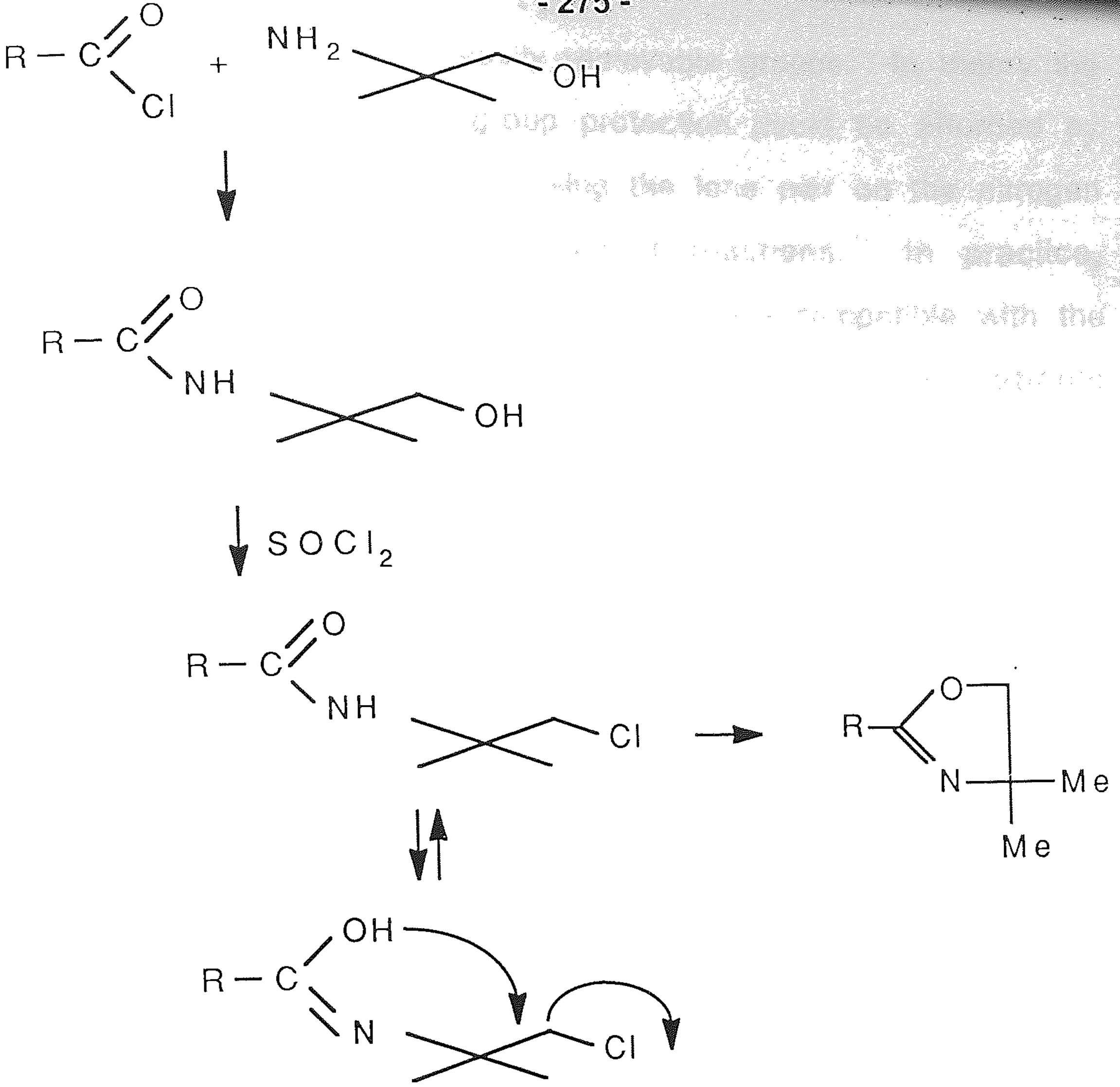
Another example of a group used to protect a carboxylic acid group is oxazoline [111] e.g. 2-alkyl-3-oxazoline



The formation and cleavage of this derivative is shown below[111]



The oxazoline ring can also be prepared by treatment of the acid chloride with the appropriate aminoalcohol followed by cyclisation of the amide in the presence of thionyl chloride.



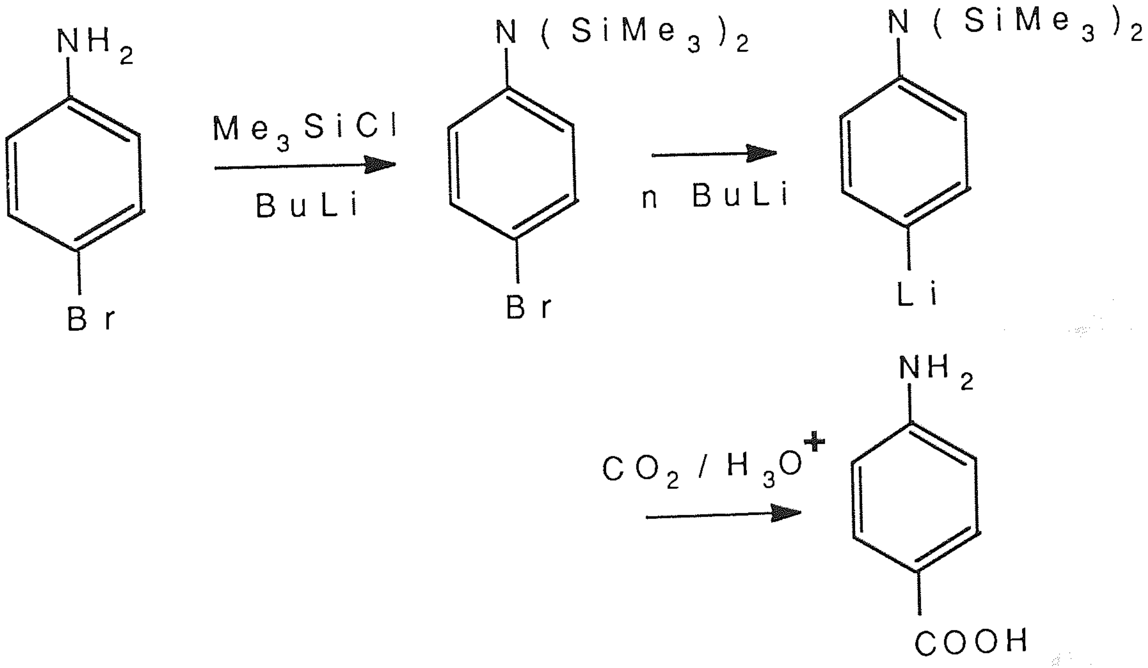
Oxazolines as masking groups for carboxylic acids are relatively inert to a variety of synthetic manipulations. Attack at the C=N link by organometallic reagents is slow; likewise it is resistant toward reduction by a variety of common reducing agents such as $NaBH_4$ and Li AlH_4.

The oxazoline can be hydrolysed to the carboxylic acid or ester in aqueous or alcoholic HCl [116].

5.2.4. Protection of the amine group

Primary and secondary amines are readily susceptible to oxidation and replacement reactions involving the N-H bond. Accordingly, in order to keep an amino group intact throughout reactions involving other parts of the molecule it is usual to protect these bonds by easily removable groups. In theory the simplest form of amino group protection could be afforded by protonation of the amine, utilising the lone pair on the nitrogen atom and preventing replacement reactions. In practice, however, very few synthetic sequences are compatible with the acidic conditions required. Indeed, during cationic polymerisation intiated by a mineral acid, protection is often required against protonation.

Another form of protection often used for amine groups is the trimethylsilyl group. This group is used as a blocking agent in reactions of the following type [114]

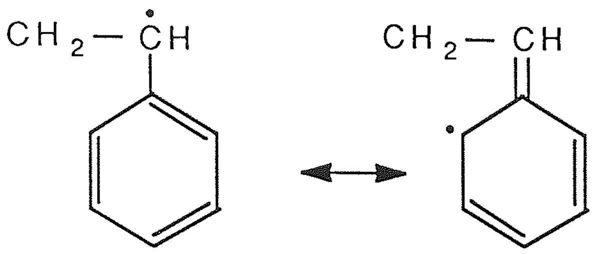


Thus the trimethylsilyl moieties block the amine nitrogen atom to the effects of n-butyllithium under the reaction conditions yet allow the more selective halogen-metal exchange to produce a highly reactive organolithium reagent.

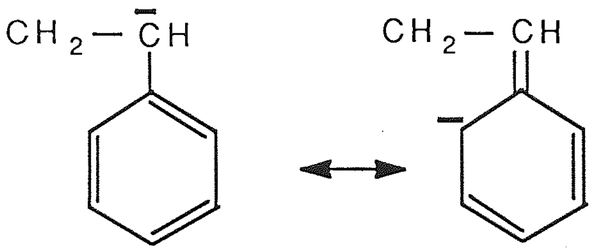
The trimethylsilyl derivative is formed by treating the amine with butyllithium followed by chlorotrimethylsilane. On completion of reaction the trimethylsilyl derivative is removed by acidic hydrolysis. Since the group is particularly prone to hydrolysis the trimethylsilyl group is an effective protecting group in anhydrous and non acidic conditions [111, 114].

5.3. Polymerisation

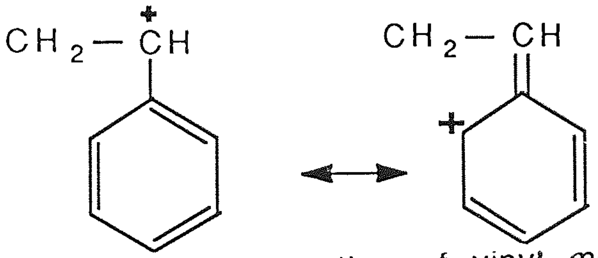
Styrene and certain of its derivatives may be polymerised free radically, anionically and cationically. In each case the propagating centre may be stabilised by delocalisation of the charge or unpaired electron over the conjugated benzene ring, thus:



etc .



etc .



etc .

The free radical polymerisation of vinyl monomers has been discussed in detail in chapter three. The cationic polymerisation of vinyl monomers is beyond the scope of this work but the anionic polymerisation of styrene derivatives has formed a substantial part of this work.

5.3.1. Anionic polymerisation

The polymerisability of a monomer using anionic initiators depends greatly on the group (R) in the vinyl monomer CH_2 =

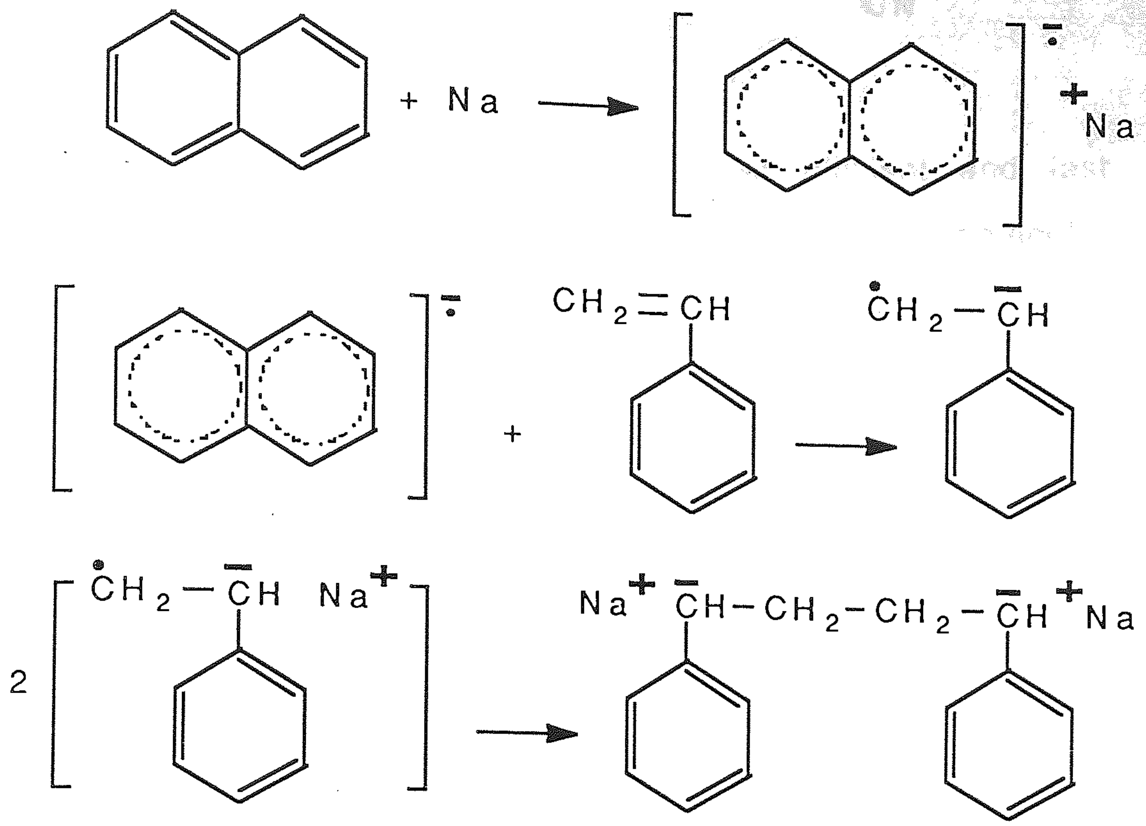
CHR. In free radical polymerisation benzene ring substituents such as electron donating methyl groups or the electron withdrawing bromine group have little effect. In contrast, the stability of the carbanion is generally enhanced when there is a combination of advantageous resonance and inductive effects. Bromostyrene is particularly suited to anionic polymerisation since the propagating carbanion can be stabilised by the resonance effect of the benzene ring which is enhanced by the inductive effect of the bromine group.

Anionic polymerisation proceeds by a chain mechanism and can be dealt with under the general headings of initiation, propagation and termination.

5.3.1.1. Initiation

The anionic polymerisation of styrene may be initiated by an electron transfer process as promoted by sodium/naphthalene complexes in THF or alkyl metal compounds. The initiation sequences can be summarised therefore as:

(i) electron transfer

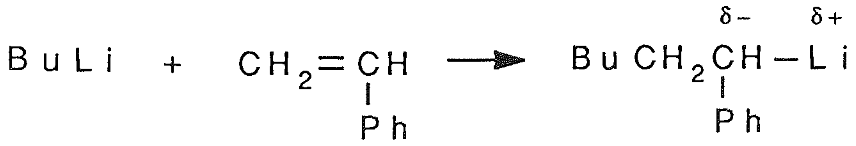


and

(ii)

$$(BuLi)_6 \rightleftharpoons 6\ BuLi$$

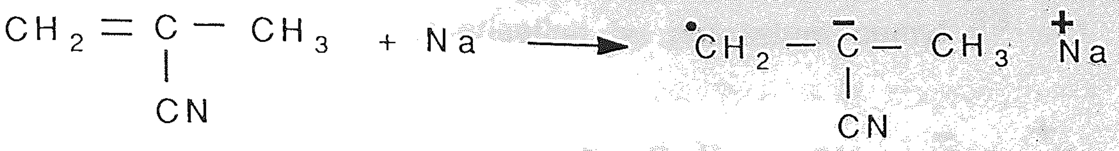
then:



$$BuLi + CH_2{=}\underset{\displaystyle Ph}{CH} \longrightarrow Bu\,CH_2\overset{\delta-}{\underset{\displaystyle Ph}{CH}}-\overset{\delta+}{Li}$$

One electron transfer initiation

Thermodynamically the initiation of styrene polymerisation by one electron transfer from sodium is effectively catalysed by the naphthalene molecule. Metallic sodium can be used as an initiator, particularly for monomers such as methacrylonitrile:



$$\mathrm{CH_2{=}\underset{\displaystyle CN}{\underset{|}{C}}{-}CH_3 + Na \longrightarrow {}^{\bullet}CH_2{-}\underset{\displaystyle CN}{\underset{|}{\bar{C}}}{-}CH_3\ \overset{+}{Na}}$$

but the use of naphthalene ensures an efficient and fast initiation process which is essential if narrow molecular weight polymers are required. The initially formed radical anions readily dimerise to form a propagating dianion.

Two electron transfer reaction

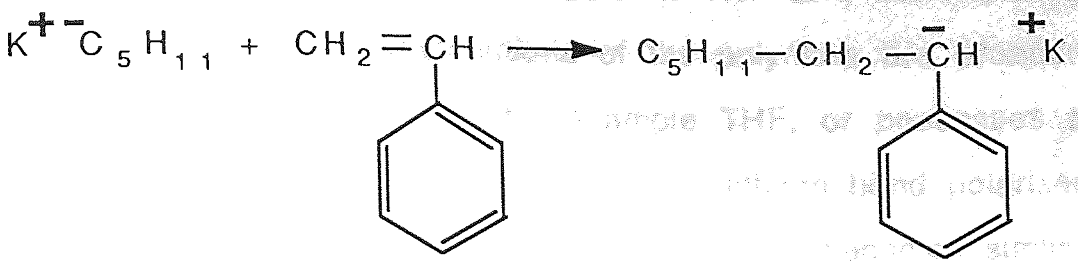
The initiation of styrene polymerisation by alkyl metal compounds can be considered to be a two electron transfer process. In this type of mechanism a suitable initiator is required which provides a sufficiently strong nucleophile to add to the carbon-carbon double bond of the monomer. The alkyl metal initiators of this type fall into two classes. Firstly there are the organolithium compounds and secondly the metal alkyl compounds of the other group 1 metals. The distinction between lithium and the other alkali metal alkyls arises from the fact that alkyllithium compounds may exist in the covalent as well as the ionic form, which is the form in which the other alkali metal alkyls exist. Such two electron transfer may be described more fully as:

$$\overset{-}{\mathrm{R}}\ \overset{+}{\mathrm{Mt}} + \mathrm{M} \longrightarrow \mathrm{R}{-}\overset{-}{\mathrm{M}}\ \overset{+}{\mathrm{Mt}}$$

$$\overset{\delta-}{\mathrm{R}}{-}\overset{\delta+}{\mathrm{Mt}} + \mathrm{M} \longrightarrow \mathrm{R}{-}\overset{\delta-}{\mathrm{M}}{-}\overset{\delta+}{\mathrm{Mt}}$$

Ionic initiators

An example of the first type of initiator mechanism is the initiation of styrene polymerisation by potassium cumyl [33]

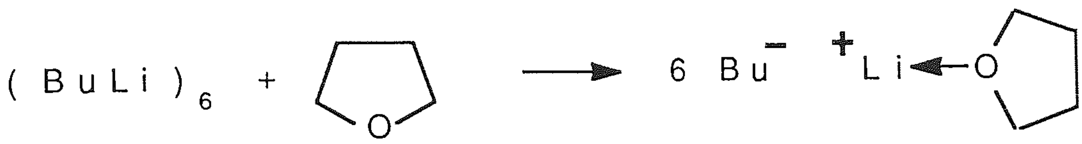


The gegen ion Mt^+ may be inorganic or organic and other examples of this type of initiator include sodium alkyls, KNH_2 and Grignard reagents. If the monomer has a strong electron withdrawing group then only a weakly positive initiator (Grignard) is required for polymerisation e.g. the polymerisation of methyl methacrylate may be initiated by a Grignard reagent. However, when the side groups are phenyl groups or the electronegativity is low a highly electropositive metal initiator such as a potassium or sodium compound is needed.

Covalent/dipolar initiators

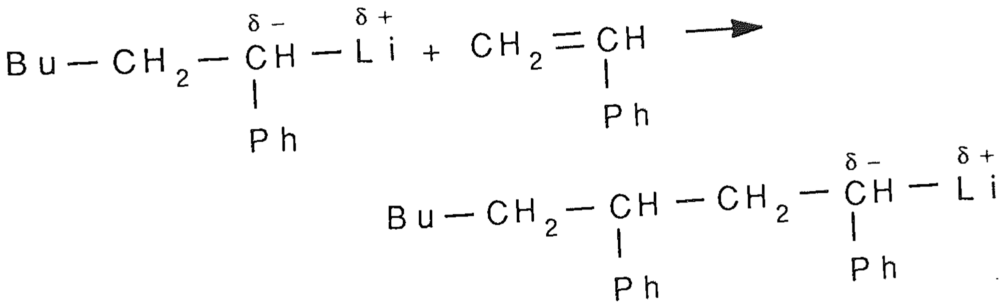
Organolithium compounds such as n-butyllithium are examples of covalent/dipolar initiators.

