LABELLED POLYMERS - SYNTHESIS, ANALYSIS

AND DEGRADATION STUDIES

A thesis

Submitted to the University of Surrey in partial fulfilment of the requirement for the Degree of Doctor of Philosophy in the Faculty of Science

by

R.J.Diamond

Cecil Davies Laboratory
Department of Chemistry
University of Surrey
Guildford
Surrey

October 1988

1153963

ProQuest Number: 11015124

All rights reserved

INFORMATION TO ALL USERS
The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript
and there are missing pages, these will be noted. Also, if material had to be removed,
a note will indicate the deletion.

ProQuest 11015124

Published by ProQuest LLC (2018). Copyright of the Dissertation is held by the Author.

All rights reserved.
This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

Abstract

The study of polymer degradation and the mechanisms involved is essential if materials with improved properties are to be developed. Isotopes and isotopically labelled compounds can be useful tools in studies of reaction mechanisms, offering some unique advantages over the more common techniques. The work presented here details the labelling and analysis of a range of monomers and polymers with deuterium and tritium followed by a preliminary investigation of their usefulness in mechanistic studies.

The thesis is divided into four sections as follows:-

Chapter one contains a literature survey which describes the use to which isotopes and isotopically labelled compounds have been put in the study of polymer chemistry.

Chapter two details the labelling with tritium and analysis by tritium NMR spectroscopy of a range of monomers and polymers.

Chapter three describes the labelling with deuterium and analysis by deuterium NMR spectroscopy of a range of monomers and polymers.

Chapter four details a study of the kinetics of the degradation of poly([G-^{3}H]-butylmethacrylate) by acid catalysed hydrolysis.

Contents

Page

Acknowledgements..... iii

Dedication..... iv

Chapter

1. The Uses of Isotopes in Polymer Chemistry..... 1

1.1 Introduction..... 2

1.2 The Preparation of Labelled Polymers..... 7

1.3 Polymerisation Studies..... 9

1.4 Polymer Characterisation by Spectroscopic Methods..... 30

1.5 Polymer Degradation Studies..... 35

1.6 Applications of Labelled Polymers..... 39

1.7 Summary..... 41

1.8 References..... 44

2. The Preparation and Analysis of Tritium Labelled Monomers and Polymers..... 54

2.1 Introduction..... 55

2.2 Materials and Equipment..... 66

2.3 Synthesis of ^{3}H-Labelled Monomers..... 67

2.4 Preparation of ^{3}H-Labelled Polymers..... 72
2.5 Results..... 74
2.6 Discussion..... 94
2.7 Conclusions..... 98
2.8 References..... 99

3. The Preparation and Analysis of Deuterium Labelled Monomers and Polymers..... 101
3.1 Introduction..... 102
3.2 Properties of Deuterium..... 104
3.3 Materials and Equipment..... 106
3.4 Synthesis of ^{2}H-Labelled Monomers and Polymers..... 107
3.5 Analysis of ^{2}H-NMR Spectra..... 111
3.6 Discussion..... 123
3.7 Conclusions..... 127
3.8 References..... 128

4. The Application of Labelled Polymers to Degradation Studies..... 129
4.1 Introduction..... 130
4.2 Experimental..... 143
4.3 Results..... 144
4.4 Discussion..... 146
4.5 Conclusions..... 149
4.6 References..... 152

Acknowledgements

I would like to thank Dr.J.R.Jones and Prof.W.W.Wright for their support and encouragement throughout this period of study. I would also like to thank Dr.A.Derome, Dr.C.Groombridge and Mr.J.Bloxsidge for their assistance with the NMR spectroscopy. Finally I am very grateful to Mrs.L.Carroll and the other members of staff and students of the Dept. of Chemistry, University of Surrey for their ideas and their help both in and out of the laboratory.

To Christine

CHAPTER ONE

The Uses of Isotopes in Polymer Chemistry

1.1 Introduction

Nowadays polymers are an integral part of most manufacturing processes, be it either at an intermediate or final stage; this is reflected in the fact that in the UK alone in 1986, 2·7m tonnes were produced at a cost of over £1·5bn with consumption of polymers up 5% over the previous year.[1] The major sector of the market consisted of low and high density polyethylenes, mainly used for packaging, of which some 900 000 tonnes were produced. The other large areas of the market were occupied by PVC (484 000 tonnes) used in the manufacture of plastic bottles, records and floor and wall coverings and polypropylene (370 000 tonnes) used for food packaging mainly, but increasingly used in the automobile industry.

The growth in consumption of polymers can be attributed to the advantages they offer over older conventional materials such as metals and glass. The mechanical properties of polymers are probably their most important feature whether as elastomers or chosen for their structural properties. An example of the significant improvements that can be offered over conventional materials by polymers is shown in Table 1.1[2], where a comparison is made between the physical properties of some metals and fibre-reinforced

Table 1.1 Typical Properties of Fibre-Reinforced (55-75% fibre) Composites and Metals

		Specific Gravity	Ultimate Tensile Strength (GPa)	Young's Modulus (GPa)	Specific Tensile Strength (GPa)	Specific Young's Modulus (GPa)
Epoxy Composites	General Purpose	1·5	1·5	110	1·00	74
	High Strength	1·5	1·9	130	1·27	87
	High Modulus	1·6	1·5	190	0·94	119
Steel		7·8	1·0	210	0·13	27
Titanium		4·5	0·96	110	0·21	25
Aluminium		2·8	0·47	75	0·17	26

epoxy composites. The specifications demonstrate that in all bar one case, the epoxy composites are lighter and stronger than common metals. Other useful properties of polymers include their electrical and thermal resistance which makes them suitable as electrical insulators, capacitor dielectrics and for thermal insulation. Many polymers have a high optical transmittance and are used in safety glass and contact lenses; others are used for surgical implants where materials are required that are inert or undergo controlled decomposition and do not induce immune reactions.

While polymers do offer advantages over metals and glass etc. there is still scope for further improvements in many areas such as dimensional and thermal stability, toughness, scratch and mar resistance, weathering, inertness to chemicals, processability and cost. The synthesis of novel polymers is one route by which polymers with improved properties may be obtained, the alternative being studies of polymer degradation with the aim of determining the reaction mechanisms involved and devising ways of inhibiting them. Reaction mechanisms and kinetics, be they concerned with the rate of polymerisation of a novel monomer or the degradation of a polymer by ultra-violet irradiation for example are usually determined by a range of physical techniques. Rates of polymerisation

are generally followed by either changes in molecular weight, changes in refractive index or volume of the monomer/polymer mixture, and degradation studies by such techniques as differential thermal analysis, thermal volatilisation analysis, differential scanning calorimetry, pyrolysis gas chromatography and ultra-violet/infra-red spectroscopy. An alternative approach to reaction mechanism studies involves the use of isotopically labelled compounds, a technique that can offer some unique advantages over the more common methods. The main advantage of using labelled compounds is the ability to follow a particular molecule or part of a molecule through a series of reactions; this is particularly true for compounds labelled with radioisotopes. Other features that make isotope labelling unique are as follows:-

1. Compounds are usually used on a very small scale (<1 g); this is a reflection of the high sensitivity of radiochemical methods as well as for reasons of safety.

2. It is necessary to be aware of kinetic isotope effects which may complicate the interpretation of the results. On the other hand, the observation of kinetic isotope effects can be a powerful probe for studying reaction mechanisms.

3. The label may be located at a site which

can undergo a separate reaction to that which is being studied; it is therefore necessary to consider carefully which site should be labelled.

4. It is possible through the use of radioisotopes to measure the rates of many kinds of different reactions eg. ionisation, radical formation etc. Because the radioactivity can be measured in such small quantities it is possible to measure very slow rates of reaction over very short time periods; this is a very big advantage.

5. At very high specific activities, radiation induced decomposition can become an important factor.

When using compounds labelled with stable isotopes, it is not always necessary to use such small quantities of material and radiation induced decomposition is no longer a problem.

While isotopes are versatile research tools for the study of reaction mechanisms, they have rarely been the first choice for studying polymer reactions and have tended to be used when standard techniques have proved inadequate. The consequence of this is that the literature contains a large amount of isotope work often playing only a small part in a much larger project. Therefore, although this review covers each field of

polymer chemistry where isotopes have been used, it has been necessary to be selective in some areas and choose only that work that has made up a significant part of a project.

1.2 The Preparation of Labelled Polymers

Isotopic labelling is the replacement of an element within a compound by an isotope. Shown in Table 1.2 are the classes of compounds found in the field of polymer chemistry and the opportunities available for isotopic labelling.

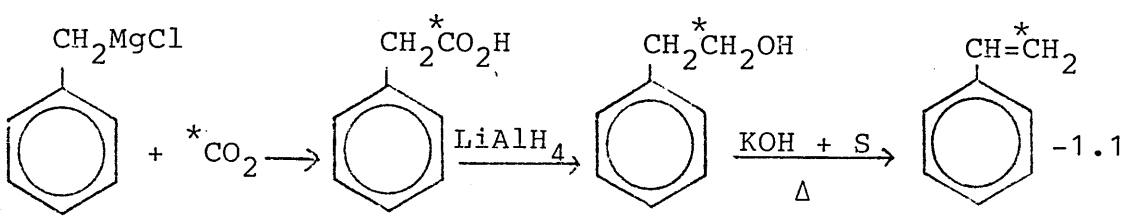
Table 1.2 Opportunities for Isotopic Labelling

Compound	C,H	O	N	S,P	Cl	Metal
Polymers	X	(X)	(X)		(X)	
Initiators	X	(X)	(X)			(X)
Inhibitors	X	(X)		(X)		
Cross Linking Agents	X			(X)	(X)	
Chain Transfer Agents	X		(X)	(X)		
Antioxidants	X	X	(X)	(X)		
UV Stabilizers	X	X	(X)	(X)	(X)	(X)
Metal Deactivators	X	X				

X - Denotes always present (X) - Denotes sometimes present

The techniques required for isotopic labelling will vary according to the isotope used and the compound to be labelled.

Two general techniques are available for isotopic labelling, direct chemical synthesis or isotope exchange. Direct chemical synthesis involves the incorporation of the label by some synthetic route; this has the advantage of labelling a molecule at a specific site but can be a time consuming process. An example of this technique is the labelling of styrene with carbon-14 in the α-position (eqn. 1.1).



-1.1

$^{14}CO_2$ is prepared from commercially available barium [^{14}C]carbonate; the reaction between $^{14}CO_2$ and benzyl magnesium chloride yields 2-phenyl[^{14}C]acetic acid which is reduced and dehydrated to form [α-^{14}C]styrene.

Isotope exchange is the catalytic exchange of one isotope for another. The exchange may be into either stable or labile sites and the catalysts range from

a simple acid or base to a phosphoric acid - boron trifluoride complex. An example of an isotope exchange reaction is shown by the deuteration of polystyrene using perdeuterated benzene. The reaction is catalysed by a diethylaluminium dichloride catalyst, after two exchanges of 100 hours, the extent of deuteration is >97%.[3]

1.3 Polymerisation Studies

1.3.1 Reactions and Mechanisms

In general the process of polymerisation can be summarised by defining three reaction stages, initiation, propagation and termination.

Initiation	$I \xrightarrow{k_i} I\cdot$	-1.2
Propagation	$I\cdot + M \xrightarrow{k_p} P'$	-1.3
	$P' + M \xrightarrow{k_p} P'$	-1.4
Termination	$P' + P' \xrightarrow{k_t} P$	-1.5
	$P' + P' \xrightarrow{k_t} PH + P(-H)$	-1.6

Where I is the Initiator

I· " " Initiator Radical

M " " Monomer

P' " " Growing Polymer Chain

P,PH,P(-H) are the Polymer Molecules

To gain an insight into the initiation step (1.2) requires knowledge of the initiator species I, the rate of initiation and the efficiency of the initiator. A radical initiator is a compound that on decomposing forms radicals; a common radical initiator used for many polymerisations is 1,1'-azobisisobutyronitrile (AIBN) that decomposes thermally to form the isobutyronitrile radical (eqn 1.7).

$$(CH_3)_2C(CN)N{:}NC(CN)(CH_3)_2 \longrightarrow 2(CH_3)_2\dot{C}CN + N_2 \quad -1.7$$

The initiation step with AIBN and other radical initiators is via addition across the double bond (eqn 1.8), this has been shown by following the polymerisation of methylmethacrylate with [^{14}C]AIBN.[4]

$$(CH_3)_2\dot{C}CN + CH_2{=}CXY \longrightarrow (CH_3)_2C(CN)CH_2\dot{C}XY \quad -1.8$$