However, kinetic analysis of the reactions shows that initiation is not a simple function of the bascity of R, owing to the characteristic tendency for organolithium compounds to associate and form tetramers and hexamers [105]. The kinetics of initiation and polymerisation are usually complicated by this feature which is solvent dependent [55(h)] and consequently fractional reaction orders are commonly found for both rate dependences. The fractional orders of reaction are particularly prevalent in non polar media such as hydrocarbons. In these instances the rate of initiation is not fast when compared with the initiation by sodium naphthalide in THF and consequently the molecular weight distributions of the polymers are broader. When the solvent is polar, for example THF, or possesses a donor atom, such as dioxane, the carbon-lithium bond polarises to form ions and the behaviour of the initiator becomes similar to the behaviour of alkai metal alkyl initiators i.e. fast initiation rates occur resulting in narrow molecular weight distribution polymers. The lone pairs of electrons of the oxygen atoms in THF and dioxane are responsible for cleaving the hexamer and tetramer complexes. Thus:



5.3.1.2. Propagation

Whether the initiator step has led to a monanion or dianion propagation takes place by the further addition of monomers to the growing chain either by insertion of the monomer into the carbon-metal bond or by addition of the anion to a monomer molecule.



$$\mathrm{Bu-CH_2-\underset{Ph}{\overset{\delta -}{CH}}-\overset{\delta +}{Li} + CH_2{=}\underset{Ph}{CH} \longrightarrow Bu-CH_2-\underset{Ph}{CH}-CH_2-\underset{Ph}{\overset{\delta -}{CH}}-\overset{\delta +}{Li}}$$

5.3.1.3. Termination

Termination involves the destruction of the growing species possibly by recombination with the counterion or another species; carbanions are frequently neutralised by small quantities of water, alcohols, carbon dioxide and oxygen which act as effective terminating agents [32,33]. However, termination never involves the reaction between two growing chains as in the case of free radical polymerisation and in many instances termination does not take place at all resulting in the formation of "living" polymers.

5.3.1.4. Living polymers

One of the first "living" polymer systems studied was the polymerisation of styrene initiated by sodium naphthalide. This results in the formation of a dianion capable of propagating from both ends as described earlier.

$$Na^{+-}[PhCHCH_2CH_2CHPh]^{-+}Na$$

The validity of the assumption that in the absence of a terminating agent the carbanion remains intact and alive was demonstrated by (a) adding more styrene to the living polystyryl carbanions when an increase was observed in $\overline{M}_n$ and (b) by adding another monomer such as isoprene to form block copolymers.

5.3.1.5. Solvent and gegen ion effects

Effect of the gegen ion on stereochemistry

The gegen ion itself can influence the stereochemical course of the reaction. The stereoselectivity of the reaction decreases sharply with an increase in cation size and degree of coordination of the solvent. For example, polymerisation using organolithium or organosodium reagents is highly stereospecific in that predominantly the isotactic product is obtained

$$H{-}[CH_2CHR]_n{-}CH_2\bar{C}HR\ {}^{+}M$$

M = Li or Na

R = 2 - pyridyl

When the reaction, however, is carried out in the presence of "crowned" Na ions approximately equal proportions of isotactic and atactic products are obtained.[117] This suggests that when the counterion is small and the charge density on such an ion is high co-ordination of the monomer may take place prior to propagation. When this type of coordination takes place, if it is found to take place in a specific manner, then the propagation step would be expected to regenerate the propagating centre at each step producing a high isotactic content.

Effect of gegen ion and solvent on the rate of reaction

The interactions of the gegen ion with the solvent have an effect on the polymerisation rate. Smaller Li^+ ions can be solvated to a greater extent than larger ions and in general the more polar the solvent the greater its solvating power will be; as the solvating power decreases there is an increasing tendency for ion pairs to become the initiating species. Chain propagation will depend significantly on the separation of the ions and this separation will also control the mode of entry of an adding monomer. For example, the rate of propagation of polystyryllithium decreases as the dielectric constant of the solvating medium does [32]. This was also discussed in terms of initiation previously.

5.4 Applications to polymers

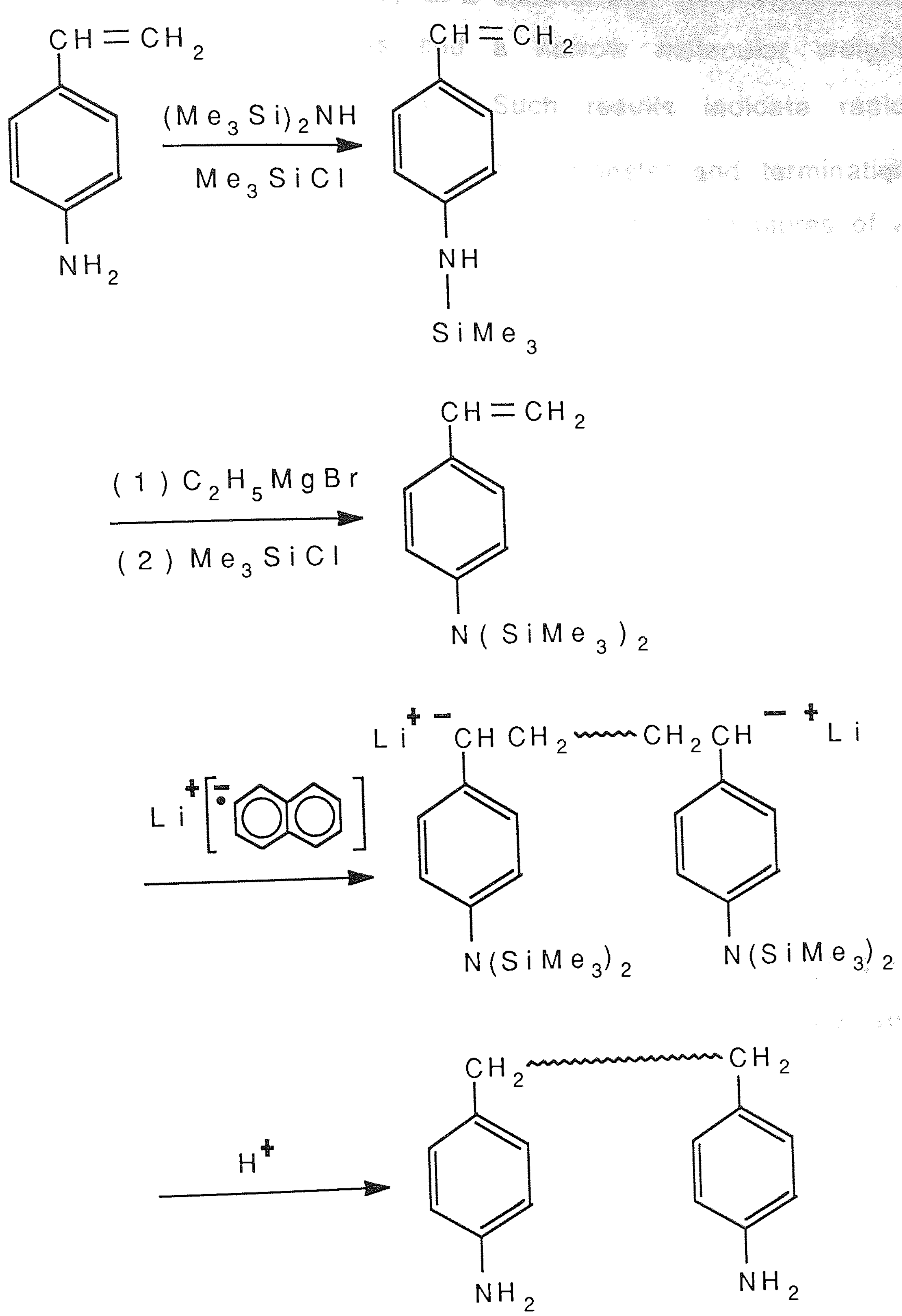
In view of the protection afforded by certain derivatives of specific functional groups to reagents such as organometallic compounds, new synthetic routes to functionalised polymers which were previously unsuitable and unsatisfactory can now be put into operation. There are recent reports in the literature where this concept has been applied to polymerisation procedures.

5.4.1. Protection of monomers

Work has been undertaken with regard to the anionic polymerisation of several protected functionalised monomers and these are discussed in detail below.

5.4.1.1. Anionic polymerisation of p-N,N-bis-(trimethylsilyl)aminostyrene.

Previously p-aminostyrene had been polymerised free radically which was discussed earlier. However, dificulties were encountered using this method and there are no references cited regarding the anionic polymerisation of this monomer. However the amino-protected monomer p-N,N-bis-(trimethylsilyl)aminostyrene was successfully polymerised anionically initiated by lithium naphthalide in THF [118]. A summary of the preparation and polymerisation of the protected monomer is given below



On completion of polymerisaion no cleavage of the trimethylsilyl protective group could be detected by NMR analysis. Furthermore, it was found that the nitrogen-silicon bond was stable in THF - methanol.

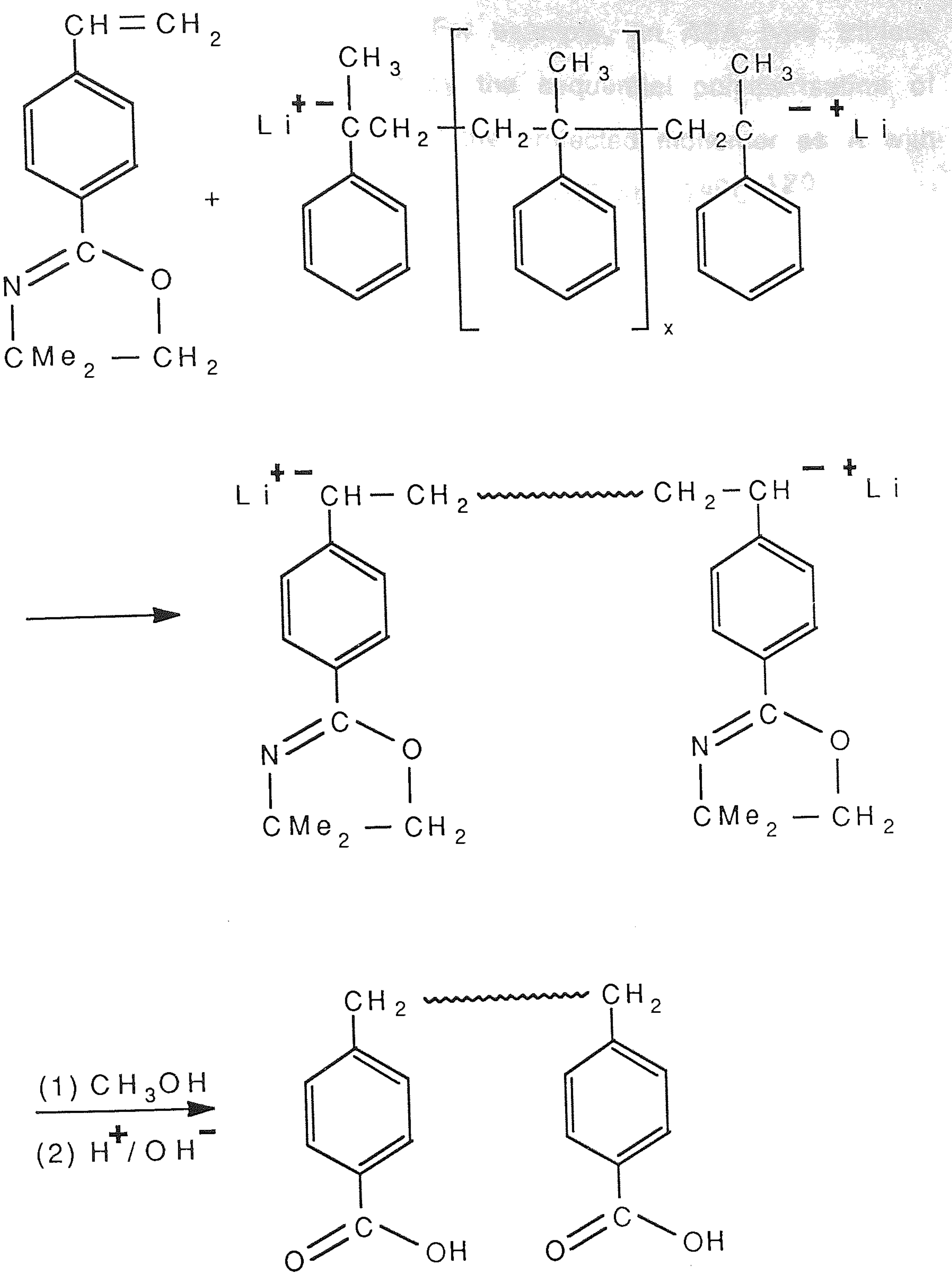
Analysis of the polymer by GPC showed that the polymers had high molecular weights and a narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n$<1.1). Such results indicate rapid initiation and the absence of chain transfer and termination reactions during the course of polymerisation, all features of a living polymerisation. Additional proof of a living polymerisation was provided by block copolymerisation of the protected monomer with styrene.

5.4.1.2. Anionic polymerisation of 2-(4-vinylphenyl) -4,4-dimethyl-2-oxazoline

Previously 4-vinylbenzoic acid had been polymerised free radically but it has been reported that a narrow molecular weight distribution was difficult to obtain using such methods because of the reactivity of the carboxyl group causing termination and chain transfer reactions[119].

However the protected monomer 2-(4-vinylphenyl)-4,4,-dimethyl-2-oxazoline was successfully polymerised anionically [119, 120].

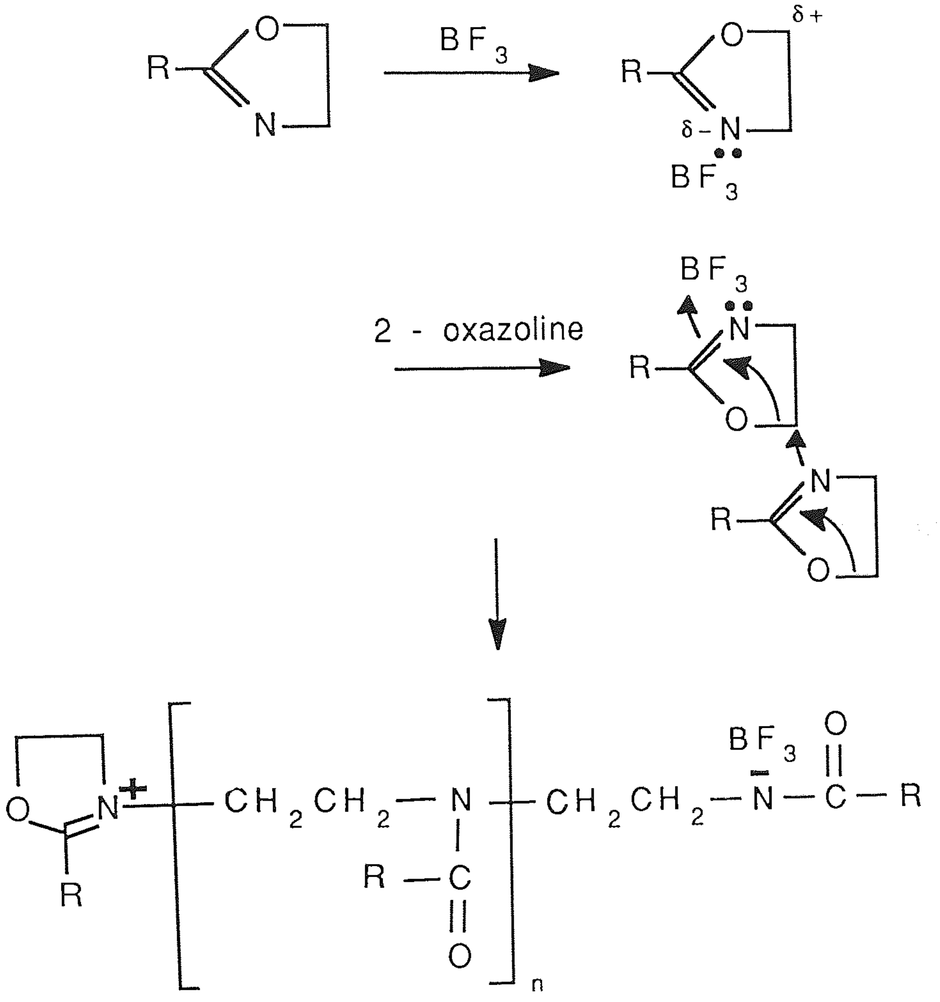
The oxazoline derivative was prepared by the reaction of 4 vinylbenzoyl chloride and 2-amino-2-methyl-1-propanol, followed by treatment with thionyl chloride to cyclise the corresponding oxazoline ring. Polymerisation was then carried out using an oligomeric (α-methylstyryl)dilithium as initiator i.e.



GPC analysis of the polymer product showed that the polymer had a high molecular weight and a narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n$=1.13). Such facts clearly indicate the rapidity of initiation and lack of chain transfer and termination reactions during the course of polymerisation.

Some copolymerisation studies have also been carried out using the protected monomer. For example, an ABA type triblock copolymer was prepared by the sequential polymerisation of styrene as monomer B and the protected monomer as A with oligo(α-methylstyryl)dipotassium in THF at - 78°C [120].

Although oxazolines show such inertness to anionic polymerisation conditions they have been reported to polymerise by a ring opening mechanism in the presence of cationic initiators such as borontrifluoride [121].



5.4.1.3. Anionic polymerisation of 4-(tert-butyldimethylsilyloxy)styrene

As a functionalised polymer poly(4-vinylphenol) has many potential uses such as a polymeric nucleophile [122]. However, previous to the method involving protection of the functional group poly(4-vinylphenol) had been prepared by cationic and free radical methods but the polymers were of dubious "purity". Such polymers also had low molecular weights and a broad molecular weight distribution owing to termination and chain transfer by the highly reactive hydoxyl group as described earlier.

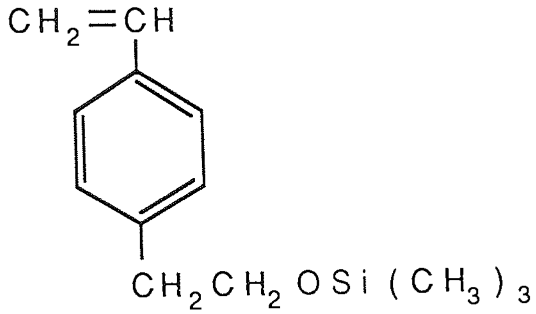
However anionic polymerisation of the protected monomer 4-(tert-butyldimethylsilyloxy)styrene initiated by lithium naphthalide or butyllithium takes place in THF at -78^{o}C[123,124]. GPC analysis of the resulting product showed that the polymers had high molecular weights with a narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$=1.01) again indicating rapid initiation and the absence of chain transfer. Further proof of a living system was provided by the formation of ABA block copolymers with methylstyrene.

No cleavage of the tert-butyldimethylsilyl ether linkage could be detected by NMR showing that the derivative is stable to water and methanol under mild alkaline and neutral conditions.

Although the anionic polymerisation of this monomer was instantaneous at the reaction temperature of - 78^{o}C there was a 40% loss in activity of the styryl anion when the reaction was carried out at 30^{o}C. This was explained by the fact that the carbanion attacks the polymer chain at the silicon atom resembling the substitution reactions of alkoxysilane compound with organolithium reagents [125].

The 4-(tert-butyldimethylsilyloxy)styrene derivative was made by treating 4-vinylphenol with tert-butyldimethylsilyl chloride in the presence of imidazole and on completion of reaction was removed by reaction with concentrated hydrochloric acid in 1,4-dioxane.

The trialkyllsiyl group has also been used as a means of protection during the anionic polymerisation of 2-(4-vinylphenyl) - ethanol. The monomer was treated with hexamethyldisilazane to produce the protected monomer shown below [126]



The polymerisation was initiated by lithium naphthalide and carried out at -78^{o}C. Again the temperature was found to be critical; when the temperature was raised to 20^{o}C there was a loss in activity of the styryl anion due to attack on the silicon atom in the protecting group by the carbanion at the polymer end.

On completion of reaction the trimethylsilyl group was removed by the addition of acidified methanol.

GPC analysis of the polymer product again showed that the materials produced had high molecular weights and a narrow molecular weight distribution.

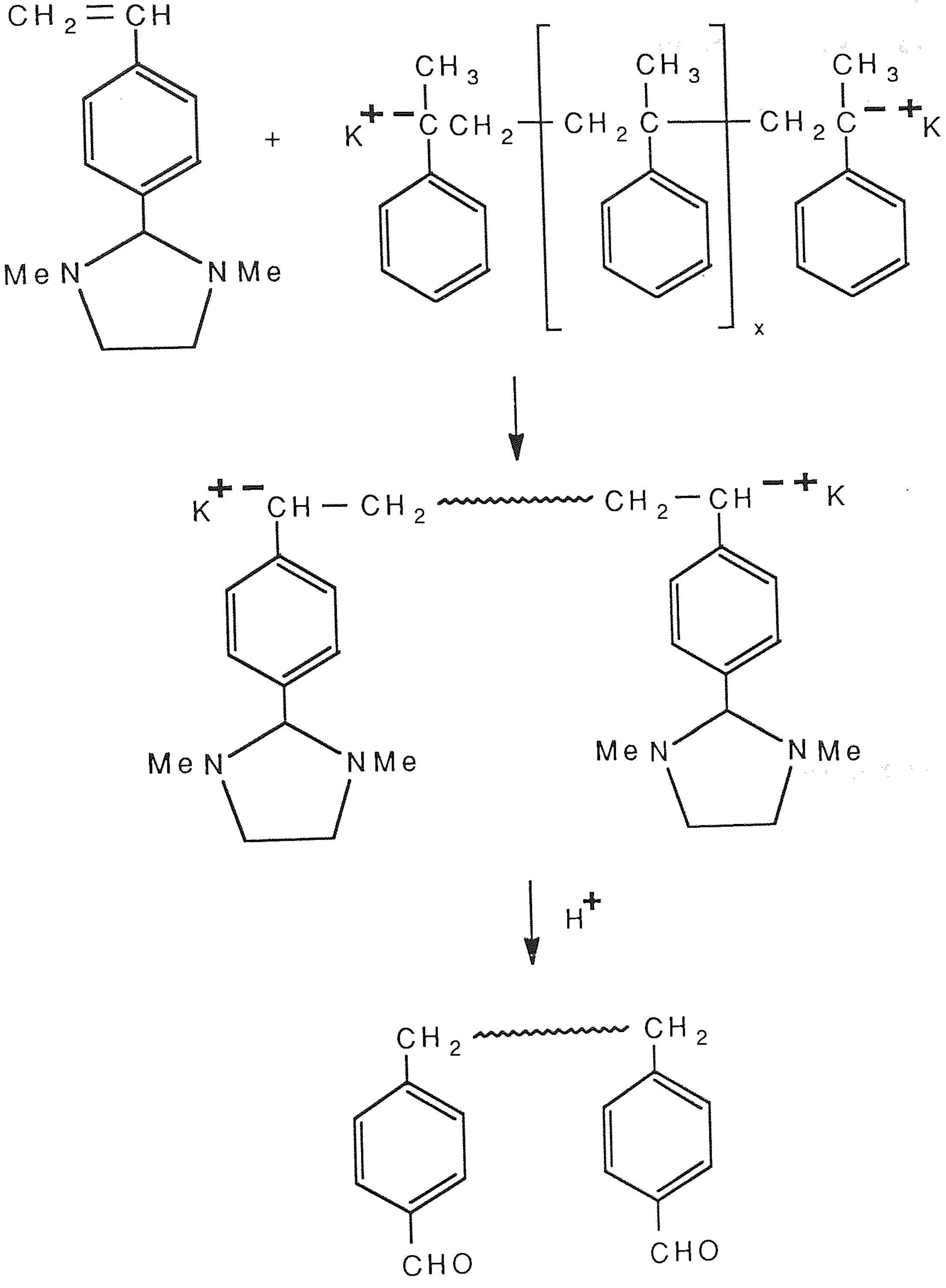
5.4.1.4. Anionic polymerisation of 1,3-dimethyl-2-(4-vinylphenyl)imidazolidine

Poly(4-vinylbenzaldehyde) is of considerable interest due to its potential use as polymer supports and polymer chelates. Also of interest is that an aldehyde group attached to a polymer chain can undergo a number of reactions such as oxidation, reduction etc. Previous to this method of protection 4-vinylbenzaldehyde had been polymerised free radically but chain transfer resulted in broad molecular weights of the polymer products.

However 1,3-dimethyl-2-(4-vinylphenyl)imidazolidine was successfully polymerised anionically [127] and GPC analysis of the product showed that the polymer had a high molecular weight and a narrow molecular weight distrbution ($\bar{M}_w/\bar{M}_n$=1.1). This is indicative of the absence of chain transfer and termination reactions.

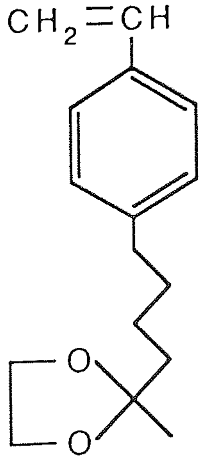
1,3-dimethyl-2-(4-vinylphenyl)imidazolidine was prepared from 4-vinylbenzaldehyde and NN'-dimethylethylenediamine and was removed on completion of reation by hydrolysis using 2M HCl.

A summary of the polymerisation of the protected monomer and recovery of the original functionalised monomer is given below:


CH 2 = CH
+
MeN
NMe
K+ −C CH2
CH3
CH2 C
x
CH2 C − +K
K+ −CH − CH2
CH2 − CH − +K
H+
CH2
CHO

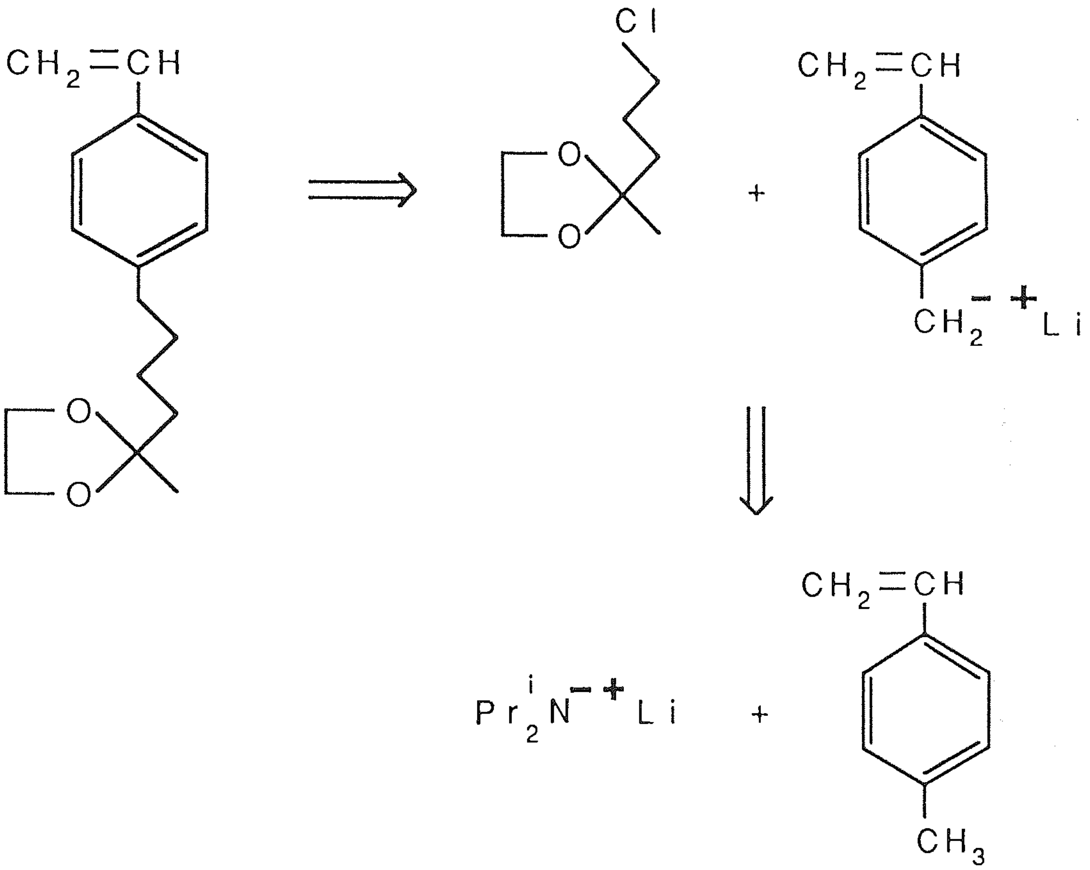
5.5. Experimental results

It is obvious that polymers containing any one of the following functional groups COOH, C=O, OH, have many potential uses. Earlier studies showed that the most effective way of producing functionalised polymers is by polymerisation of a functionalised monomer. However, the functional group often has to be protected during the polymerisation process. In the literature reviewed previously it can be seen that work has been carried out in relation to the preparation and polymerisation of monomers containing protected aldehydic, carboxylic acid and hydroxyl functions. However, to date there have been no references cited regarding polymers containing protected ketone functions. Hence it appeared logical to devise a method of producing polymers of this type. Since monomers containing protected ketone groups are not available commercially it was necessary to create a means of synthesising them. Suitable synthons of this product seemed to be vinyltoluene and 2-(3-chloropropyl)-2-methyl-1,3,-dioxalane (CPMD). Vinyltoluene was chosen since it contains a site where polymerisation can occur and labile hydrogen atoms in the pendant methyl group whilst CPMD was chosen since dioxalanes are the agents most commonly used for the protection of the ketone moiety and the chlorine atom enables this precursor to take part in Gilman-type exchange reactions. The aim was, therefore, to synthesise the following protected monomer



It was thought that this type of monomer could thus be synthesised by a Gilman-type exchange reaction. However, this first necessitated the formation of the highly reactive anion CH_2^- by abstraction of a hydrogen from the methyl group of vinyltoluene. As seen in chapter four the base lithium diisopropylamide, is capable of performing this type of abstraction whilst leaving the highly reactive vinyl group of the monomer intact.

Thus the synthetic route devised may be represented as follows:



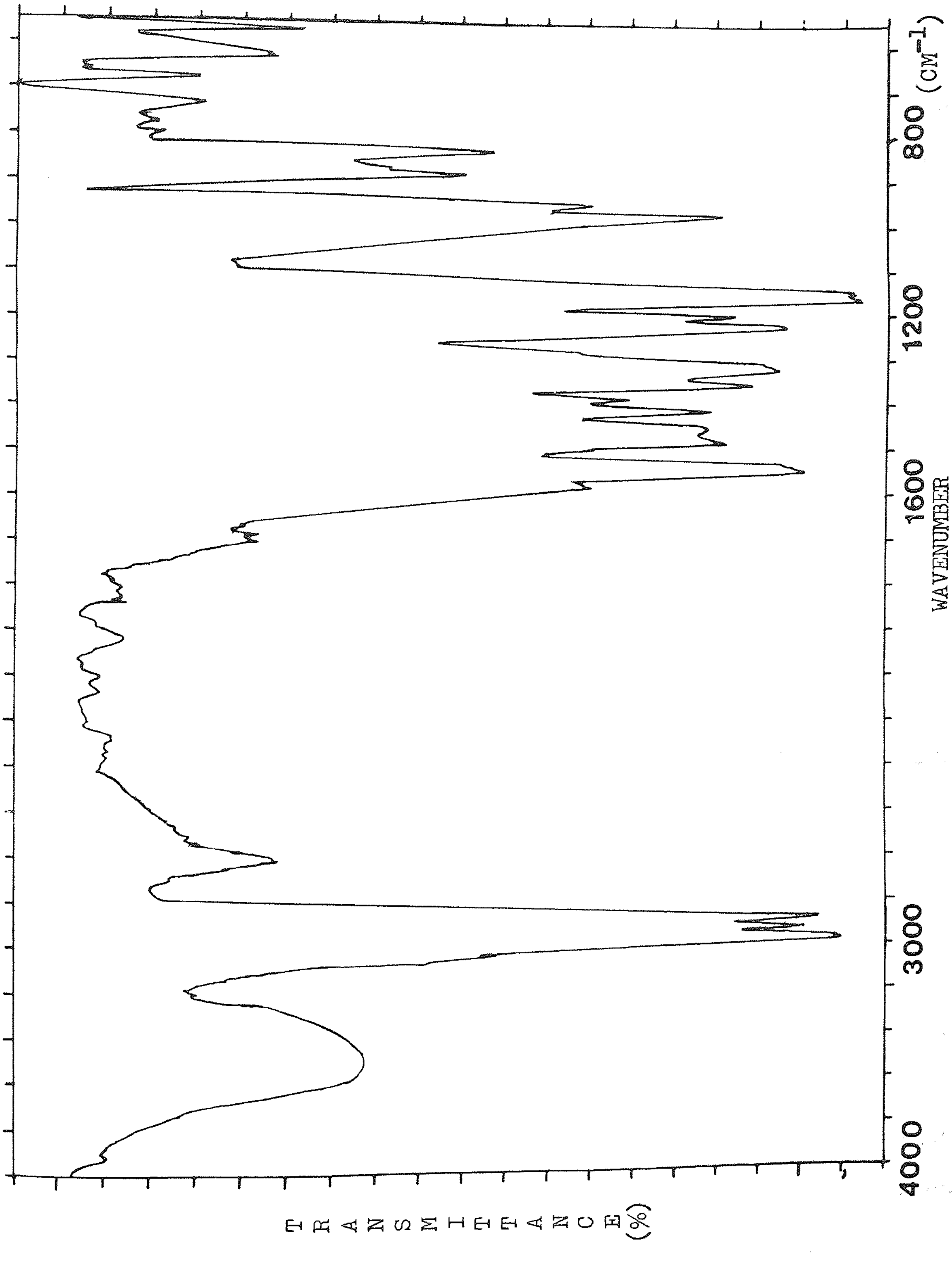


Figure 5.1

5.5.1. Synthesis of 2-methyl-2(4-(vinylphenyl)-butyl)-1,3-dioxalane

5.5.1.1. Method one

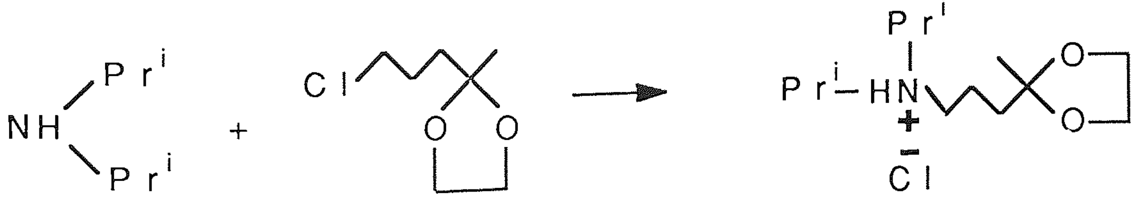
Lithiation of vinyltoluene using lithium diisopropylamide was carried out by the procedure described in section 4.2.4.3.1. However, on completion of lithiation 7.5ml (0.05mol) of 2-(3-chloropropyl)-2-methyl-1,3-dioxalane (CPMD) were added to the reaction flask. A white precipitate formed which was removed by filtration and dried.

5.5.1.1.1. Analysis of the product

Both the precipitate and the supernatant liquid were analysed by FT IR.

The precipitate was analysed as a KBr disc and the spectrum is shown in figure 5.1.

The absorbance at 2628cm^{-1} due to the -NH group, would seem to indicate that the precipitate is an amine salt. This conclusion is supported by the presence of strong absorbances in the infrared at 1385cm^{-1}, due to the presence of an isopropyl group, and at 1126cm^{-1} due to the presence of a cyclic ether. This tends to suggest that the solid was formed by the reaction between the dioxalane and an excess of diisopropylamine in the reaction:



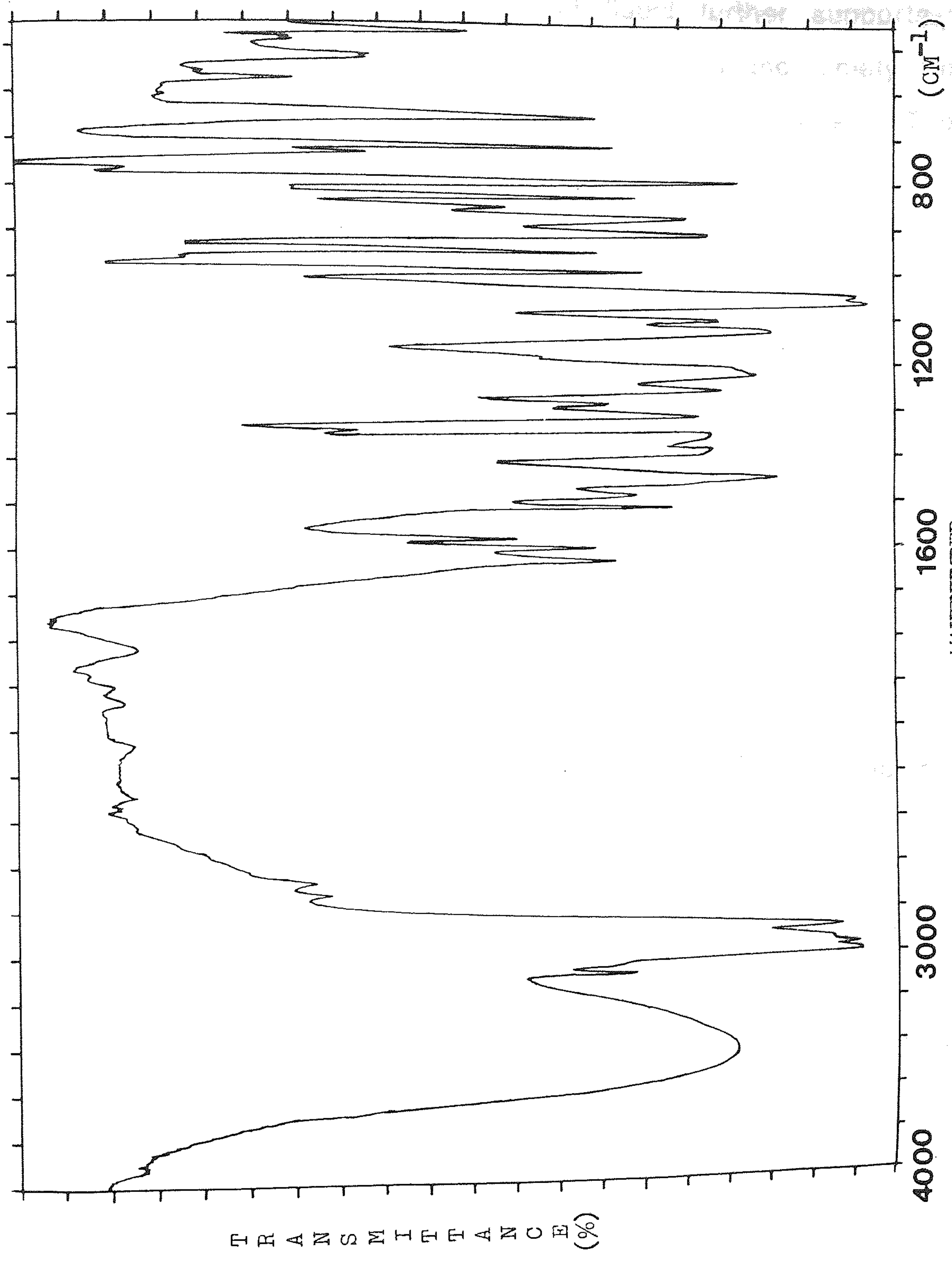


Figure 5.2

Confirmation of this possible reaction scheme comes from the disappearance of the absorbance due to C-Cl bond at 650cm^{-1}.

IR analysis of the supernatant liquid further supports this conclusion since it appears that the dioxalane moiety reacts with the amine in preference to the lithiated monomer. The IR spectrum of the liquid shows possible evidence of vinyltoluene and unreacted 2-(3-chloropropyl)-2-methyl-1,3-dioxalane (CPMD). The spectrum is shown in figure 5.2.

5.5.1.2. Method two

The generation of a reactive anion from a monomer such as vinyltoluene, whilst maintaining the unsaturation, presents a number of problems. As discussed previously the removal of a labile proton requires reaction with a strong base. If the base is also a strong nucleophile, then the nucleophile may add across the carbon-carbon double bond rather than abstract a labile proton. This would be expected to happen if butyllithium was used as the base with or without a complexing agent such as K Bu^{t}O or tertiary amines, such as TMEDA. Secondary and primary bases such as diisopropylamine possess a labile hydrogen atom and so it is possible to carry out the following reaction before metallation:

$$(Pr^{i})_2-NH \xrightarrow{BuLi} (Pr^{i})_2-N^{-}\,{}^{+}Li + BuH$$

The isopropylamide ion is a sufficiently strong base to abstract a proton, but not a sufficiently powerful enough nucleophile to add across a carbon-carbon double bond of vinyltoluene. Were it not for the fact that excess amine is present to react with

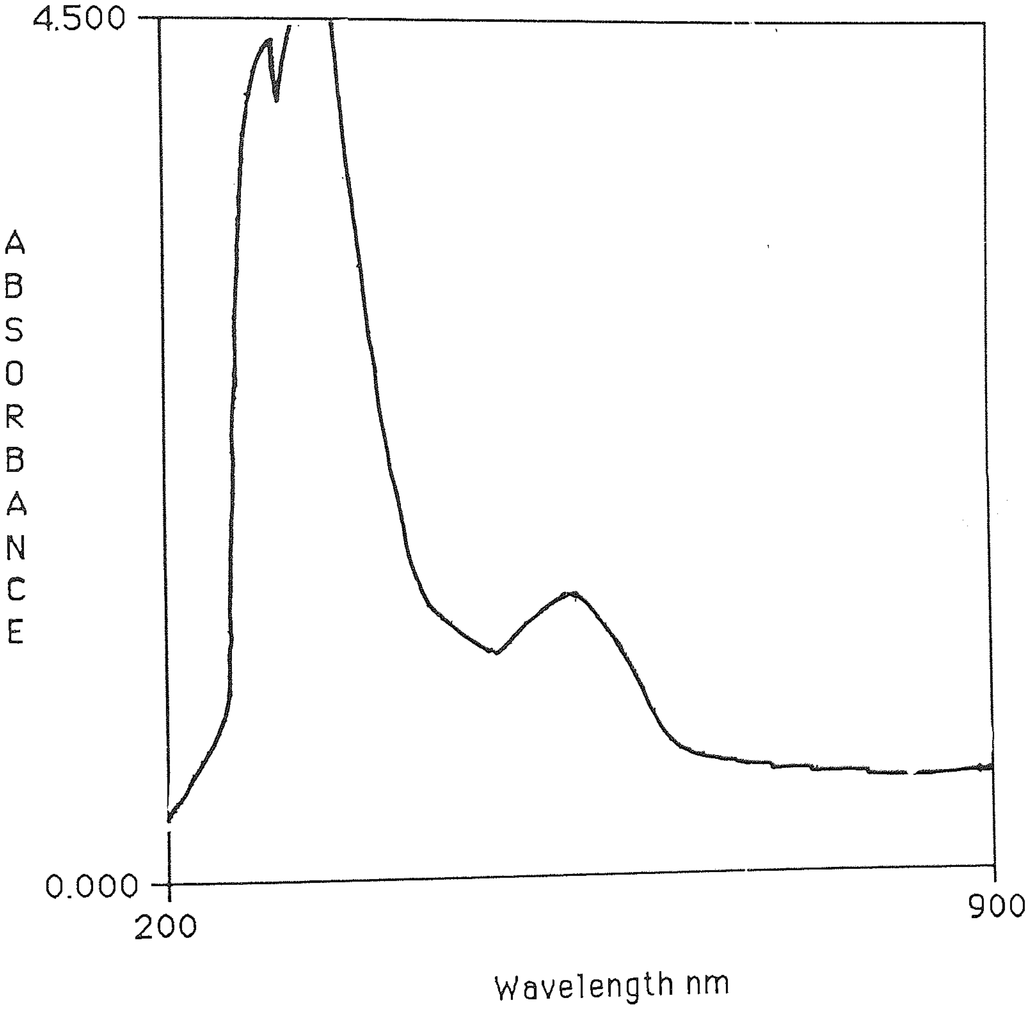
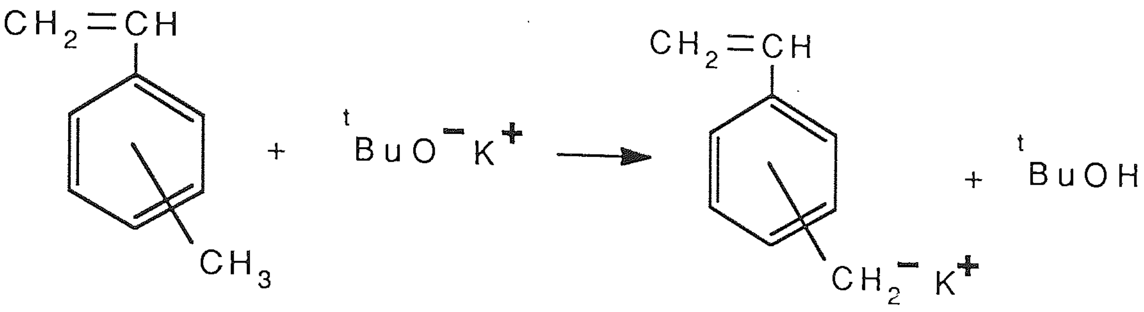


Figure 5.3

the substitited dioxalane, this would have provided a satisfactory metallation route. It was therefore necessary to look at an alternative route to metallate vinyltoluene (VT) and for this reason K Bu^{t}O was chosen as a strong base - weak nucleophile combination. Thus K Bu^{t}O was used in an attempt to abstract a labile hydrogen atom from the methyl group of vinyltoluene i.e.