The experimental results showed that the reaction was first order with respect to the monomer concentration and half order with respect to the initiator concentration. This result can be deduced theoretically from the mechanism above (eqn 1.2-1.6)[5] using the steady state theory for all free radicals including the growing polymer chain and assuming also that k_p is constant for all growing polymer chains (eqn 1.9).

$$\text{Rate} = \left(\frac{k_i}{k_t}\right)^{\frac{1}{2}} k_p[\text{AIBN}]^{\frac{1}{2}}[\text{MONOMER}] \qquad -1.9$$

It has been suggested that AIBN may also decompose to form a diazoradical (eqn 1.10).[6]

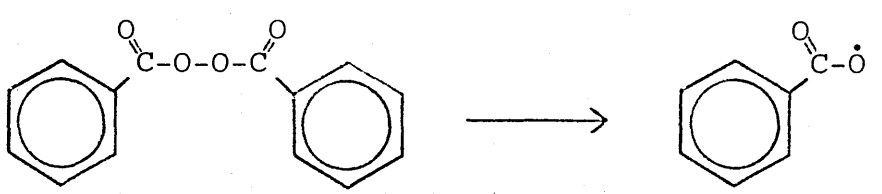
$$(CH_3)_2C(CN)N{:}NC(CN)(CH_3)_2 \longrightarrow (CH_3)_2C(CN)N{:}\dot{N} + \dot{C}(CN)(CH_3)_2 \qquad -1.10$$

The diazoradical would then attack the monomer to form a thermally unstable diazo end group (eqn 1.11).

$$(CH_3)_2C(CN)N{:}\dot{N} + CH_2{=}CXY \longrightarrow (CH_3)_2C(CN)N{:}NCH_2\dot{C}XY \qquad -1.11$$

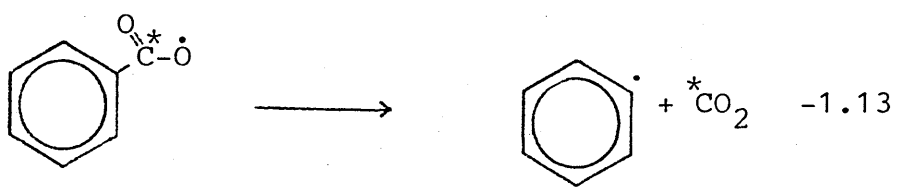
Polystyrene prepared with [^{14}C] AIBN[7] showed no loss of radioactivity on heating however, indicating that the above reaction was unlikely to be important in the polymerisation process.

Another common radical initiator, benzoyl peroxide (BPO), decomposes thermally to form a benzoyloxy radical (eqn 1.12).



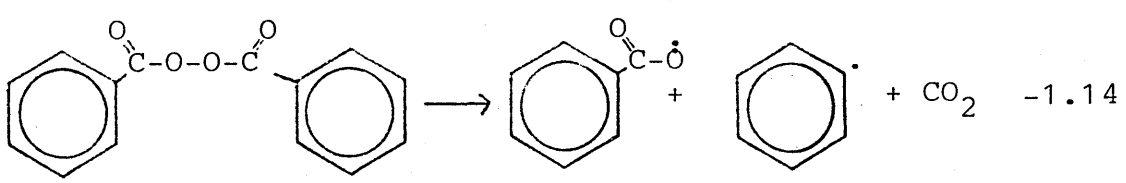
-1.12

The initiation mechanism for the polymerisation of styrene with BPO has been studied using initiator labelled with carbon-14 in the carbonyl group[8] over a range of concentrations and temperatures. The radioactivity of the polymer decreased and $^{14}CO_2$ was evolved at higher polymerisation temperatures suggesting that the benzoyloxy radical decomposed further to form a phenyl radical and $^{14}CO_2$ (eqn 1.13), with the phenyl radical initiating the polymerisation.



-1.13

Other studies with carbon-14 labelled BPO[9] have shown that, under ultraviolet irradiation, the initiator decomposes rapidly to the phenyl radical which then initiates the polymerisation reactions (eqn 1.14).



-1.14

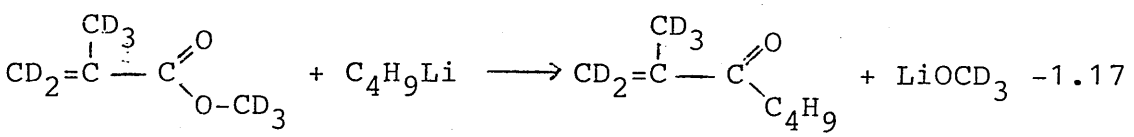
The sulphate radical formed by the decomposition of the persulphate ion (eqn 1.15) is one of a range of initiators used in aqueous polymerisation systems.

$$S_2O_8^{2-} \longrightarrow 2SO_4^{\cdot-} \qquad -1.15$$

Sodium [^{35}S]persulphate has been used to determine the type of termination reaction occurring during the emulsion polymerisation of styrene.[10] Measuring the number of sulphur atoms per chain indicates the type of termination reaction; a combination mechanism (eqn 1.5) would produce a polymer chain with sulphur atoms at each end and a disproportionation reaction (eqn 1.6) one sulphur atom per chain only. The results of the experiments were inconclusive as washing the polymer during the repurification process, to remove any unused initiator, reduced the activity of the polymer considerably due to what was believed to be a chain transfer reaction between the monomer and the initiator. Later experiments carried out at a lower temperature[11] (to prevent chain transfer reactions) with a redox system in the form of an iron(II) salt (eqn 1.16) to increase the rate of decomposition of the initiator gave reproducible results indicating that the process was terminated by a combination mechanism.

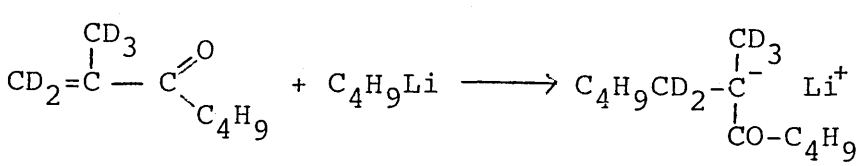
$$S_2O_8^{2-} + Fe^{II} \longrightarrow SO_4^{2-} + Fe^{III} + SO_4^{\cdot-} \qquad -1.16$$

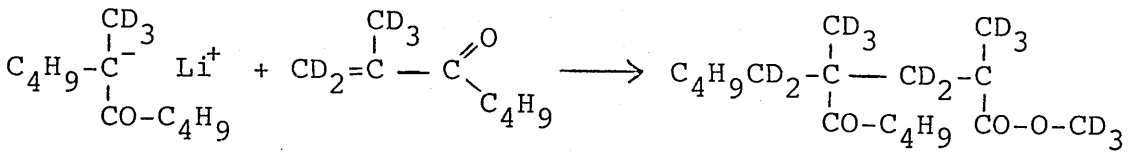
The anionic polymerisation of methylmethacrylate frequently uses butyl lithium as the initiator to produce a growing polymer chain with an anionic end group. The reaction has been studied using perdeuterated methyl-methacrylate and butyl lithium initiator in toluene.[12] The polymerisation reaction was terminated with methanol and the various molecular weight fractions analysed by proton nuclear magnetic resonance spectroscopy. The proton in the methine group from the reaction of methanol with the anionic end group was visible in the nuclear magnetic resonance spectrum suggesting that the initiation reaction commenced by the attack of butyl lithium on the ester group (eqn 1.17).