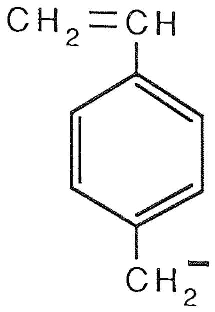


5.5.1.2.1. Metallation

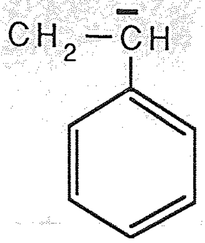
The reaction between K Bu^{t}O and VT was carried out as described in section 2.6.2.3.2.1. A typical reaction system consisted of a suspension of 10.21g (0.09mol) of K Bu^{t}O in 40ml of THF and 12ml (0.09mol) of vinyltoluene in 10ml of THF. The reaction was left for four hours at 20°C, when the reactants had produced a lilac solution which had increased in viscosity.

5.5.1.2.1.1. Analysis of the product

UV analysis was carried out on the solution obtained from the reaction flask by removal of a 20ml sample as described in section 2.6.2.3.2.2. The spectrum is shown in figure 5.3. UV analysis of the solution showed a λmax at 550nm. This can be compared with λmax for the propagating polystyryl anion which is known to show a λ max at 338nm [128]. The increased conjugation afforded by the carbon-carbon double bond in the structure:

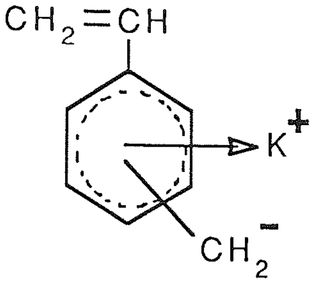


over



could explain the shift of λmax to a longer wavelength.

The relatively high value of λmax of the product could also be explained by the formation of a charge transfer complex between the potassium ion and the π orbitals of the benzene ring in the monomer i.e.



5.5.1.2.1.2. Reaction with Michlers ketone

After removal of a sample of the lilac solution for UV analysis the remainder was reacted with 25ml of a 2M solution of Michlers ketone in THF. The contents of the flask were immediately seen to change from lilac to red when the solution of Michlers ketone was added by syringe.

5.5.1.2.1.2.1. Analysis of the reaction product

A 20ml sample was removed from the reaction flask by the method described in section 2.6.2.3.2.2. for analysis by FT IR and UV.

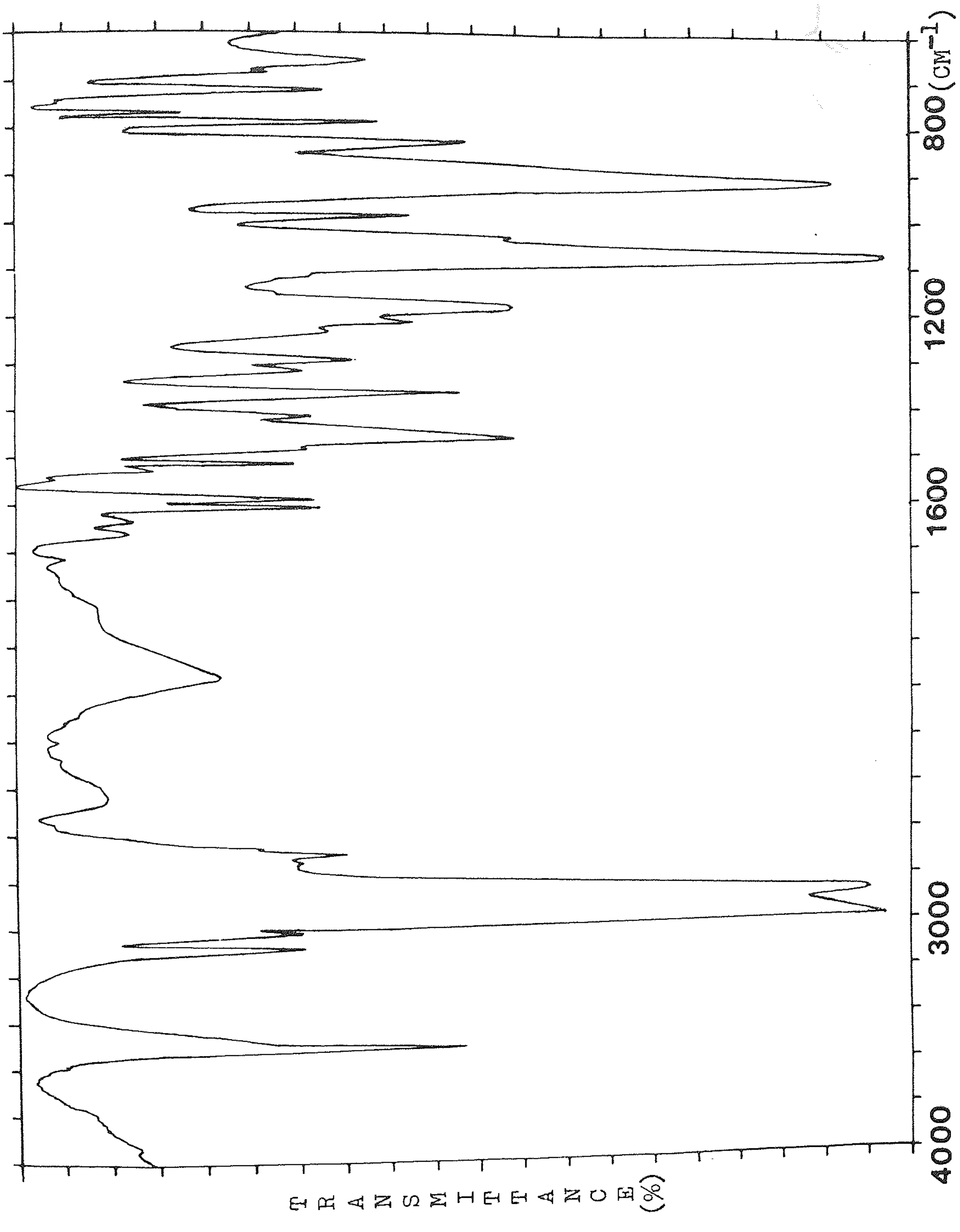
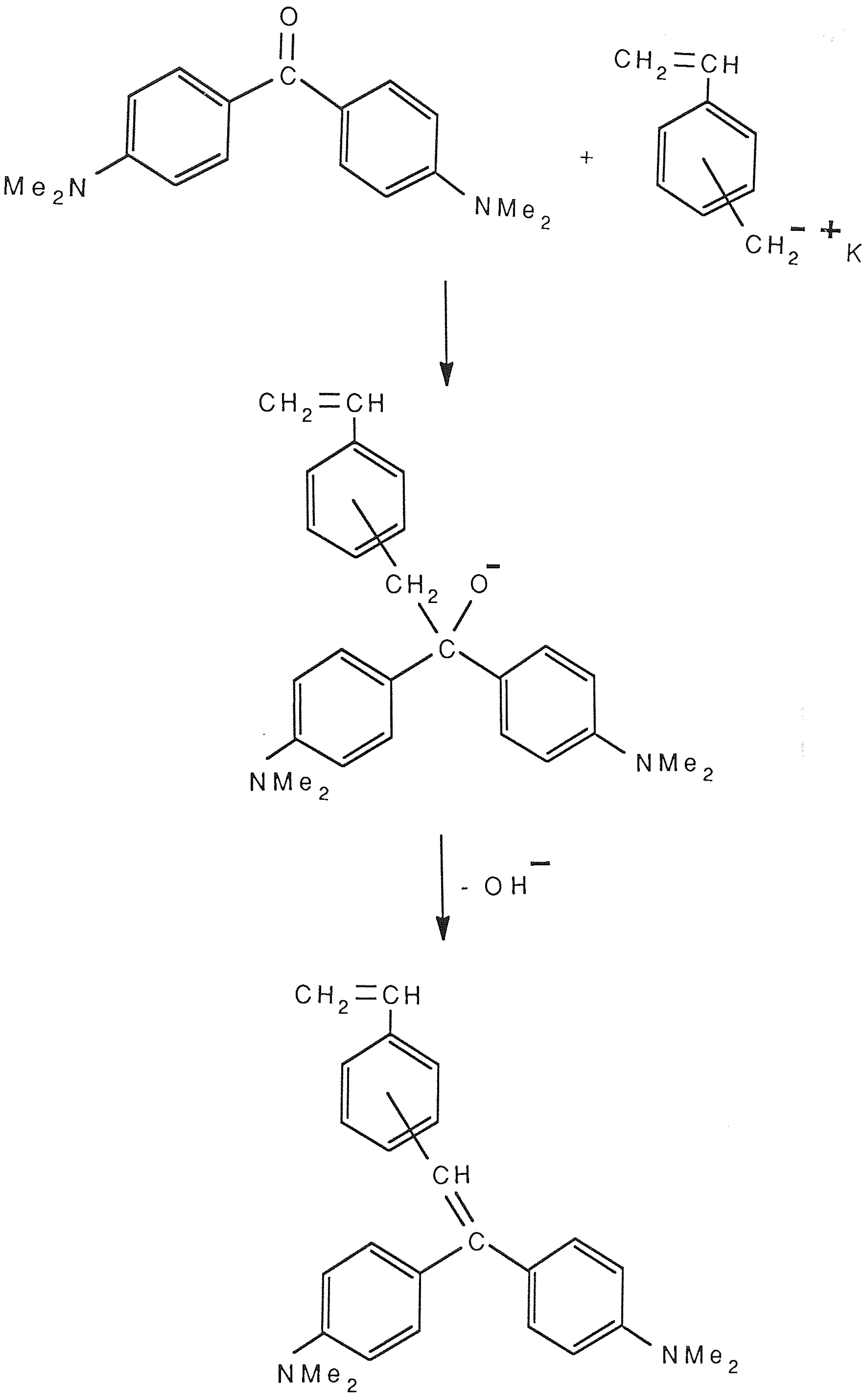


Figure 5.4

Figure 5.5



Structure (A)

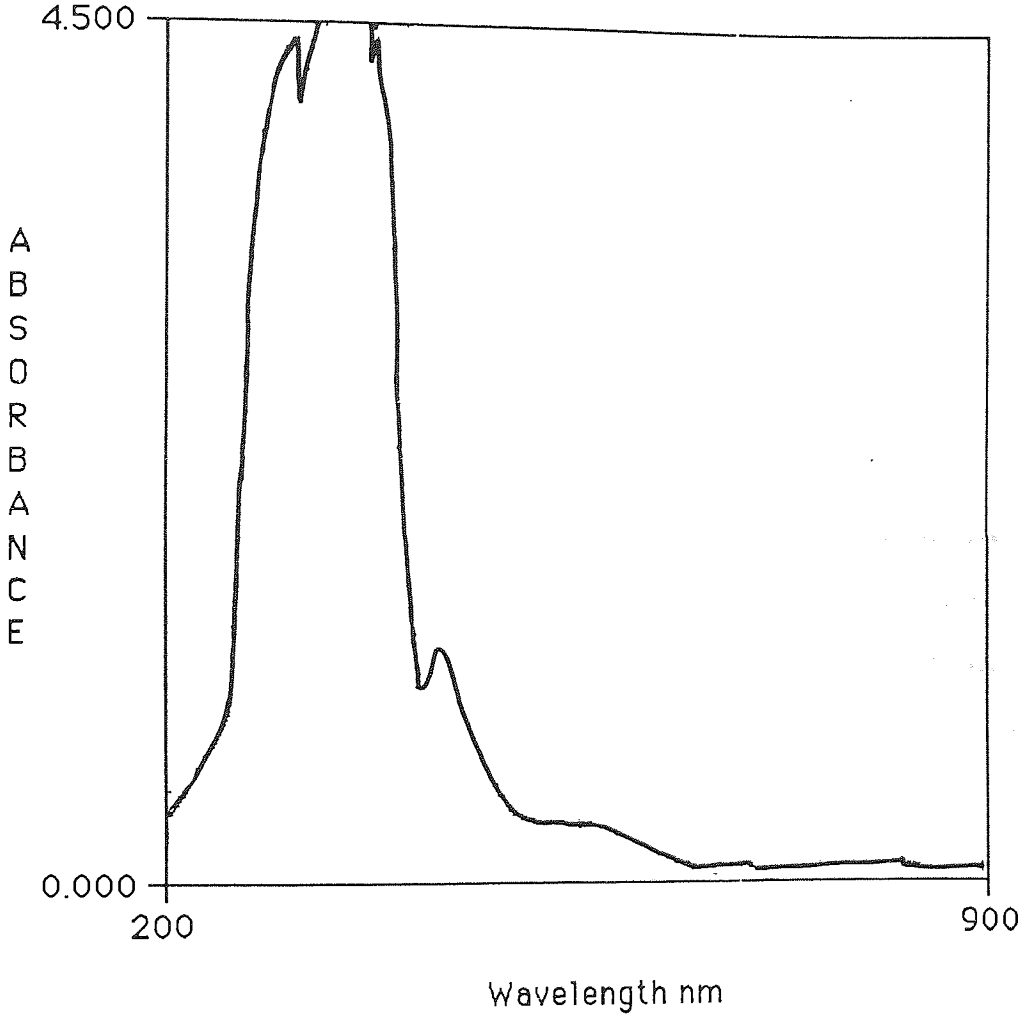


Figure 5.6

IR analysis

The product was analysed immediately after removal from the reaction flask as a thin liquid film between sodium chloride plates. The spectrum obtained is shown in figure 5.4. The reaction scheme proposed for the sequence of reactions is shown in figure 5.5.

Michlers ketone shows a strong infrared absorbance at $1601cm^{-1}$ attributable to a carbonyl group conjugated to two substituted benzene rings; this specific absorbance is absent from the product. The spectrum of the product shows absorbances at $3024cm^{-1}$ and $3082cm^{-1}$ which are respectively associated with R-CH=CR'R' and R-CH=CH_2 structures. It is likely that these carbon-carbon double bonds are conjugated systems because the peak at $1615cm^{-1}$ is indicative of such conjugation; there are no strong absorbances in this region of the spectrum that would normally be associated with conjugated double bonds such as occur in vinyltoluene. The structure (A) would seem to be a reasonable postulate.

UV analysis

UV analysis was carried out on a solution extracted directly from the reaction flask. The spectrum is shown in figure 5.6.

On analysis it can be seen that the sample shows a λmax at 442nm in the visible region. It is also seen that the absorbance band at 550nm is greatly reduced in intensity. Again the absorbance band at 442nm could be explained by the presence of a highly conjugated product such as a structure (A).