(I)

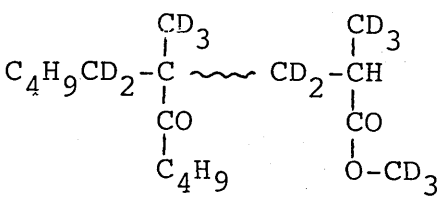
It was proposed that the butyl ketone (I) would have a more reactive double bond than the monomer and so be attacked by another butyl lithium molecule to form the initiating species (eqn 1.18).





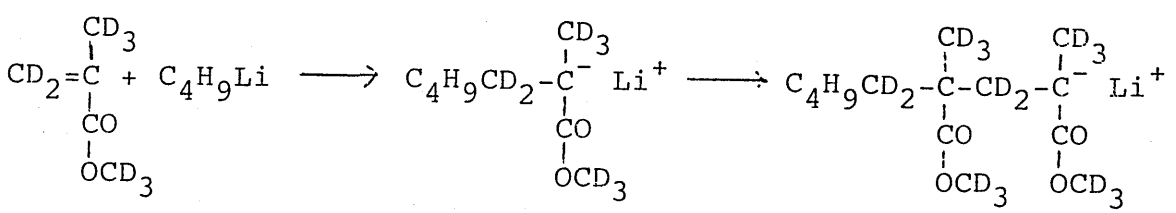
-1.18

Termination of the reaction with methanol would produce a non-ionic end group via the formation of a methine group (II).



(II)

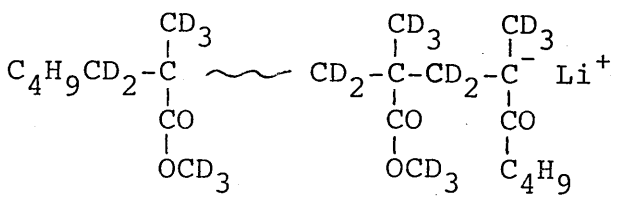
Analysis of oligomers formed in the same system by mass spectrometry[13] indicated the presence of more than one active species suggesting the following reaction scheme: the butyl lithium attacks the double bond in preference to the ester (eqn 1.19).



Growing Chain

-1.19

The butyl lithium also attacks the ester as previously described in reaction (eqn 1.17). Were ketone (I) to have a higher reactivity than the monomer, it would attack the growing chain in preference to the monomer to give III.

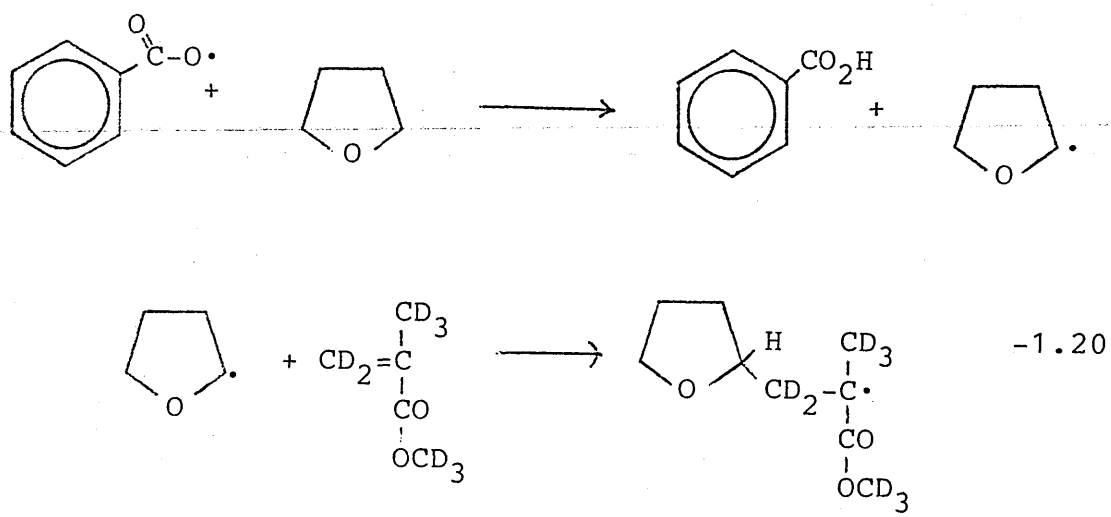


(III)

This reaction to some extent deactivates the end group and therefore addition of the monomer would occur more slowly until another monomer unit was added increasing again the reactivity of the anion. This system would lead to an average of one ketone unit per chain. When the reaction is performed in tetrahydrofuran (THF)[14] each polymer chain contains 3-4 ketone units on average, possibly explained by a solvent effect which increases the reactivity of butyl lithium to the ester carbonyl group producing a higher concentration of I, leading to more frequent attack on the growing polymer chain of I and hence more ketone units per chain.

The same technique was used to study the termination of perdeuterated methylmethacrylate in THF and toluene using undeuterated BPO and AIBN as radical initiators.[15]

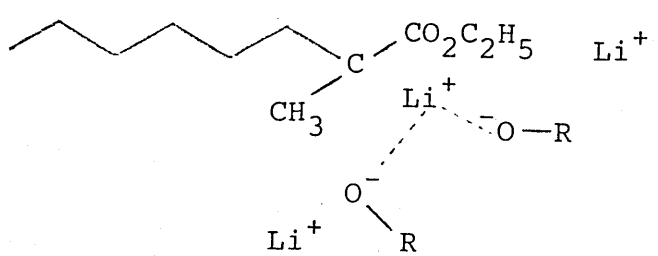
The presence of aliphatic protons in the nuclear magnetic resonance spectrum of the AIBN initiated polymer in both solvents indicated that the termination reaction was predominantly by disproportionation. Likewise the presence of phenyl protons in the nuclear magnetic resonance spectrum indicates disproportionation is ocurring during the BPO/toluene polymerisation. However, after the BPO/THF polymerisation, no phenyl protons were observable in the nuclear magnetic resonance spectrum indicating that the polymerisation was not initiated by either benzoyl or phenyl radicals. The presence of signals from the THF solvent in the spectrum indicated the involvement of the solvent in the process by hydrogen abstraction from the solvent by the radical initiator (eqn 1.20).



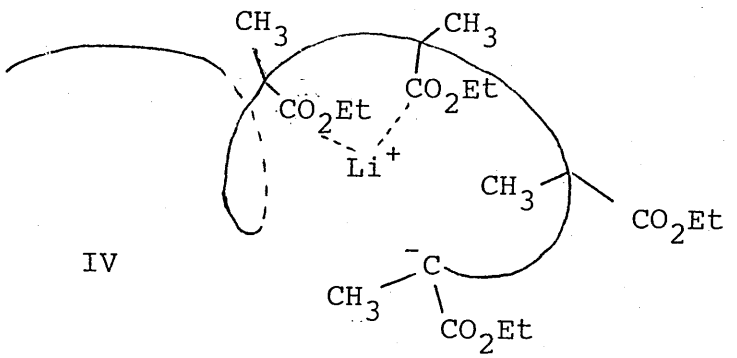
-1.20

By a similar method, the polymerisation of perdeuterated styrene with a titanium(IV) chloride - ethyl aluminium dichloride catalyst in toluene has been studied.[16] In this system, a significant amount of chain transfer from the solvent was shown to occur.

The polymerisation of ethylmethacrylate by butyl lithium in toluene yields a polymer containing both isotactic chains (those with all the side groups in the same plane) and syndiotactic chains (those with side groups alternating between one side of the chain and the other at regular intervals).[17] Perdeuterated ethylmethacrylate was polymerised with butyl lithium and the polymer fractions analysed by nuclear magnetic resonance spectroscopy. Three different chemical structures were found to be present in the polymer and the explanation for this is believed to lie in the orientation of polymer chains in solution. The lithium cation on the syndiotactic chains forms a complex with ethoxide groups formed at the initiation stage, forcing the chain to open up in solutions allowing attack from both sides by the monomer.



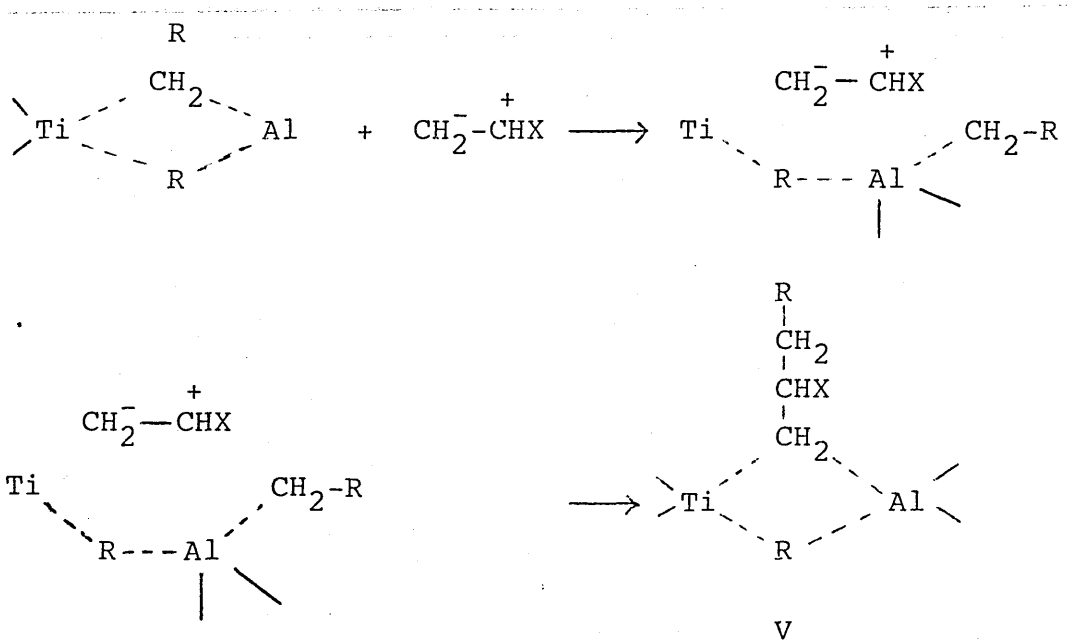
The isotactic polymer chain is forced into a helix when the lithium cation cyclises, forming a complex with a previous ester group allowing attack from one side only.



IV

The polymerisation of vinyl monomers using Ziegler-Natta catalysts involves the ionisation of the double bond followed by the formation of an organo-metallic complex with a titanium (III) aluminium complex[18] (eqn 1.21).

$$CH_2{=}CHX \longrightarrow CH_2^{-}\text{-}\overset{+}{C}HX \qquad -1.21$$



V

For complete comprehension of the catalytic processes involved, it is necessary to be able to determine the concentration of active centres (V) on the catalyst as this affects the efficiency of the catalyst and therefore the choice of catalyst. The number of active centres can be determined by quenching the catalyst using a tritiated alcohol.[19] The alcohol breaks the metal polymer bond (MPB) and incorporates the label in the polymer molecules, so determining the radioactivity of the polymer and therefore allowing the calculation of active centre concentration (eqn 1.22).