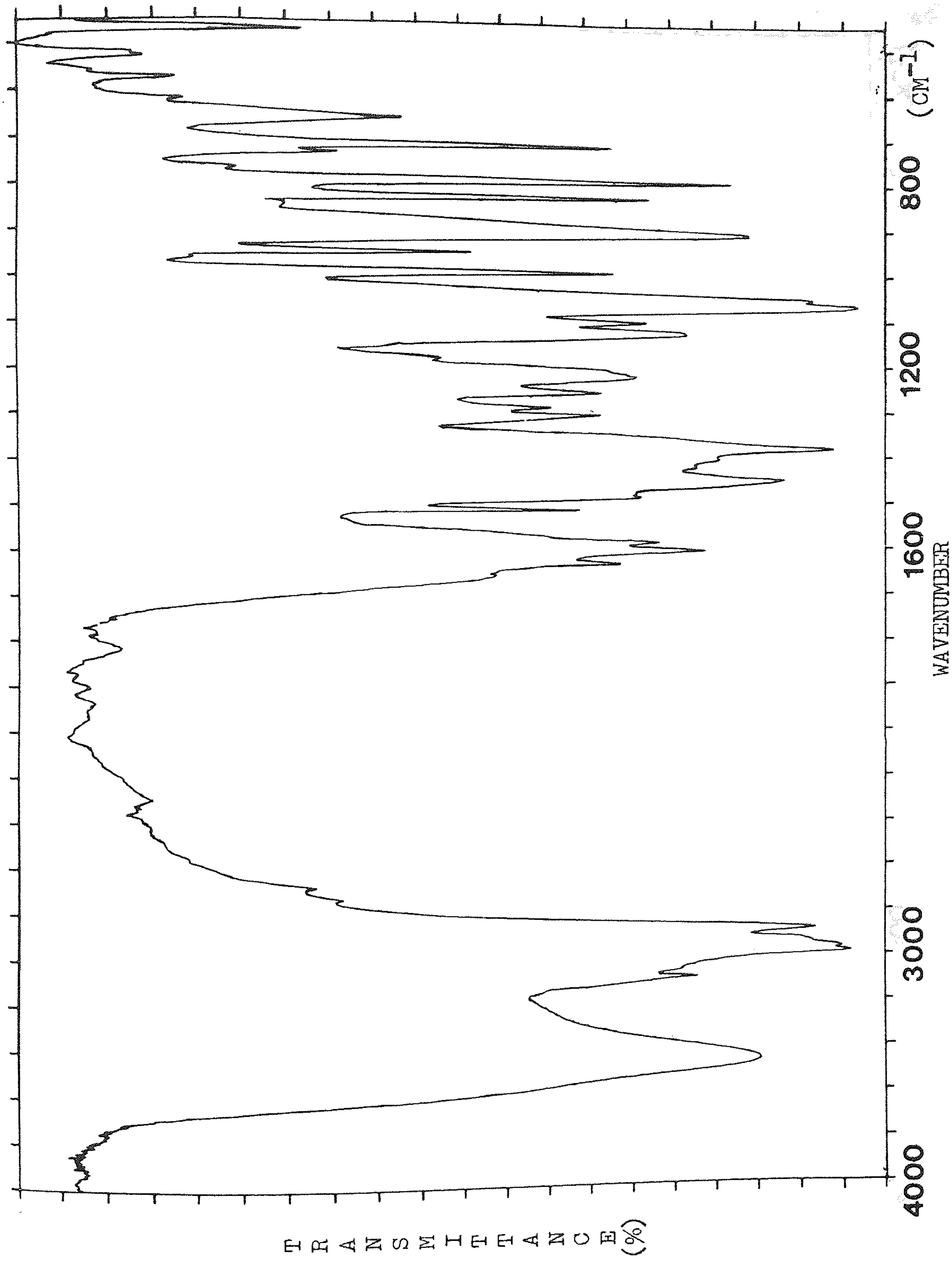


Figure 5.7

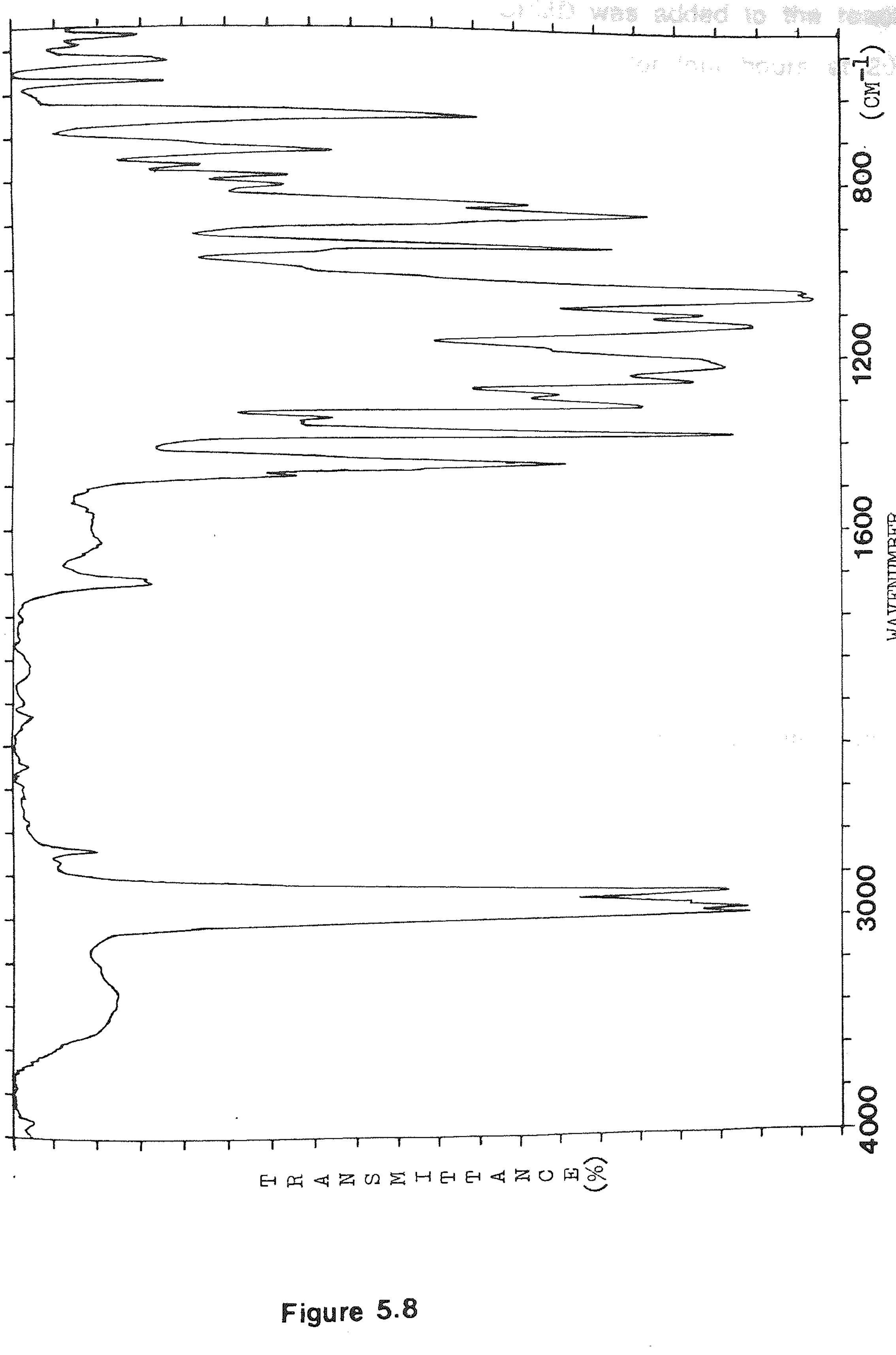


Figure 5.8

5.5.1.2.2. Reaction with CPMD

On completion of the metallation reaction described in section 5.5.1.2.1. 13.5ml (0.09mol) of CPMD was added to the reaction system. The reaction mixture was left for four hours at 20^{o}C when the contents were orange/brown.

5.5.1.2.2.1. Analysis of the product

Immediately after injection of CPMD a 5ml sample was removed from the reaction flask as described in section 2.6.2.3.2.2. for analysis by UV. A further 10ml sample was removed after four hours' reaction time for UV and FT IR analysis.

IR analysis

The product was analysed immediately after removal from the reaction flask as a thin liquid film between sodium chloride plates. The spectrum is shown in figure 5.7.

The strong absorbances at 1124 and 1220cm^{-1} which are indicative of cyclic ethers show that the dioxalane moiety remained intact during the reaction. On comparison with the spectrum of 2-(3-chloropropyl)-2-methyl-1,3-dioxalane, shown in figure 5.8, it is seen that there is a slight reduction in intensity of the absorbance at 655cm^{-1} which can be attributed to the C-Cl group. However, the full extent of this reduction is difficult to estimate since vinyltoluene also shows a comparatively strong absorbance at this wavelength. The vinyl group of the monomer is seen to remain unchanged as indicated by absorbances at 992cm^{-1} and 3088cm^{-1}.

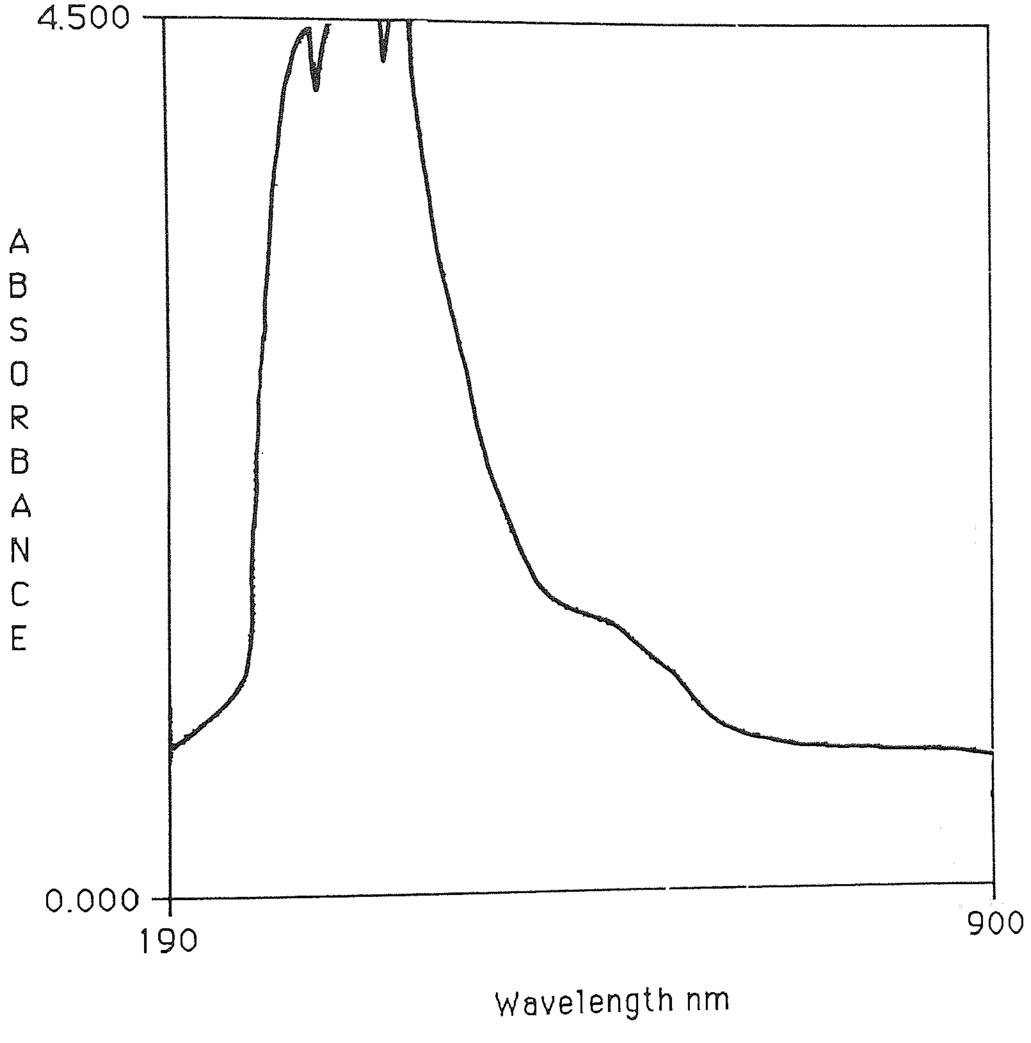


Figure 5.9

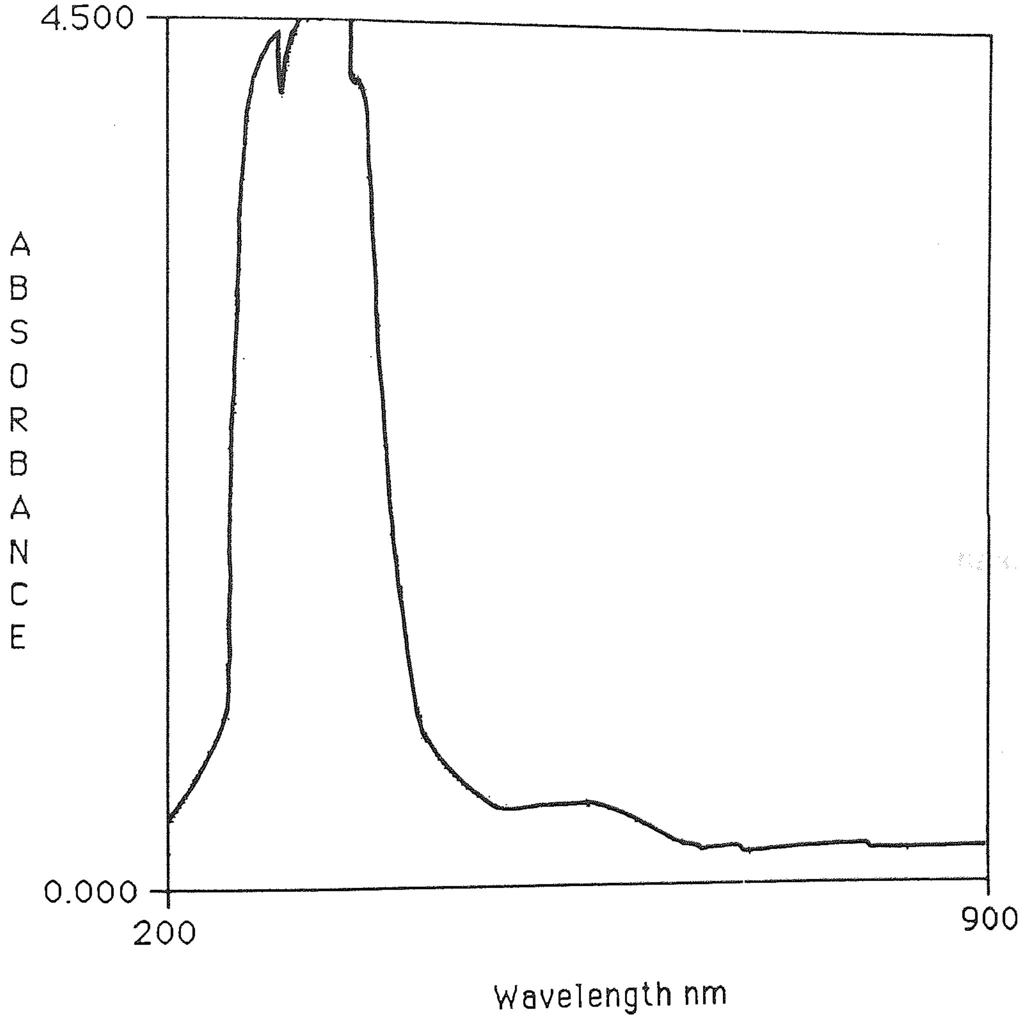


Figure 5.10

UV analysis

UV analysis was carried out on solutions obtained directly from the reaction flask. Samples were analysed at the start of the reaction and after four hours. The spectra obtained are shown in figures 5.9 and 5.10 respectively. On analysis of the spectra it can be seen that there is progressive disappearance of the absorbance band at 550nm; after reaction for four hours the absorbance at 550nm has virtually disappeared. This can be explained by the disappearance of the highly delocalised carbanion during the course of the reaction with the chlorinated compound.

5.5.2 Anionic polymerisation of 2-methyl-2(4-(vinylphenyl)-butyl)-1-3-dioxalane

On completion of reaction with CMPD 0.6ml (0.009mol) of butyllithium solution was injected into the reaction flask and the flask placed in an ice bath for 8 hours. The contents were seen to become red. The resulting viscous solution was poured into methanol and a white polymer precipitated. The polymer was dried under vacuum and purified by reprecipitating into methanol from THF solution. The polymer was dried once again and weighed; the yield was found to be 15.8g.

5.5.2.1. Analysis of the product.

The polymer produced was analysed by FT IR and GPC.

5.5.2.1.1. IR analysis

The polymer was analysed as a film cast from a solution of the

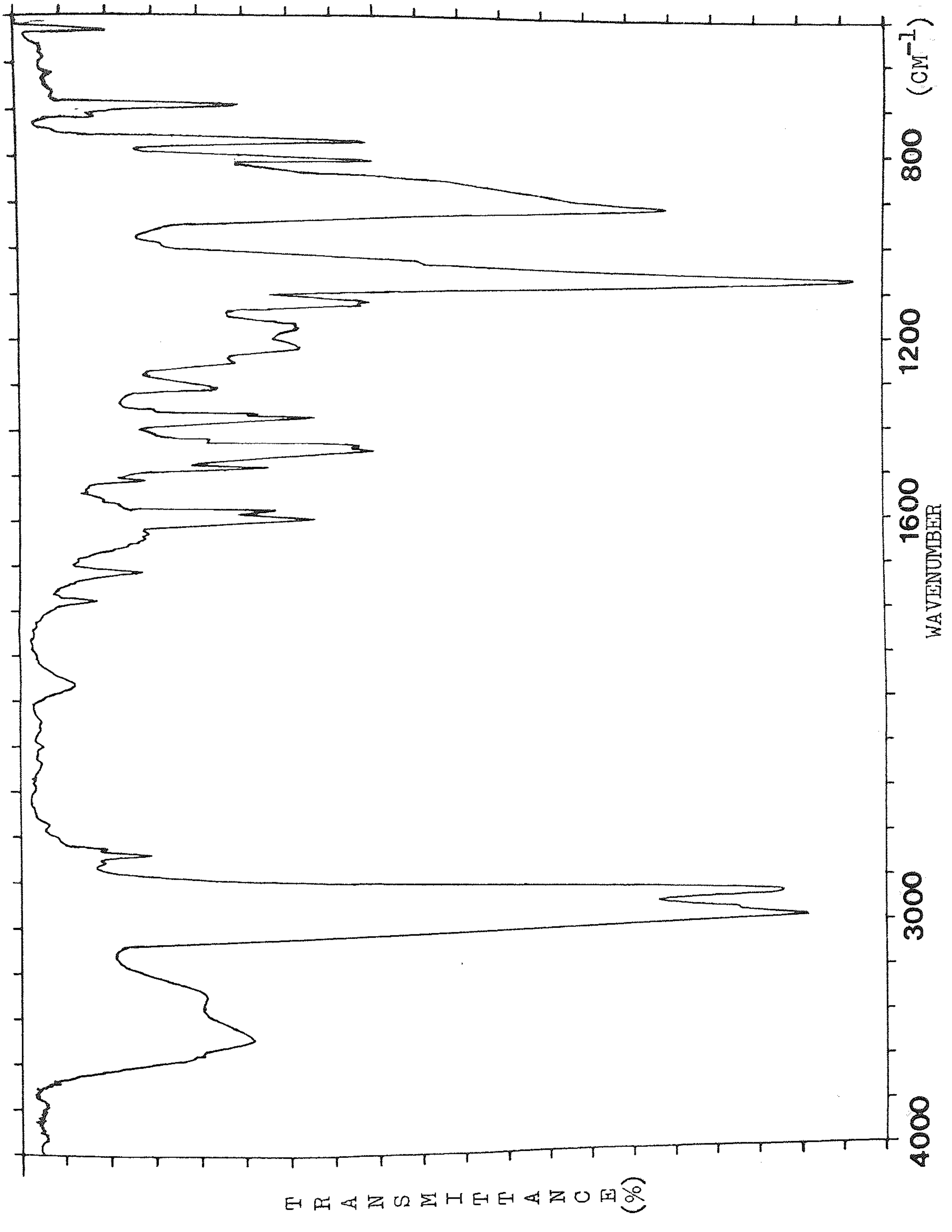


Figure 5.11(a)

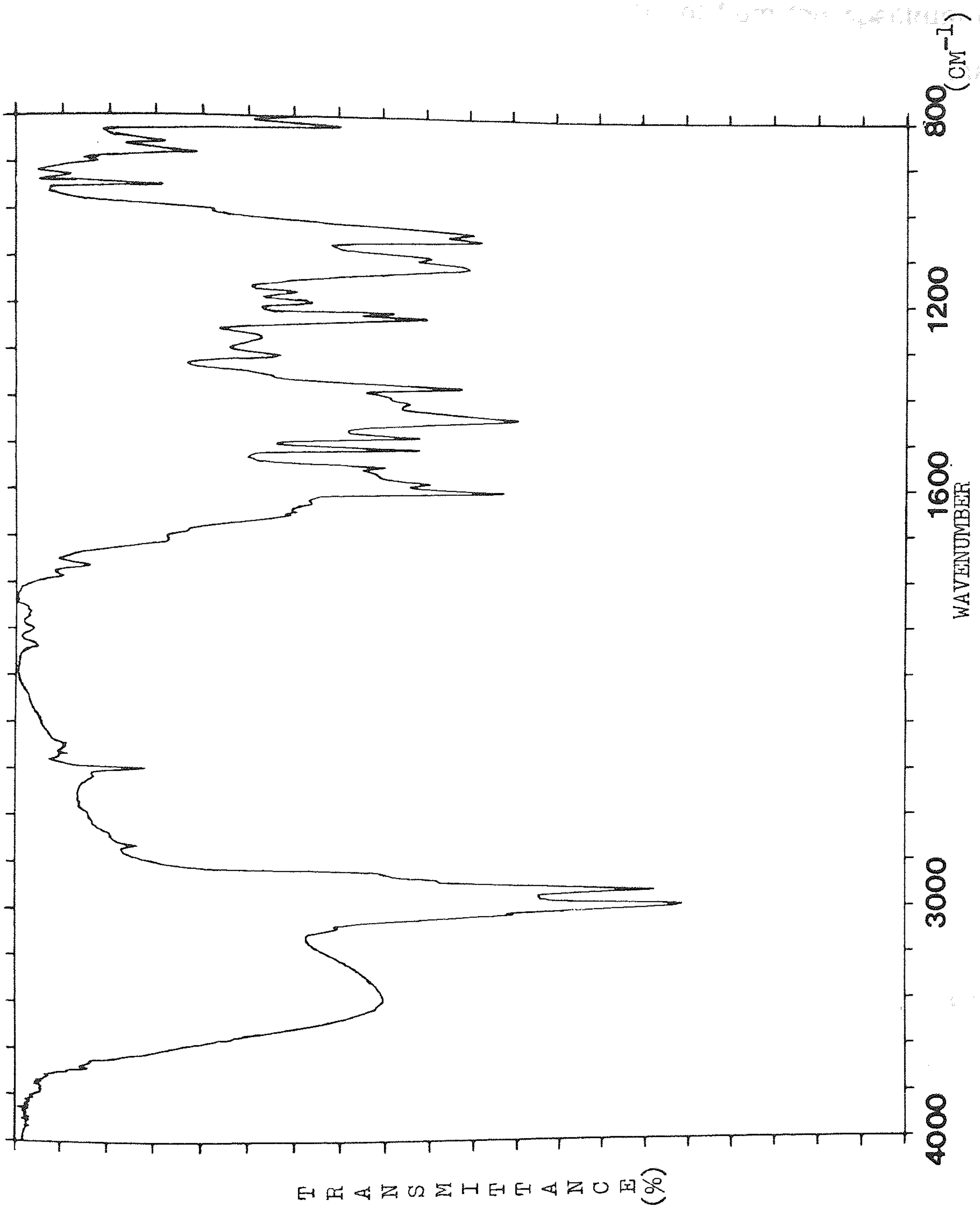


Figure 5.11(b)

polymer in THF. The spectrum obtained is shown in figure 5.11(a).

The absorbance at 650cm^{-1} which has been attributed to both C-Cl bonds and C-C double bonds is absent from the spectrum of the polymer. It seems reasonable to suggest, therefore, that the absorbance at 650cm^{-1} displayed by the monomer was due to C-C double bonds. The removal of these bonds by the polymerisation reaction would leave only the C-Cl bond to absorb in this region. That there is no absorbance would suggest that the C-Cl bond was cleaved in the synthesis step. The disappearance of absorbances at 992cm^{-1}, 1632cm^{-1} and 3088cm^{-1} is indicative of the disappearance of the vinyl group. However, it can be seen that the polymer does contain the dioxalane moiety due to absorbances at 1122cm^{-1} and 1228cm^{-1}. To eliminate any absorbances due to THF the polymer product was also analysed by IR as a KBr disc. The spectrum is shown in figure 5.11(b)

GPC analysis

The polymer produced was analysed as a 2% solution in THF. The chromatogram obtained is shown in figure 5.12. The weight average molecular weight ($\bar{M}_w$) was seen to be 185,000 and the number average molecular weight 175,000. The polydispersity of the sample was 1.05.

The degree of polymerisation $\overline{DP}_n$ may be calculated from the equation:

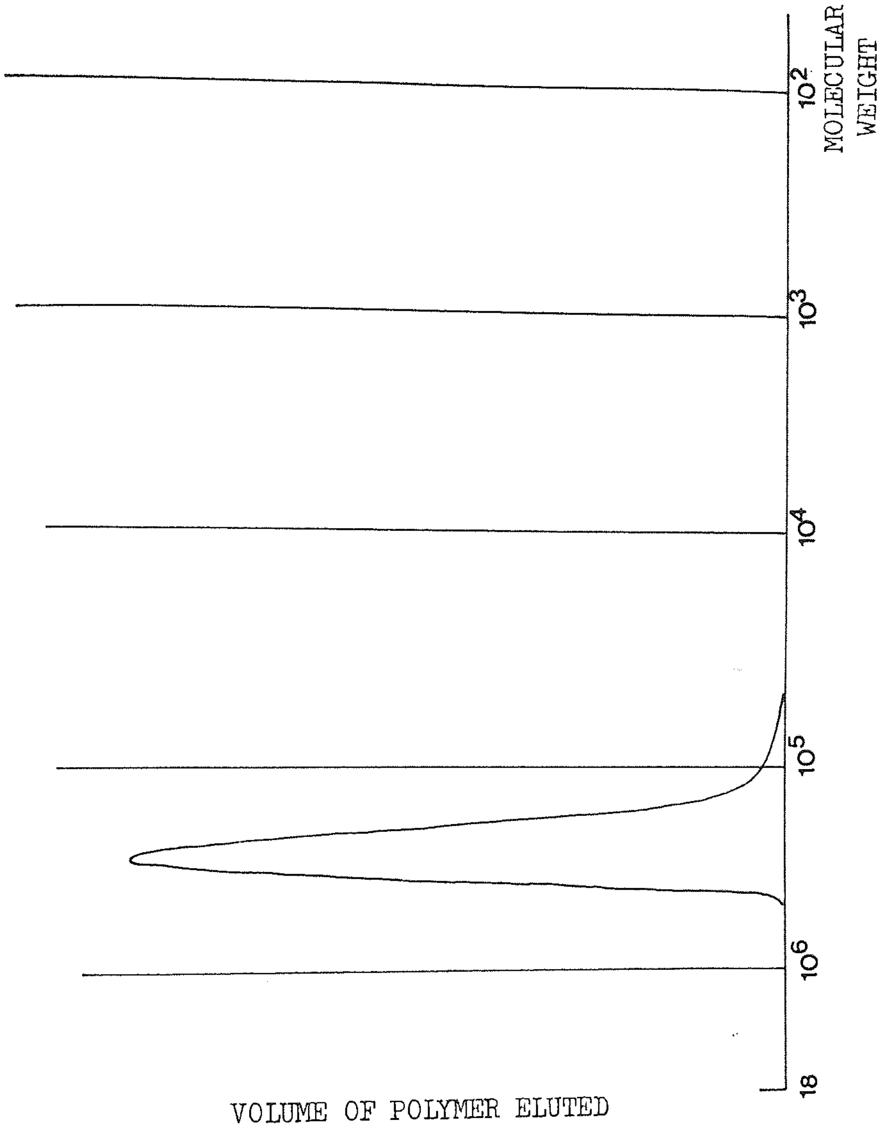
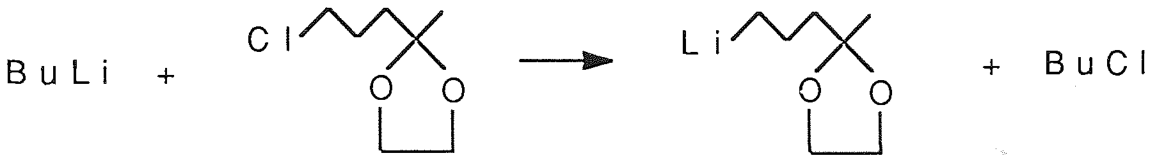

MOLECULAR WEIGHT
10²
10³
10⁴
10⁵
10⁶
18
VOLUME OF POLYMER ELUTED

Figure 5.12

$$\overline{DP}_n = \frac{\text{no of moles of monomer polymerised}}{\text{no of moles of BuLi initiating}}$$

As a ratio of monomer to initiator of 100:1 was used, if initiation was 100% efficient, one would expect 100 monomer units in each polymer chain giving a number average molecular weight of 24,600. However, the actual $\bar{M}_n$ obtained was 7 times greater than this value showing that initiation was not 100% efficient. The inefficiency could be accounted for by the fact that BuLi reacts with any unreacted CPMD in the following reaction leaving only a fraction of the BuLi present to initiate anionic polymerisation.



5.5.3. Removal of protecting group from poly-(2-methyl-2(4-(vinylphenyl)-butyl)-1,3,-dioxalane)

The polymer obtained by the procedure described in section 5.5.2 contains the dioxalane ring which as seen previously is a protected C=O. The ketone group must be protected during anionic polymerisation but in order for the resulting polymer to be useful the protecting group must be subsequently removed.

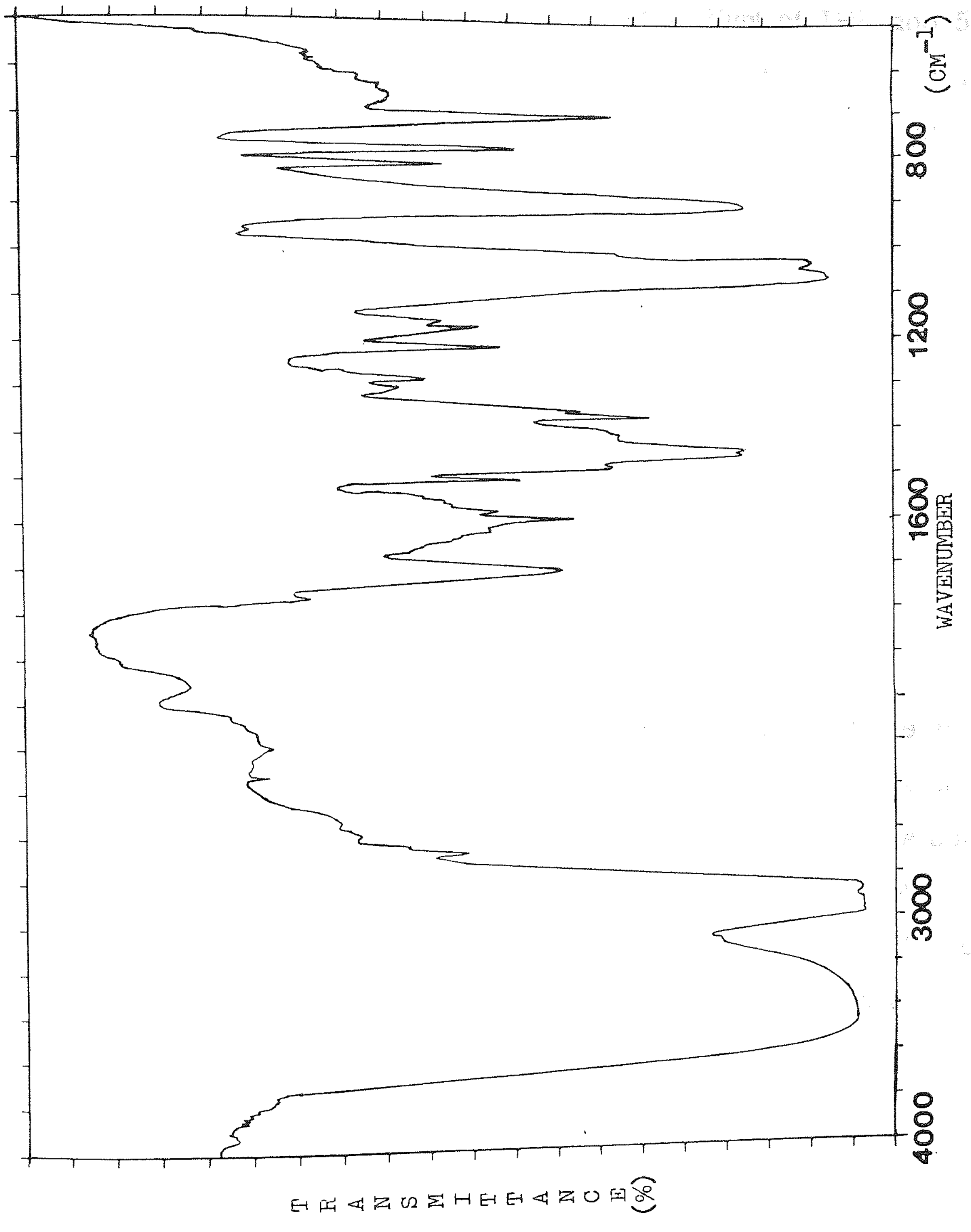


Figure 5.13

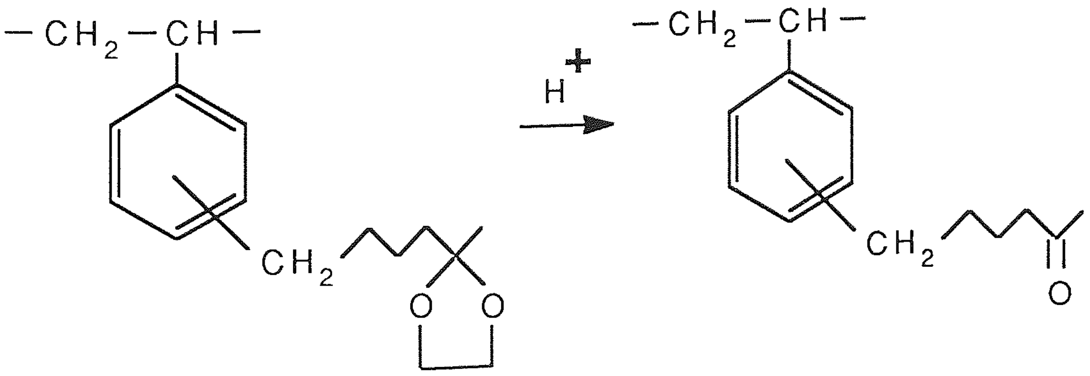
1,3,-dioxalanes are particularly useful protecting groups since they are cleaved comparatively easily by an acid medium.

A typical reaction system consisted of 1g of polymer prepared as described in section 5.5.2 dissolved in 20ml of THF and 5ml of 2M HCl. The reaction mixture was refluxed for ten hours and the product was precipitated by adding the reaction mixture to an excess of water. The product was then dried under vacuum and purified by dissolving in THF and reprecipitation into water. The product was dried once again under vacuum.

5.5.3.1. Analysis of the product

A solution of the polymer produced was analysed as a thin liquid film between sodium chloride plates. The spectrum obtained is shown in figure 5.13.

On analysis of the spectrum of the polymer product the most notable points are the appearance of the absorbances at 1722cm^{-1}, which is characteristic of an aliphatic carbonyl group, and the disappearance of the absorbance at 1120cm^{-1}, which is characteristic of a cyclic ether. Thus it would seem that the dioxalane group has been hydrolysed by the addition of acid in the following manner:



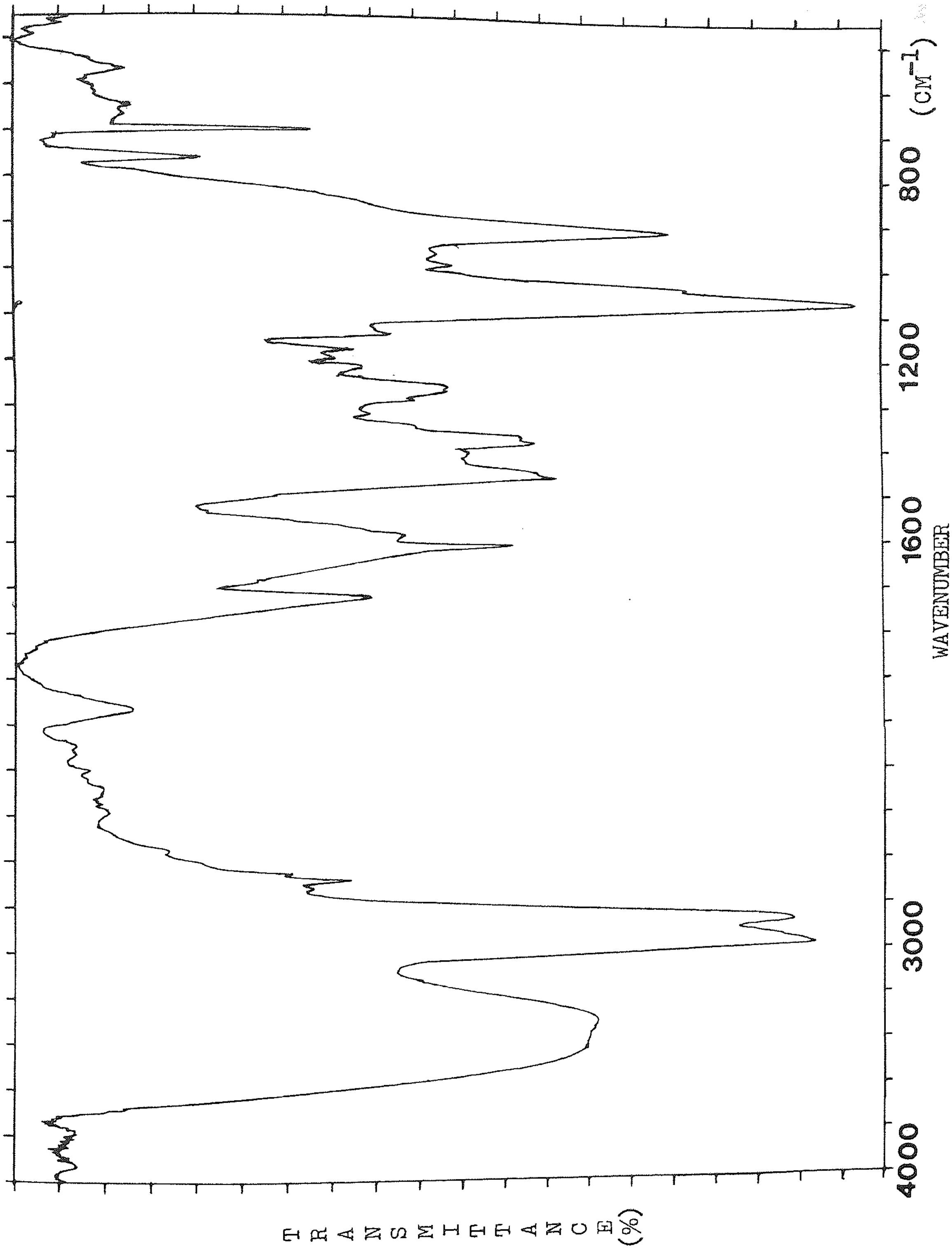


Figure 5.14

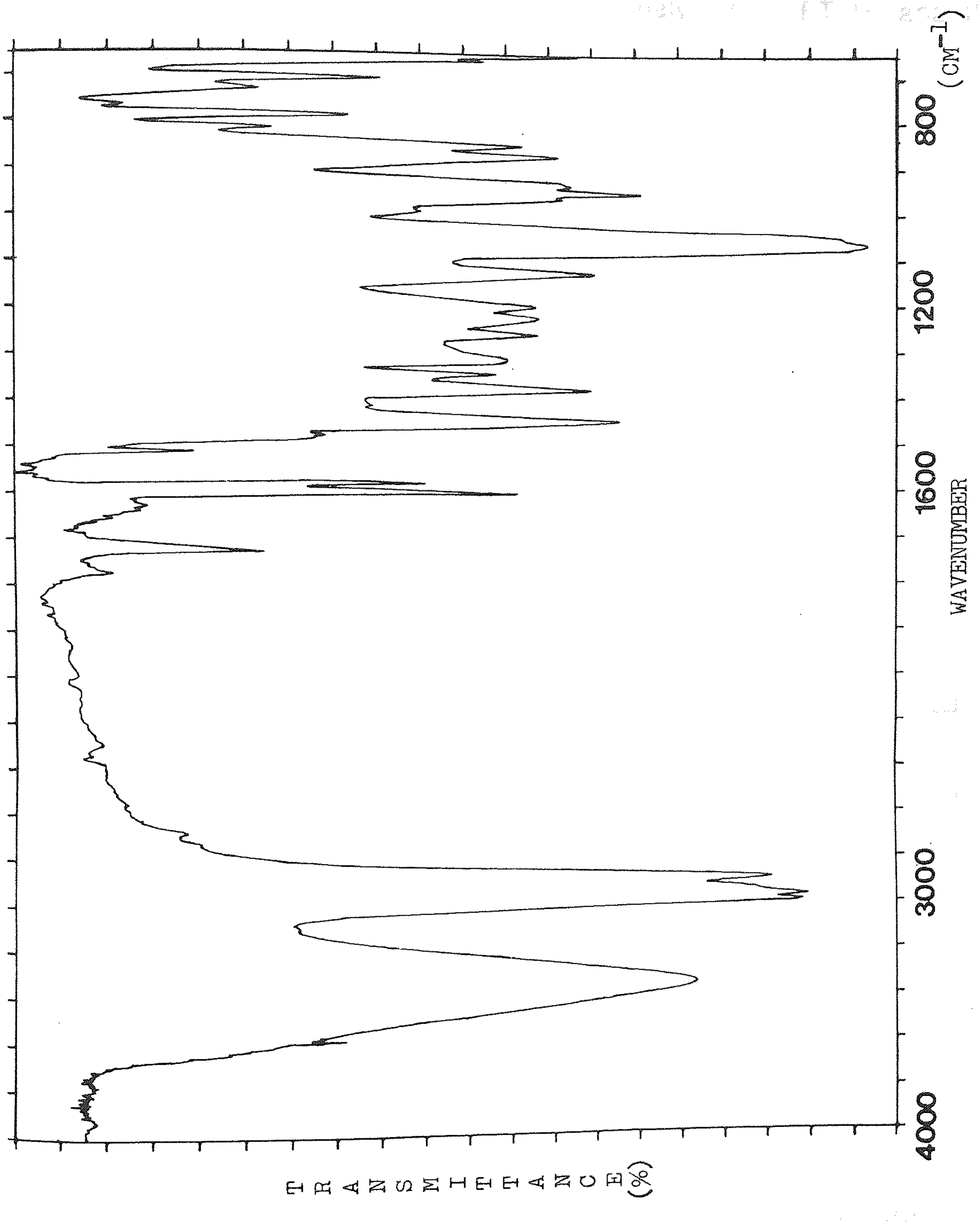


Figure 5.15

5.5.3.2. Effect of reaction time on the extent of hydrolysis of the protecting group

The hydrolysis reaction was also carried out for eight and six hours. The polymer products were analysed by FT IR and the spectra obtained are shown in figures 5.14 and 5.15 respectively. On comparison of the spectra with that obtained after 10 hours it is seen that there is a increase in the amount of carbonyl group formed with reaction time. The degree of reaction after six hours, eight hours and ten hours can be estimated by comparison of the absorbance at 1722cm^{-1} with that of the benzene ring which remains constant at 1605cm^{-1}:

Reaction time (hours)	$\frac{\text{Absorbance } 1722\text{cm}^{-1}}{\text{Absorbance } 1605\text{cm}^{-1}}$
6	0.36
8	0.51
10	1.03

5.5.3.3. Reaction with 2,4 Dinitrophenylhydrazine

A standard test for the presence of a ketone group is reaction with 2,4,-dinitrophenylhydrazine; the primary amine group of the hydrazine reacts with the carbonyl group to form a C=N group. The proposed reaction scheme for the sequence of reactions of the polymer produced by the procedure described in section 5.5.3 with 2,4,-dinitrophenylhydrazine is shown in figure 5.18.