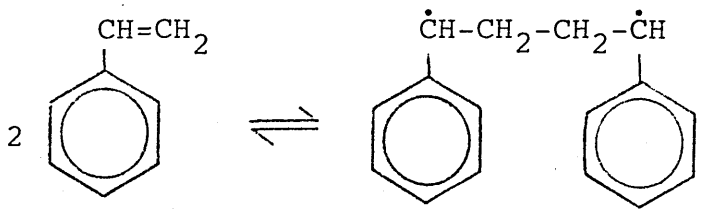
$$Cat\text{-}CH_2 \sim\sim P + ROT \longrightarrow Cat\text{-}O\text{-}R + CH_2T \sim\sim P \quad -1.22$$

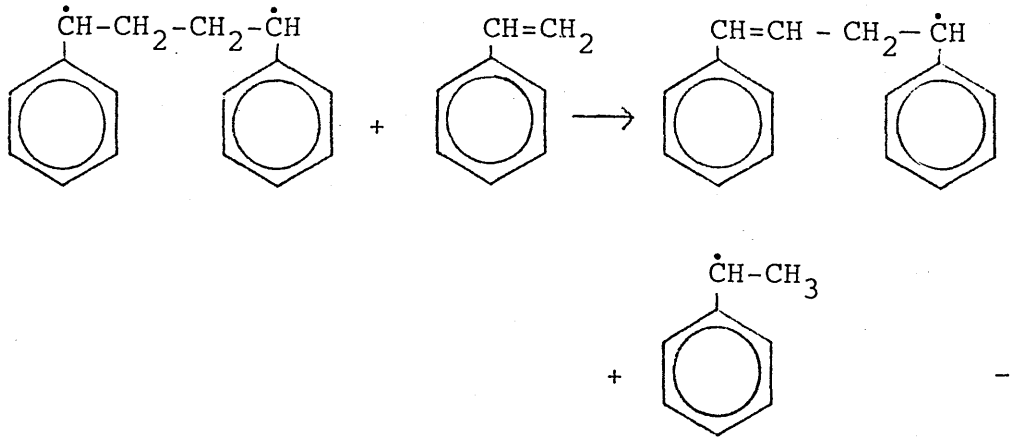
The rate of the reaction can be followed by taking samples of the reaction mixture at various time intervals and quenching them with the labelled alcohol.[20] The active site concentration was altered by studying the polymerisation using a range of aluminium alkyl-vanadium halide catalysts.[21] The rate of polymerisation was found to be independent of the alkyl aluminium indicating that the active site was probably at the vanadium atom.

It has been shown that, when the hydroxyl hydrogen of the alcohol is replaced by deuterium or tritium, an isotope effect is observed;[22] also insertion of the label into the

inactive aluminium polymer bond (as well as the active transition metal polymer bond) can occur leading to inaccurate experimental results. These two problems may be overcome by the use of a 'specific' quenching agent in the form of [^{14}C]carbon monoxide,[23] which attacks only the transition metal polymer bond leaving the inactive aluminium polymer bond alone. This technique has been combined with the alcohol quenching method enabling chain transfer reactions between the catalyst and the polymer to be studied.[24] Similar studies have been performed using carbon-14 labelled aluminium alkyls to determine the chemical nature of the active site,[25] their concentrations[26,27] and follow the kinetics of polymerisation.[28]

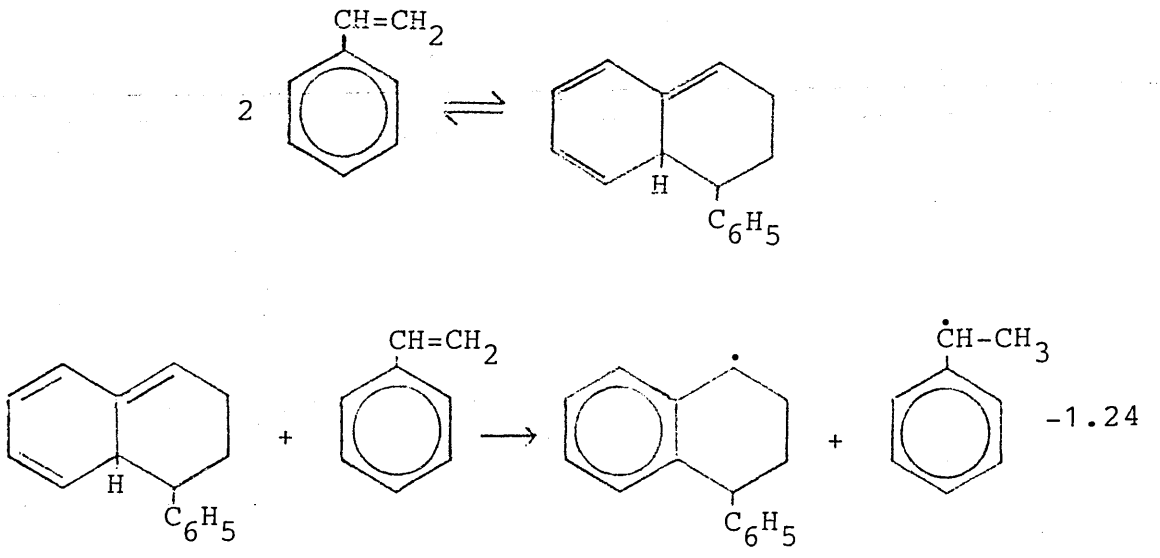
The mechanism for the thermal initiation of styrene was believed to proceed by the formation of a diradical dimer[29] (eqn 1.23).





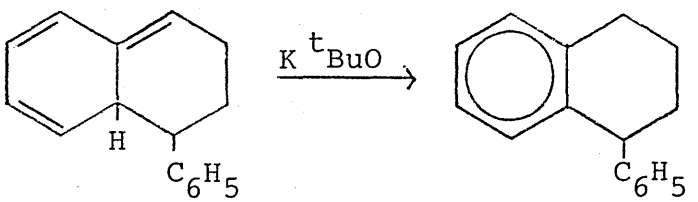
-1.23

Specific labelling of styrene with deuterium in the α-position produced no observable kinetic isotope effect for the polymerisation.[30] A study of the polymerisation of a range of styrenes deuterated in various positions showed that the ortho-position of the aromatic ring played a large part in the process.[31,32] The reaction is believed to proceed via the formation of a monoradical (eqn 1.24).



-1.24

The addition of potassium t-butoxide to the polymerisation mixture decreases the rate of polymerisation by a factor of 17 due to the competing reaction (eqn 1.25).

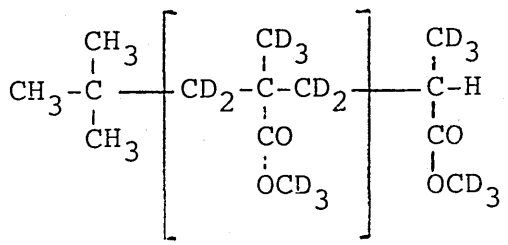


-1.25

1-Phenyltetralin can be removed from the polymerisation mixture.