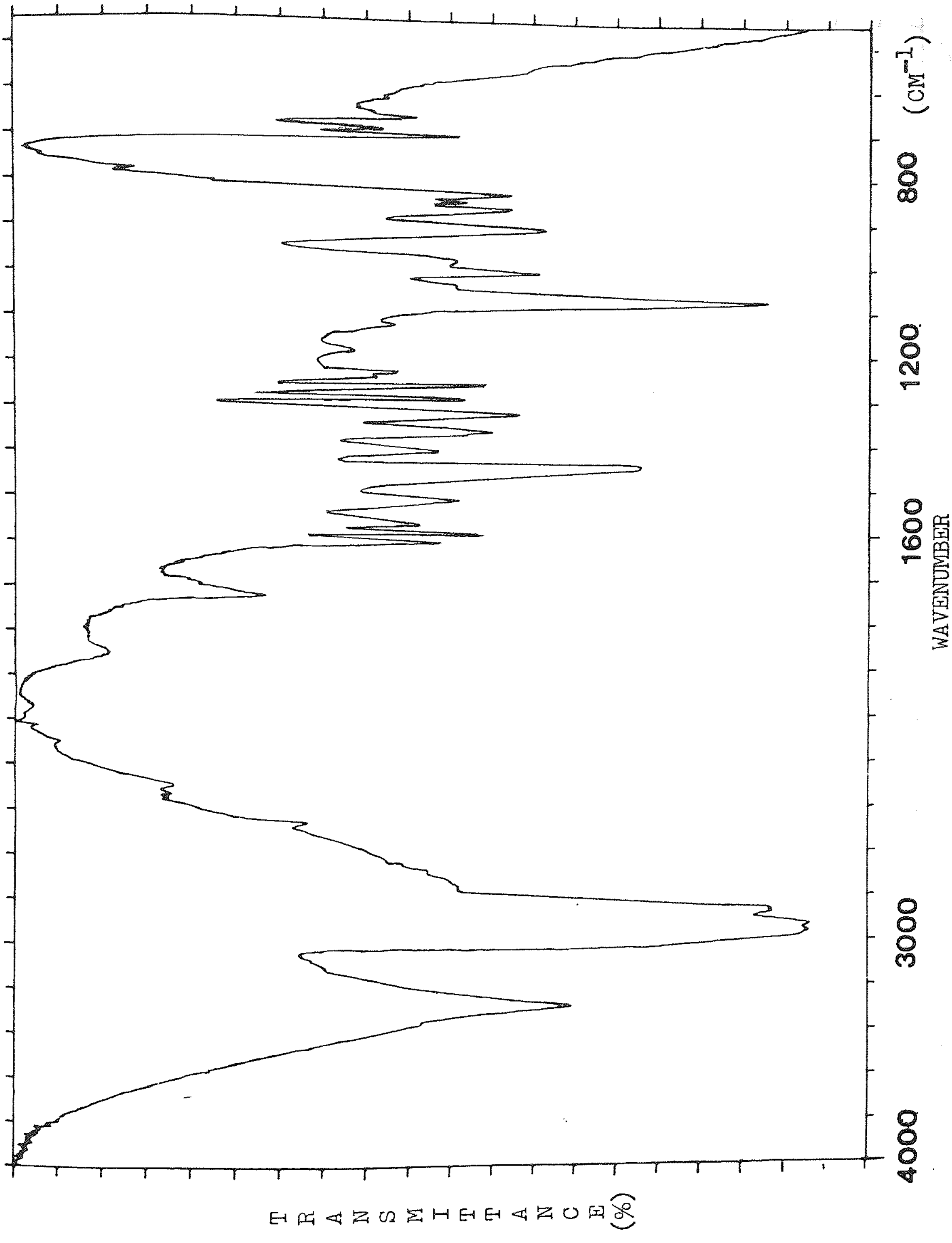


Figure 5.16

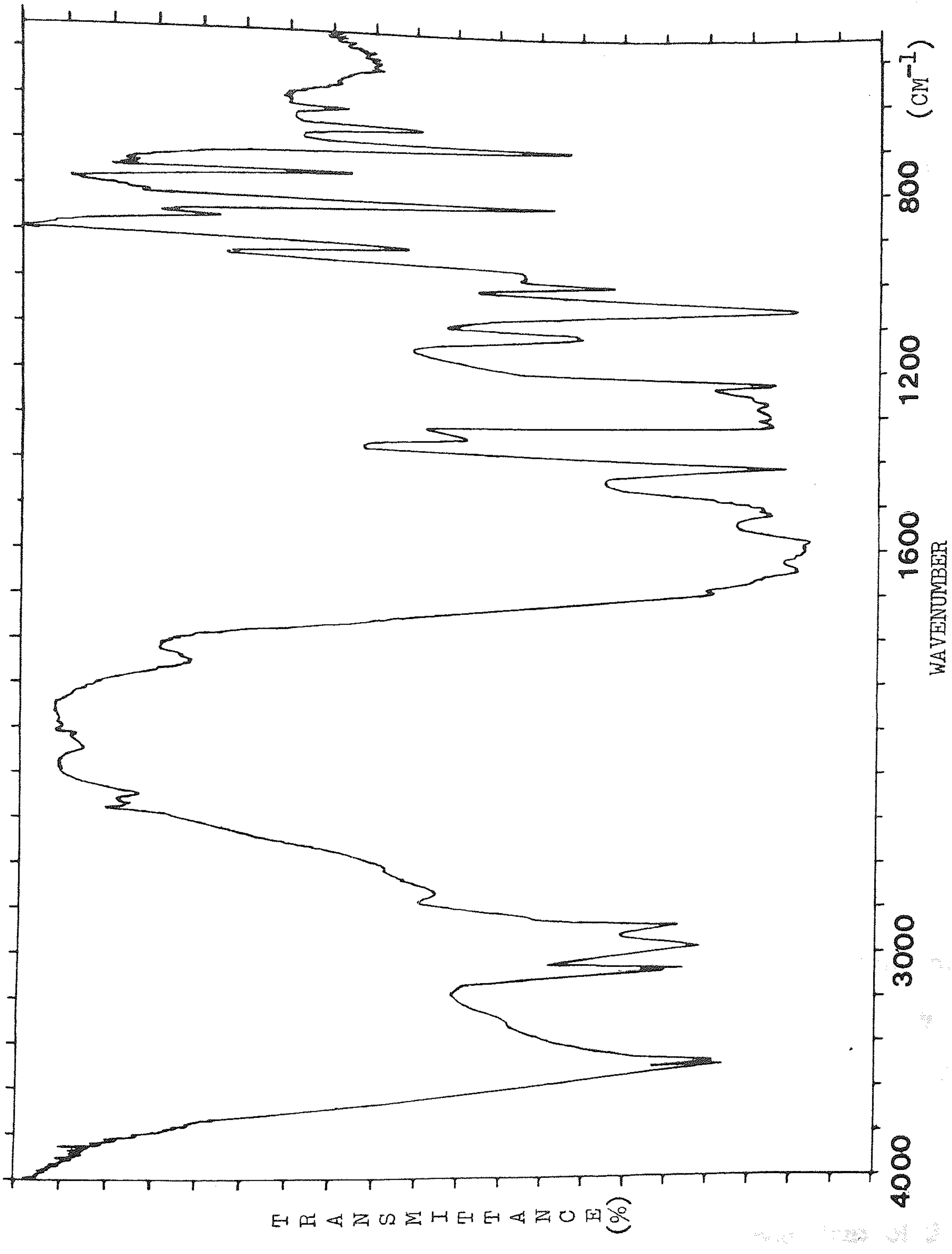


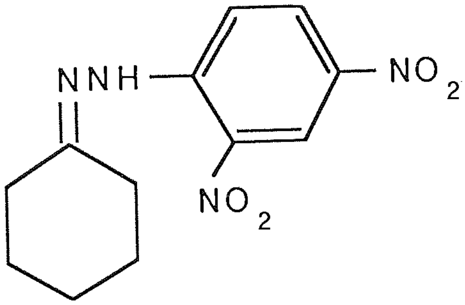
Figure 5.17

5ml of 0.25M solution of 2,4,-dinitrophenylhydrazine was added to 0.002 moles of the polymer produced in section 5.5.3 dissolved in 10ml of THF.

5.5.3.3.1. Analysis of the product

A solution of the product in THF was analysed by FT IR as a thin liquid film between sodium chloride plates. The spectrum obtained is shown in figure 5.16.

On comparison of the spectrum obtained with that of poly(6-(vinylphenyl)hexan-2-one it is seen that there is a reduction in the intensity of the absorbance due to the carbonyl group at 1720cm^{-1}. There is also the appearance of a new absorbance at 1620cm^{-1}. If reference is made to the spectrum of cyclohexanone 2,4-dinitrophenylhydrazone



produced by Aldrich Chemical Company it is seen that this compound shows an absorbance at 1619cm^{-1}. Therefore it seems reasonable to postulate that the absorbance at 1620cm^{-1} is due to a C=N group.

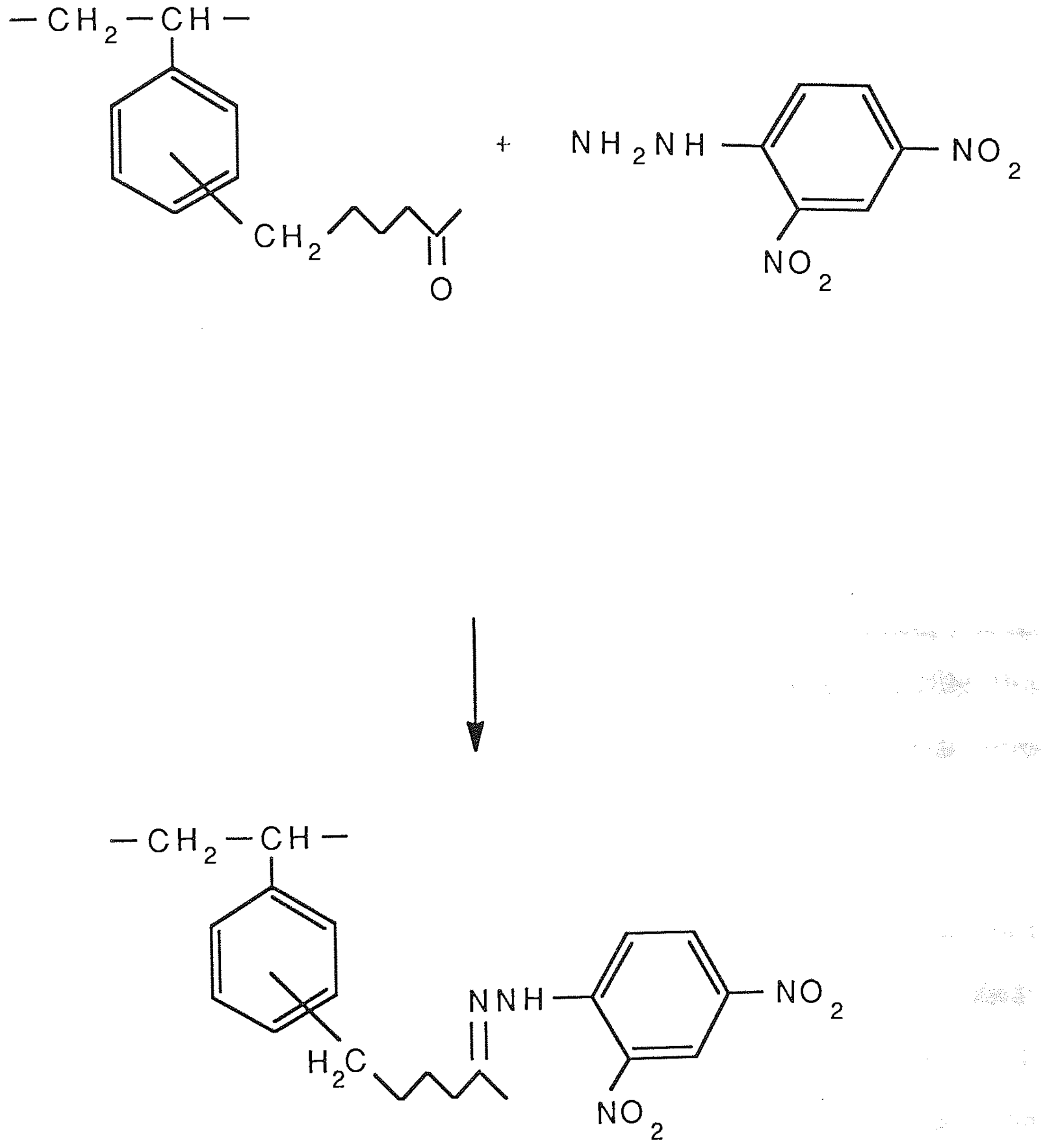
On comparison of the spectrum of the product with that of 2,4 dinitrophenylhydrazine (shown in figure 5.17) it can be seen that the absorbance at 1648cm^{-1} (which is probably due to a primary amine group) has completely disappeared in the product. Furthermore, 2,4,-dinitrophenylhydrazine shows two absorbances between 3300cm^{-1} and 3400cm^{-1} which are characterSistic of a primary amine whereas the product only shows one absorbance in this region. Thus it would appear that the 2,4 dinitrophenylhydrazine reacts completely via its NH_2 group.

The carbonyl group does not disappear completely since poly(6-(vinylphenyl)hexan-2-one was present in excess and therefore does not react to completion.

Figure 5.18

poly(6-(vinylphenyl) hexan-2-one)

2,4-dinitrophenylhydrazine

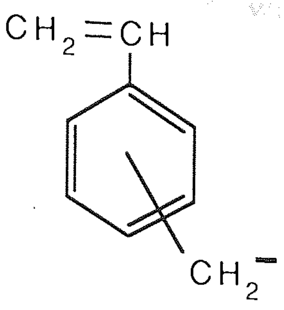


poly(6-(vinylphenyl)hexan-2-one 2,4-dinitrophenylhydrazone

5.6 Discussion and conclusions

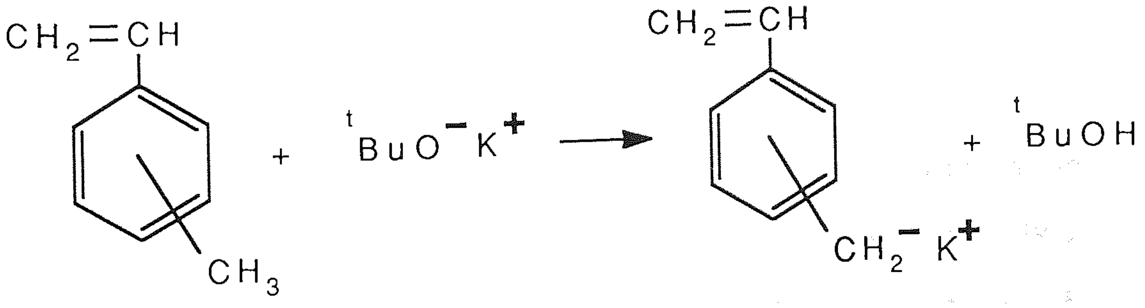
The work described previously in chapter four on the synthesis of carboxylated vinyltoluene showed that a lithiated intermediate could be prepared by the reaction of vinyltoluene with lithium diisopropylamide. In this way the anionic polymerisation of the monomer was inhibited by the judicious selection of reacting base (the diisopropylamide ion). Indeed, reactions of this type on vinyltoluene must be carried out under conditions such that all the butyllithium used in the reaction has been removed to form the diisopropylamide ion. This is achieved by reacting butyllithium with an excess of diisopropylamine and in this case the excess amine reacted preferentially with CPMD thus abrogating this method as a suitable synthetic route. The only way to overcome this disadvantage of lithium diisopropylamide (LDPA) would be to titrate the amine with butyllithium so that the effective molar ratio Li:N was exactly 1:1 or separately prepare and purify the LDPA. Both these methods were beyond the scope and time available in this project.

The ease with which the methyl group of vinyltoluene reacted with LDPA suggested that the methyl protons were somewhat acidic. Alkoxides are commonly used as the catalytic bases in reactions such as the Claisen and aldol condensation reactions where the base ($^{-}$OR) reacts with an acidic proton. Although KBu^tO has not been used as a metallating agent, as far as is known, it seems reasonable to suggest that the methyl proton of vinyltoluene is sufficiently acidic to be removed by the t-butoxide ion ($pk_aBu^tOH=18$; $pk_a{}^{-}NH_2=33$) because all the evidence from the monomer synthesis through the production of polymer, suggests that the intermediate



is formed.

Reaction of KBu^{t}O with vinyltoluene resulted in a deep lilac solution which was shown by UV to be highly conjugated. Evidence for this degree of conjugation could be accounted for by delocalisation of the charge on the CH_2^- anion by interaction with the ring π system and the carbon double bond of the vinyl group or the formation of a charge transfer system between the ring π system and the potassium counterion. Reaction of this intermediate with Michlers ketone gave the expected IR and UV spectra associated with the production of a highly conjugated product. Accordingly it is concluded that the KBu^{t}O is a sufficiently strong base to react with vinyltoluene.



It should be noted that the other product of this reaction is expected to be Bu^{t}OH. The advantage of using this technique of metallation in this instance is that the intermediate does not polymerise prematurely and also contains no functional group that will undergo side reactions with the dioxalane.

Sequential UV analysis of the product of the reaction of the metallated monomer with CPMD showed the progressive disappearance of the absorbance due to a possible charge transfer complex. During the course of a successful reaction the chlorine atom of the dioxalane moiety reacts with CH_2^- and KCl is produced as a by-product. Thus the disappearance of this complex and therefore the degree of reaction of the monomer with the chlorinated dioxalane was seen to increase with reaction time.

Evidence for the formation of the desired product is more conclusive when the polymerisation data are considered. It was difficult to obtain definitive structural evidence that the monomer was the desired product because of the occurrence of absorbances from the reactant and expected products in the same region of the IR. However, the disappearance of the absorbance at 550nm in the UV when the intermediate reacted with CPMD showed that the conjugated system was destroyed and replaced by material that showed absorbances only in the region below 350nm. This would be expected but the reaction needs to be studied in greater detail to ascertain the optimum reaction conditions.

Confirmatory evidence of the success of the reaction is required; mass spectrometry and NMR analysis are two techniques that might provide such data. Other routes to the monomer, particularly the reactive intermediate anion, should be investigated, for example, reaction of bromostyrene with magnesium to form a styryl Grignard derivative.

IR analysis of the product of the anionic polymerisation of the protected monomer provided more corroboratory evidence concerning structure; the most notable point is that whilst the spectrum of the polymer sample showed the expected reduction in absorbaces due to the vinyl group, the dioxalane ring appeared to remain intact during polymerisation process. Furthermore, there were no absorbances in the region characteristic of the C-Cl group providing evidence that the dioxalane group reacts with the monomer by displacement of its chloride ion.

Further supportive evidence was provided by subsequent reactions of the polymer; IR analysis of the hydrolysed material showed that the dioxalane group disappeared and was replaced by a ketone group. The IR spectrum showed a strong absorbance characteristic of the carbonyl group at 1720cm^{-1}. Furthermore, when the IR spectra of polymer samples hydrolysed for different periods of time were compared, the progressive appearance of the carbonyl group at 1720cm^{-1} and the progressive disappearance of absorbances due to the dioxalane ring could be seen.

However, proof that the absorbance at 1720cm^{-1} was due to a ketone group was provided by reaction of the hydrolysed polymer sample with 2,4,-dinitrophenylhydrazine. It seemed reasonable to suggest that this reaction resulted in the formation of the corresponding hydrazone as shown in figure 5.18, when the IR spectrum of the sample was compared with the published spectrum of an analogous hydrazone.

GPC analysis of the polymer product showed that it had a very narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n$=1.05) which is the characteristic of a living polymer system. However, the molecular weight was higher than expected showing that initiation was not 100% efficient; the inefficiency could possibly be accounted for by reaction of butyllithium with either t-butanol, a side product of metallation of the monomer, or excess CPMD. This problem could be overcome by purification of the monomer before addition of butyllithium. One possible method by which these substances could be removed is by vacuum distillation. However, difficulties could be then encountered due to the relatively high boiling point of CPMD. Nevertheless, there is a need for a controlled synthesis and methods for controlling the molecular weight of the polymer must be looked into.

Further proof for the existence of a living system was provided by the fact that the polymerisation solution was red which is characteristic of the $^{-}C(Ph)H$ group produced during an anionic polymerisation process.

In conclusion, all the evidence suggests that a successful method of producing a polymer which possesses ketone groups and has a narrow molecular weight distribution has been devised.

CHAPTER SIX

SUGGESTIONS FOR

FURTHER WORK

6. Suggestions for further work

The aim of the project was to produce polymeric materials possessing functional groups. The main conclusion to arise from this work is that it is very difficult to functionalise polymers directly and a more successful route is functionalisation and subsequent polymerisation of the monomer. This is exemplified by comparing the work on metallation of polymers with that involving formation and polymerisation of a monomer with a protected ketone group.

Since a pathway has been devised to produce a polymeric ketone, further work could be concerned with investigating ways by which to control the reaction at various stages of the synthesis and to develop optimum reaction conditions by carrying out kinetic studies. In addition work needs to be carried out to ascertain structural information on the intermediate products thus giving conclusive evidence of the occurrence of the proposed reaction pathway.

Future work could be carried out with regard to developing other routes to the polymeric ketone using alternative protecting groups or reagents such as Grignards in place of potassium t-butoxide. Routes to other functionalised polymers other than ketones could be devised using the appropriate protecting groups. Some examples are shown below:

$-OH \longrightarrow -OSiMe_3$

$-NH_2 \longrightarrow -N(SiMe_3)_2$

$-COOH \longrightarrow$ - Oxazoline

Furthermore the synthetic route to the polymeric ketone could be developed further by looking at subsequent reactions of the polymeric product in more detail.