Monomers specifically labelled with deuterium have been used to study the initiation reactions involved when Grignard reagents are used as initiators. Phenyl magnesium bromide was used to polymerise isopropyl (α-cis-β-$^2H_2$)acrylate.[33] The coupling of the remaining proton in the methine group in the proton nuclear magnetic resonance spectrum was studied when coupled and decoupled to the deuterium atoms. The results indicated that the acrylate double bond opened trans; cis opening is possible but is sterically inhibited. The polymerisation of methylmethacrylate by t-butyl magnesium bromide in toluene yields a highly isotactic polymer with a low molecular weight distribution. The polymerisation was studied

using perdeuterated monomer and undeuterated initiator.[34] Analysis of the proton nuclear magnetic resonance spectrum of the polymer showed that each chain had a methine proton at one end and a t-butyl group at the other as in structure VI.



VI

Hence the reason for the low molecular weight dispersity of the polymer is due to the lack of side reactions which would alter the proportions of the methine and t-butyl groups to the numbers of chains.

Similarly, the radical polymerisation of methyl (α,β-$^2H_2$)acrylate is initiated by either cis or trans double bond opening; however anionic initiation with lithium aluminium hydride is by attack of the catalyst specifically cis or trans. Further work is required to determine which mode is involved.[35]

The mechanism of epoxide polymerisation has been studied using ethylene oxide prepared with cis and trans deuterium labels.[36] Analysis of the subsequent polymers by infra-red spectroscopy[37] indicated that polymerisation

proceeded by ring opening with inversion of configuration.

Chain transfer occurs when the growing polymer chain extracts a labile atom from any component present (eqn 1.26), be it monomer, polymer, the initiator or an impurity. Chain

$$P + AS \longrightarrow PA + S\cdot \qquad -1.26$$

transfer agents may be used to control the molecular weight of a polymer[38] but this requires knowledge of the rate of chain transfer compared with the rate of polymerisation. Thiols are often used as chain transfer agents and [^{35}S] thiols have been used to determine these rate constants for the polymerisation of methylmethacrylate[39] and styrene.[40]

The site of chain transfer on allyl acetate was determined by the polymerisation of [1-$^{2}H_2$] allyl acetate. A deuterium isotope effect at this position inhibited chain transfer, so the rate of polymerisation was on average 2·5 times faster and the molecular weight of the polymer 2·4 times that of the unlabelled polymer.

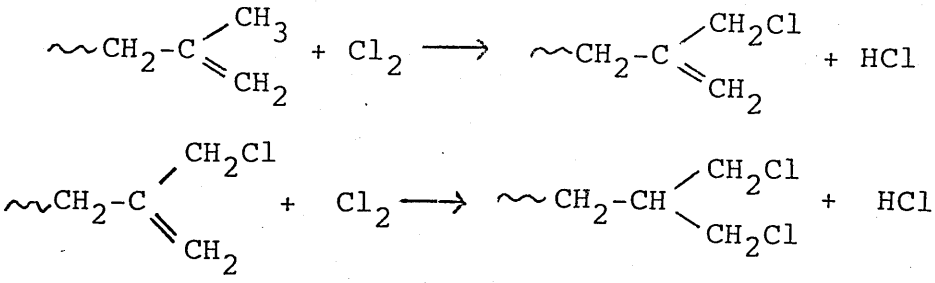
Chain transfer reactions play a significant part in emulsion polymerisation of vinyl acetate. The reaction has been studied by following the molecular weight of

the polymer by measuring its intrinsic viscosity in a range of solvents;[40] a mechanism was suggested showing chain transfer occurring in the acetyl group. However, polymerisation of [1,2-$^{2}H_3$] vinyl acetate produced a polymer with three times the molecular weight of the unlabelled polymer suggesting that chain transfer was in fact occurring at the vinyl hydrogens.[41]

1.3.2 Purification and Analysis

The compositional analysis of co-polymers can be difficult, particularly in cases where the co-polymer consists of monomers that are either chemically similar or indistinguishable by spectroscopic techniques. The use of isotopically labelled co-monomers may help to overcome these problems; for example [^{14}C] polyethylene has been used to calibrate a spectroscopic method for analysing polyethylene/polypropylene co-polymers;[42] a range of other examples are available in the literature.[43-48]

The degree of unsaturation of a polymer may be determined by the addition of chlorine-36 across the double bond as shown in equation 1.27.



-1.27

The radioactivity of the polymer is an indication of the degree of unsaturation present in the polymer; the technique is particularly good for low levels of unsaturation (ca. 0·01 mole %).[49]

The efficiency of polymer fractionation procedures used for the purification of a polymer have been studied by two different techniques. As part of a study on chain transfer in styrene polymerisation, an unsuccesful attempt was made to separate [^{14}C] polystyrene (prepared by the polymerisation of [2-^{14}C] styrene inside an unlabelled polystyrene matrix) from the unlabelled polymer by fractional precipitation.[50] A combination of this technique, in conjunction with end-labelled polymers (by polymerisation with a labelled radical initiator) has shown that it is possible however to separate completely polystyrene and polymethyl-methacrylate by careful fractionation.[51]

Small angle neutron scattering techniques used in conformational studies of polymers require polymers with a low molecular weight dispersity and of known composition. Deuterium labelled polymers for use in these kinds of studies have been characterised by gel permeation chromatography,[51] light scattering and high speed membrane osmometry[52] and pyrolysis gas chromatography.[53,54]

1.3.3 Additives

The sensitivity of radiochemical methods of counting and in particular liquid scintillation counting makes radioisotopes extremely useful when studying additives in polymer systems, usually present in very low concentrations.

The migration of additives such as antioxidants and accelerators can have a detrimental effect on the properties of elastomers leading to a loss of adhesion, staining and faster than normal ageing. Using labelled additives, migration in the following have been studied; ^{35}S-labelled accelerators and ^{14}C-labelled phenolic antioxidants in polybutadiene and styrene/butadiene copolymers,[55] ^{14}C-labelled additives and plasticizers in polyvinyl chloride[56] and [^{14}C] tricaprylin in polyethylene, poly(vinyl chloride) and polystyrene.[57]

In each case, two discs of the polymer were prepared, one of which contained the labelled additive. The discs were pressed together and any migration of the additive manifested itself as an increase or decrease in the radioactivity of the discs (followed by liquid scintillation counting).

The mechanism and efficiency of the UV stabilization of polypropylene by 2-hydroxy-4-octyloxybenzophenone has been determined using the tritium labelled additive.[58] On irradiation with UV light of the stabilized polymer, the evolution of various radioactive gases was observed from the breakdown of the stabilizer, thereby allowing the reaction to be followed.