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APPENDIX ONE

SUPPLEMENTARY SPECTRAL DATA RELATING TO NMR STUDIES

Table (A) Chemical Shift values for poly(bromostyrene)

Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (-C)	121	119.78, 121.56
C 2 (CH)	131	131.24, 131.33 131.59
C 3 (CH)	130	127.73, 128.94 129.12
C 4 (-C)	147	143.06
C 5 (CH)	40.96	40.01
C 6 (CH$_2$)	49.96	43.42

Table (B) Chemical Shift values for p-bromostyrene monomer

Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (-C)	121	119.78, 121.56
C 2 (CH)	131	131.24, 131.33, 131.59
C 3 (CH)	130	127.73, 128.94 129.12
C 4 (-C)	135	135.70
C 5 (CH)	136	136.67
C 6 (CH$_2$)	112	114.58

Table (C) Chemical Shifts for derivative (A) produced by the Grignard reaction

Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (CH)	126	126.25
C 2 (CH)	128	127.66, 128.51
C 3 (CH)	128	127.66, 128.51
C 4 (-C)	137	136.93
C 5 (-C)	148	152.3
C 6 (CH_2)	104	108.85
C 7 (CH_2)	55.86	56.81

Table (D) Chemical shifts for derivative (B) produced during the Grignard reaction

Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (-C)	121	124.62
C 2 (CH)	131	136.93
C 3 (CH)	130	136.93
C 4 (-C)	147	145.46, 146.01
C 5 (CH)	53.96	56.81
C 6 (CH_2)	46.96	40.30

Table (E) Chemical shifts for derivative (C) produced during the Grignard reaction

Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (-C)	121	124.62
C 2 (CH)	131	136.93
C 3 (CH)	130	136.93
C 4 (-C)	135	136.93
C 5 (CH)	125	124.62
C 6 (CH)	137	136.93

Table (F) Chemical Shifts for derivative (D) produced during the Grignard reaction

Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (-C)	121	124.62
C 2 (CH)	131	136.93
C 3 (CH)	130	136.93
C 4 (-C)	147	145.46, 146.01
C 5 (CH_2)	33.86	29.72, 30.58
C 6 (CH_2)	42.65	40.30

Table (G) Chemical Shifts for p-methylstyrene monomer

Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (CH_3)	20-21	20.87, 21.05
C 2 (-C)	135	134.74
C 3 (CH)	128	128.22, 128.30 128.41, 129.03
C 4 (CH)	128	128.22, 128.30 128.41, 129.03
C 5 (-C)	135	134.74
C 6 (CH)	136	136.70, 136.96
C 7 (CH_2)	112	112.38, 113.10

Table (H) Chemical Shifts for m-methylstyrene monomer

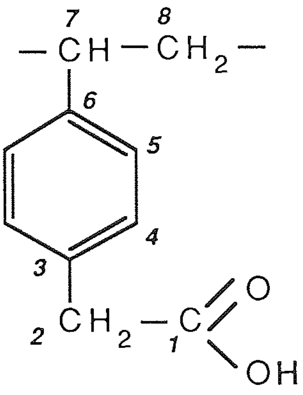
Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (CH_3)	20-21	20.87, 21.05
C 2 (-C)	137	137.18, 137.40 137.66
C 3 (CH)	128	128.22, 128.30 128.41, 129.03
C 4 (-C)	137	137.18, 137.40 137.66
C 5 (CH)	126	126.01, 126.87
C 6 (CH)	128	128.22, 128.30 128.41, 129.03
C 7 (CH)	126	126.01, 126.87
C 8 (CH)	136	136.70, 136.96
C 9 (CH_2)	112	112.30, 113.10

Table (I) Chemical Shift values of poly(p-methylstyrene)

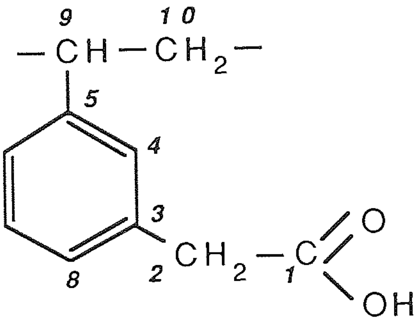
Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (CH_3)	20-21	21.03, 21.39
C 2 (-C)	135	134.67, 134.66
C 3 (CH)	128	127.68, 128.56 128.85, 129.19
C 4 (CH)	128	127.68, 128.56 128.85, 129.19
C 5 (-C)	147	145.46, 146.30
C 6 (CH)	40.96	39.84, 40.25
C 7 (CH_2)	49.96	42.32, 43.78 45.97

Table (J) Chemical Shift values for poly(m-methylstyrene)

Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (CH_3)	20-21	21.03, 21.39
C 2 (-C)	137	136.91, 136.97 137.15, 137.49
C 3 (CH)	128	127.68, 128.56 128.85, 129.19
C 4 (-C)	149	145.46, 146.30
C 5 (CH)	126	127.68
C 6 (CH)	128	127.68, 128.56 128.85, 129.19
C 7 (CH)	126	127.68
C 8 (CH)	40.96	39.84, 40.25
C 9 (CH_2)	49.96	42.32, 43.78 45.97

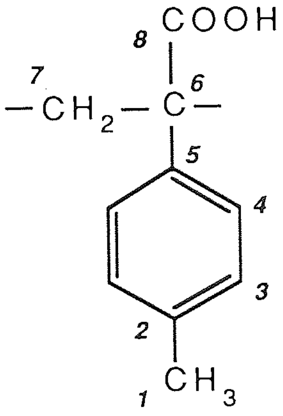


(A)

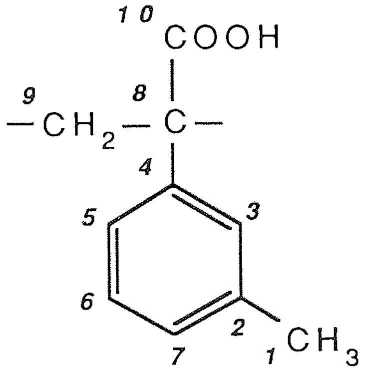


(B)

Figure A1.1 Chemical structures of derivatives formed during lithiation and carboxylation reactions



(C)



(D)

Table (K) Chemical Shifts of derivative (A) formed by the lithiation and carboxylation reactions

Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (COOH)	166-181	181.49
C 2 (CH_2)	41	41.91
C 3 (-C)	135	137.87
C 4 (CH)	138	128.58
C 5 (CH)	128	128.58
C 6 (-C)	147	146.91
C 7 (CH)	40.96	41.91
C 8 (CH_2)	49.96	52.89

Chemical shift at 89δ = Delrin rotor

Table (L) Chemical Shifts of derivative (B) formed by lithiation and carboxylation reactions

Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (COOH)	166-181	181.49
C 2 (CH_2)	41	41.91
C 3 (-C)	137	137.87
C 4 (CH)	128	128.58
C 5 (-C)	149	146.91
C 6 (CH)	126	128.58
C 7 (CH)	128	128.58
C 8 (CH)	126	128.58
C 9 (CH)	40.96	41.91
C 10 (CH_2)	49.96	52.89

Chemical Shift at 89δ= Delrin rotor

Table (M) Chemical Shifts of derivative (C) formed by the lithiation and carboxylation reactions

Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (CH_3)	20-21	23.79
C 2 (-C)	135	137.87
C 3 (CH)	128	128.58
C 4 (CH)	128	128.58
C 5 (-C)	147	146.91
C 6 (-C)	47.96	41.91, 52.89
C 7 (COOH)	166-181	181.49
C 8 (CH_2)	51.96	52.89

Chemical Shift at 89δ = Delrin rotor

Table (N) Chemical Shifts of derivative (D) formed by the lithiation and carboxlyation reactions

Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (CH_3)	20-21	23.79
C 2 (-C)	137	137.87
C 3 (CH)	128	128.58
C 4 (-C)	149	146.91
C 5 (CH)	126	128.58
C 6 (CH)	128	128.58
C 7 (CH)	126	128.58
C 8 (-C)	47.96	41.91, 52.89
C 9 (COOH)	166-181	181.49
C 10 (CH_2)	51.96	52.89

Chemical Shift at 89δ= Delrin rotor

Table (O) Chemical Shifts of the p-amide formed by the reaction of lithium-(p-vinylphenylacetate) with lithium diisopropylamide

Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (CH_3)	16.36	19.82
C 2 (CH)	15.34	19.82
C 3 ($CONR_2$)	162-179	164.82
C 4 (CH_2)	41	38.85
C 5 (-C)	135	141.71
C 6 (CH)	128	127.53
C 7 (CH)	128	127.53
C 8 (-C)	147	127.53
C 9 (CH)	40.96	38.85
C 10 (CH_2)	49.96	46.31

Chemical Shift at 89δ = Delrin rotor

Table (P) Chemical Shifts of the m-amide formed by the reaction of lithium(m-vinylphenylacetate) with lithium diisopropylamide

Type of carbon	Expected chemical shift (δ)	Obtaineded chemical shift (δ)
C 1 (CH_3)	16.36	19.82
C 2 (CH)	15.34	19.82
C 3 ($CONR_2$)	162-179	164.82
C 4 (CH_2)	41	38.85
C 5 (-C)	137	141.71
C 6 (CH)	128	127.53
C 7 (-C)	149	141.71
C 8 (CH)	126	127.53
C 9 (CH)	128	127.53
C 10 (CH)	126	127.53
C 11 (CH)	40.96	38.85
C 12 (CH_2)	49.96	46.31

Chemical Shift at 89δ = Delrin rotor

Table (Q) Chemical Shifts of poly(p-vinylphenylacetic acid) formed by lithiation using lithium diisopropylamide

Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (COOH)	166-181	181.01
C 2 (CH_2)	41	38.85
C 3 (-C)	135	141.71
C 4 (CH)	128	127.53
C 5 (CH)	128	127.53
C 6 (-C)	147	141.71
C 7 (CH)	40.96	38.85
C 8 (CH_2)	49.96	46.31

Chemical Shift at 89δ = Delrin rotor

Table (R) Chemical Shifts of poly(m-vinylphenylacetic acid) formed by lithiation using lithium diisopropylamide

Type of carbon	Expected chemical shift (δ)	Obtained chemical shift (δ)
C 1 (COOH)	166-181	181.01
C 2 (CH_2)	41	38.85
C 3 (-C)	137	141.71
C 4 (CH)	128	127.53
C 5 (-C)	149	141.71
C 6 (CH)	126	127.53
C 7 (CH)	128	127.53
C 8 (CH)	126	127.53
C 9 (CH)	40.96	38.85
C 10 (CH_2)	49.96	46.31

APPENDIX TWO

A COMPUTER PROGRAM FOR
THE DETERMINATION OF
$\overline{M}_n$ AND $\overline{M}_w$ FROM
GPC RESULTS

```
SPEED=155

]LIST

2  DIM V(100),H(100),M(100),W(100),N(100),X(100),Y(100)
5  HOME :D$ =  CHR$ (4)
10  PRINT D$;"OPEN";"CALIB GPC"
15  PRINT D$;"READ";"CALIB GPC"
18  INPUT N
19  DIM D(N),B(N),L(N)
20  FOR I = 0 TO N - 1
22  INPUT D(I)
23  INPUT B(I)
24  INPUT L(I)
25  NEXT
27  INPUT G
29  INPUT C
30  INPUT R
35  REM "D(I)=MOL.WT.AT B(I)(ELUTION VOL)"
40  PRINT D$;"CLOSE";"CALIB GPC"
45  VTAB 12
50  PRINT "PROGRAM FOR CALCULATION OF MN AND MW OF"
51  PRINT "POLYMER FROM GPC TRACE"
52  PRINT
53  PRINT
55  INPUT "WHAT IS THE CODE NAME FOR THIS SAMPLE?";NAME$
56  IF NAME$ = "" THEN  GOTO 55
57  INPUT "DATE OF ANALYSIS";TIME$
60  PRINT "HOW MANY SETS OF DATA HAVE YOU?"
70  INPUT K
72 K = K - 1
76  PRINT
77  PRINT
85  PRINT
86  PRINT "PRESS ANY KEY TO CONTINUE"
90  GET A$
100  HOME
105  SPEED= 155
110  PR# 2
113  PRINT "GPC ANALYSIS FOR SAMPLE ";NAME$;" ";TIME$: PRINT : PRINT
114  PR# 0
130  PRINT "YOU MAY EITHER TYPE IN EACH ELUTION VOL OR IF THEY ARE AT REGULAR INTERVALS YOU"
131  PRINT "MAY TYPE IN THE FIRST AND LAST VALUES   TOGETHER WITH THE INTERVAL"
132  PRINT "1-INDIVIDUAL VALUES"
133  PRINT "2-FIRST LAST AND INTERVAL"
134  PRINT "PRESS THE APPROPRIATE KEY"
135  GET ANS$
136  IF ANS$ = "1" GOTO 150
137  IF ANS$ = "2" GOTO 140
```

```
138  GOTO 135
140  GOSUB 8000
145  GOTO 175
150  HOME : PRINT "TYPE IN YOUR DATA IN PAIRS AS ELUTION   VOLUME(RETURN) AND HEIGHT (RETURN)"
152  PRINT  TAB( 2)"ELUTION VOL(ML)"; TAB( 25)"HEIGHT(MM)"
153 I = 0
155  INPUT "VE(ML)= ";V(I): INPUT "H(MM)=";H(I)
160 I = I + 1
170  IF I <  = K GOTO 155
175  GOSUB 4000
176  GOSUB 6000
180 S1 = 0
190 S2 = 0
200 S3 = 0
210  FOR I = 0 TO K
215  REM  "FIND VALUE OF M(I)"
220  GOSUB 2000
230 S1 = S1 + (H(I) * M(I))
240 S2 = S2 + H(I)
250 S3 = S3 + (H(I) / M(I))
254 W(I) = H(I)
256 N(I) = H(I) / M(I)
260  NEXT I
270 MW = S1 / S2
280 MN = S2 / S3
290 D = MW / MN
300 MW =  INT (MW / 10) * 10
310 MN =  INT (MN / 10) * 10
320 D =  INT (D * 100) / 100
330  PR# 2
340  PRINT "WEIGHT AVERAGE M WT= ";MW
342  PRINT
343  PRINT
350  PRINT "NO.AVERAGE M WT = ";MN
352  PRINT
354  PRINT
356  PRINT "POLYDISPERSITY= ";D
360  PR# 0
400  PRINT "DO YOU WANT INFORMATION ON THE DISTRIBUTION? Y?N"
410  INPUT A$
420  HOME
430  IF A$ = "N" GOTO 740
435  PR# 2
437  POKE 36,2: PRINT "ELUTION VOL";: POKE 36,15: PRINT "HEIGHT";: POKE 36,32: PRINT "M WT";: PO
6,47: PRINT "WT.FRACT";: POKE
    36,60: PRINT "NO.FRACT"
455  PRINT
460  FOR I = 0 TO K
462 W(I) =  INT (W(I) * 1000 / S2) / 1000
464 N(I) =  INT (N(I) * 1000 / S3) / 1000
470  POKE 36,3: PRINT V(I);: POKE 36,16: PRINT H(I);: POKE 36,33: PRINT  INT (M(I));: POKE 36,48
INT W(I);: POKE 36,61: PRINT
     N(I)
475  PRINT
480  NEXT I
490  PR# 0
495  GOSUB 5000
500  PRINT "DO YOU WISH TO SEE A WT. FRACT.CURVE? Y/N"
510  INPUT A$
515  HOME
520  IF A$ = "N" GOTO 620
525  HOME
530  PRINT "WHAT IS THE MAX. VALUE OF W(I)?"
540  INPUT WL
545  HOME
550  GOSUB 3000
555  VTAB 22
556  PRINT "RANGE OF W(I) FROM 0 TO ";WL
560  FOR I = 0 TO K
570 X(I) = (200 * M(I) / M(0)) + 20
580 Y(I) = 150 - (140 * W(I) / WL)
590  HPLOT X(I),Y(I)
```

```
600  NEXT I
602  PRINT "DO YOU WANT TO CHANGE UPPER LIMIT? Y/N"
604  INPUT A$
605  TEXT
606  IF A$ = "Y" GOTO 525
620  PRINT "DO YOU WISH TO SEE A NO. CURVE ? Y/N"
630  INPUT A$
640  HOME
650  IF A$ = "N" GOTO 740
652  HOME
655  PRINT "WHAT IS THE UPPER LIMIT OF N( I )?"
660  INPUT NU
670  GOSUB 3000
672  VTAB 22
675  PRINT "RANGE OF N( I ) FROM 0 TO ";NU
680  FOR I = 0 TO K
690 X( I ) = (200 * M( I ) / M( 0 )) + 20
700 Y( I ) = 150 - (140 * N( I ) / NU )
710  HPLOT X( I ),Y( I )
720  NEXT I
725  PRINT "DO YOU WISH TO CHANGE THE UPPER LIMIT? Y/N"
728  INPUT A$
730  TEXT
732  IF A$ = "Y" GOTO 652
733  PRINT "DO YOU WISH TO KEEP A DISC FILE OF THESE RESULTS? Y/N"
734  GET ANS$
735  IF ANS$ = "Y" THEN  GOSUB 7000
740  PRINT "DO YOU WISH TO ANALYSE ANOTHER CURVE? Y/N"
745  SPEED= 255
750  INPUT A$
755  HOME
760  IF A$ = "Y" GOTO 55
770  END
2000 M( I ) = 10 ↑ (C + (G * V( I )))
2010  RETURN
3000  REM  SET HGR
3010  HGR
3020  REM  DRAW GRID
3030  FOR A = 20 TO 220 STEP 50
3040  HPLOT A,10 TO A,150
3050  NEXT A
3060  FOR B = 10 TO 150 STEP 70
3070  HPLOT 20,B TO 220,B
3080  NEXT B
3085  VTAB 21
3087 T =  INT (M( 0 ) / 1000 ) * 1000
3090  PRINT  TAB( 3)0; TAB( 15 )T / 2; TAB( 30 )T
3100  RETURN
4000  PRINT : PRINT "THE COLUMNS ARE CALIBRATED FOR ": PRINT "POLYSTYRENE. DO YOU WISH TO CHANGE
": PRINT "CALIBRATION CUR
     VE?"
4010  PRINT "TO DO SO YOU NEED TO INPUT THE MARK-": PRINT "HOUWINK PARAMETERS FOR POLYMER IN THE
4020  PRINT "SOLVENT USED.PRESS THE APPROPRIATE KEY": PRINT "Y- TO RECALIBRATE": PRINT "N- TO C
UE UNCHANGED"
4030  PRINT : GET ANS$
4040  IF ANS$ = "Y" THEN  GOTO 4060
4050  RETURN
4060  HOME : PRINT : PRINT "MARK-HOUWINK PARAMETERS FOR YOUR POLYMER"
4070  INPUT "K=";P2: INPUT "A=";A2
4080  PRINT "THE COLUMNS HAVE BEEN CALIBRATED USING": PRINT "CHLOROFORM AS SOLVENT THE MARK HOU
: PRINT "PARAMETERS ARE K
     =7.2*10↑5 AND A=.76"
4090  PRINT "IF THE K AND A VALUES FOR ";: FLASH : PRINT "POLYSTYRENE ";: NORMAL : PRINT "IN YO
LVENT DIFFER SIGNIFICANTL
     Y FROM THESE YOU ARE ADVISED TO CHANGE THESE   PARAMETERS."
4100  PRINT "DO YOU NEED TO CHANGE THE  PARAMETERS?   Y/N"
4110  PRINT : GET ANS$
4120  IF ANS$ = "N" THEN  GOTO 4140
4130  INPUT "K=";P1: INPUT "A=";A1: GOTO 4150
4140 P1 = 7.2 * 10 ↑ 5:A1 = .76
4150 G = G * (1 + A1) / (1 + A2):C = C * (1 + A1) / (1 + A2) + (( LOG (P1 / P2) /  LOG (10)) / (
A2))
```

```
4160  RETURN
5000  PR# 2
5010  PRINT : PRINT : PRINT "INFORMATION CONCERNING THE CALIBRATION CURVE"
5015  PRINT
5020  PRINT "THE CALIBRATION CURVE FOR YOUR POLYMER  OBEYS THE EQUATION- "
5030  PRINT "LOG M(I)=";G;"*V(I)+";C
5040  PRINT : PRINT : PRINT "THE HIGHEST MOLECULAR WEIGHT CALIBRANT WAS ";D(0);" AND THE LOWEST "
5050  PRINT "WAS ";D(N - 1)
5060  PRINT "THEIR RESPECTIVE ELUTION VOLUMES WERE ";B(0);" AND ";B(N - 1)
5065  PR# 0
5070  RETURN
6000  PRINT  TAB( 2)"SAMPLE"; TAB( 14)"ELUTION VOL"; TAB( 30)"HEIGHT"
6010  FOR I = 0 TO K
6020  PRINT  TAB( 3)I + 1; TAB( 15)V(I); TAB( 31)H(I)
6030  NEXT
6040  PRINT : PRINT "ARE THESE VALUES CORRECT? Y/N "
6050  GET ANS$
6060  IF ANS$ = "N" THEN  GOTO 6080
6070  RETURN
6080  INPUT "SAMPLE NO. TO BE CHANGED? ";I:I = I - 1
6090  PRINT "THE ELUTION VOLUME FOR ";I + 1;" IS ";V(I);" AND HEIGHT ";H(I)
6100  INPUT "ELUTION VOLUME ";V(I)
6120  INPUT "HEIGHT ";H(I)
6130  HOME : GOTO 6000
7000  SPEED= 255: PRINT : PRINT D$;"OPEN";NAME$
7010  PRINT D$;"WRITE";NAME$
7020  PRINT K + 1
7030  FOR I = 0 TO K
7040  PRINT M(I)
7050  PRINT V(I)
7060  PRINT H(I)
7070  PRINT W(I)
7080  PRINT N(I)
7090  NEXT
7100  PRINT G
7110  PRINT C
7120  PRINT R
7130  PRINT D(0)
7140  PRINT D(N - 1)
7150  PRINT B(0)
7160  PRINT D$;"CLOSE";NAME$
7180  REM  FILE K,M(I),V(I),H(I),W(I),N(I)AND CALIBRATION DATA
7190  REM  LAST 4 ENTRIES ARE MWT OF STANDARDS AND ELUTION VOLS.
7200  RETURN
8000  HOME : INPUT "LOWEST VALUE OF ELUTION VOLUME";V(0)
8010  INPUT "FINAL VALUE OF THE ELUTION VOLUME";V(K)
8020  INPUT "ELUTION VOLUME INTERVAL";U
8030  FOR I = 0 TO K
8040 V(I) = V(0) + (I * U)
8050  PRINT "HEIGHT FOR ELUTION VOLUME ";V(I)
8060  INPUT H(I)
8070  NEXT
8080  RETURN

]K

?SYNTAX ERROR
```