The efficiency of branching agents and terminators has been determined by the use of carbon-14 labelled additives.[59] Polymers (prepared using the labelled additives) were analysed by gel permeation chromatography coupled to a liquid scintillation counter allowing the effectiveness of these additives to by determined.

1.4 Polymer Characterisation by Spectroscopic Methods

1.4.1 Infra-red Spectroscopy

Infra-red spectroscopy is a valuable tool in the analysis of polymers and for structural investigations. Infra-red spectroscopy can provide information on the chemical nature of a polymer i.e. type and degree of branching, the nature of the end groups and the presence of impurities. The steric order of the polymer, the presence of cis and trans double bonds, isomerism and stereoregularity, the conformational order in the polymer and the physical arrangement of the polymer chains may also be studied. Information can be obtained on the crystallinity of the polymer, the numbers of chains per unit cell and any intermolecular forces present.

One extremely important feature of infra-red spectroscopy is the shift in frequency of a bond when isotopic substitution has taken place. The replacement of a lighter atom for a heavier one increases the bond strength altering the frequencies of the bond vibrations. The isotopic shift effect provides a powerful tool in the study of polymer structures and bond assignments and has also found applications in the study of accessibility in polymers i.e. crystallinity.

Hydrogen-deuterium exchange in the labile groups on the polymer such as amine or hydroxyl groups with deuterated water (D_2O) for example will produce a corresponding shift in the infra-red spectrum in the 2500-3500 cm^{-1} region. This technique has been used to determine the degree of crystallinity in polyacrylamide[60] and cellulosic fibres[61] by carrying out an isotope exchange with D_2O vapour at the labile groups on the polymers. Labile groups in the amorphous regions of these polymers undergo exchange readily leaving the less accessible crystalline regions unaffected. Study of the polymer using infra-red energy polarised both parallel and perpendicular with respect to the fibre axis yields a measure of the orientation of these crystalline regions.

The steam setting of nylon brings about marked changes in the crystallinity of the polymer and so affecting such properties as the diffusion of dyestuffs, swelling and moisture uptake. D_2O vapour exchange experiments[62,63] have shown that steam setting increases the crystallinity but decreases the number of intermolecular bonds in the remaining amorphous region so increasing dyestuff diffusion. Dry heat setting has the opposite effect, increasing the number of bonds in the amorphous region so decreasing diffusion rates.

Specific labelling of various positions on the monomer followed by polymerisation and study by infra-red spectroscopy has enabled bond assignments to be carried out on a range of polymers, such as polypropylene,[64] polyacetylene,[65] and polyacrylonitrile.[66] Other labelling experiments of various specifically labelled polymethylmethacrylates[67,68] have enabled bond assignments to be made for stereoregular polymethylmethacrylates[69-72] and allowed the measurements of conformational energies to be made of the different conformational states of the backbone and side chains in temperature dependent infra-red absorption studies.[73]

1.4.2 Nuclear Magnetic Resonance Spectroscopy

Solid state nuclear magnetic resonance spectroscopy can provide information on the type and timescale of molecular motions occurring within solid polymers, and hence allow a better understanding of their mechanical properties. Solid state proton and carbon-13 nuclear magnetic resonance spectra suffer from small anisotropy of molecular shielding in the aliphatic groups and the shielding tensors are not axially symmetric making for difficult experiments with complex analysis of the results. The deuterium has a spin quantum number of 1 and is almost exclusively governed by quadrupole interactions; also

the field gradient tensor is at the deuteron site and axially symmetric about the bond. These features allow molecular motions to be monitored through the orientation of the bond directions so simplifying the data and analysis. The spectral line shapes can provide information on the different types of molecular motion;[74] the dynamic range over which the polymer dynamics can be followed is large and the spin-lattice relaxation times T_1 can be obtained right upto the nuclear magnetic resonance frequency.[75,76,77] Relatively inefficient spin diffusion also means that T_1's can differ widely between the motional and rigid environment of the polymer so motional heterogeneity can be studied in semi-crystalline and glassy polymers.[78] Deuterium nuclear magnetic resonance spectroscopy is highly selective; therefore specific labelling can produce information on selected portions of the molecule[79] and, in addition to providing dynamic information, can also offer information on the molecular order in orientated polymers eg. drawn systems.[80,81]

Solution deuterium nuclear magnetic resonance spectroscopy, as for infra-red spectroscopy, has been used on selectively labelled compounds to assign the signals in the proton spectrum;[82] studies have also been carried out on the molecular motion of polymers in solution.[83,84]

1.4.3 Small Angle Neutron Scattering

Conformational studies on polymer solutions are often performed by light scattering techniques,[85] but this method can not usually be used to make measurements of coil radii because the wavelength of light is too large. Such measurements can be made using X-ray scattering,[86] but the contrast between the solute and solvent is frequently weak and, for very dilute solutions, the scattering is too weak to be measured.

Because the wavelength of neutron beams is smaller still, averaging 5.7 Å, this technique has been developed for studies of polymer solutions in the dilute and semi-dilute concentration ranges at which the polymer chains start to overlap.[87] The technique has been used to measure radii of gyration of polymer coils[88,89] and the persistence length of the polymer molecules.[90] This technique can be used to obtain information on the behaviour of one chain amongst many by using tagged chains, usually deuterated polymer, in unlabelled polymer to study inter-chain interactions.[91,92]

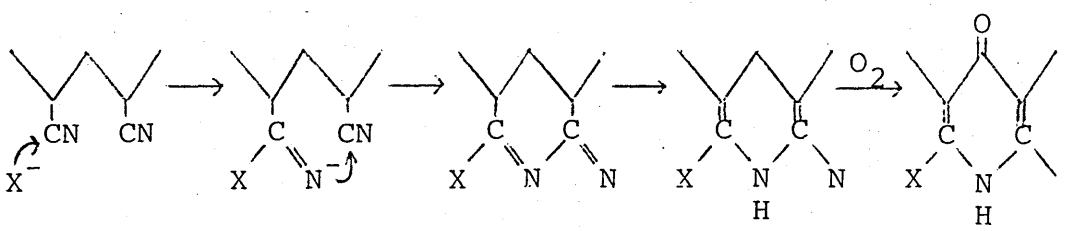
Small angle neutron scattering has also been used to study concentrated polymer solutions[93,94] and solid polymers;[95,96,97] hence it has been possible to study

aggregation occurring during the cooling of a polymer melt[98,99,100] and diffusion in solid/solid polymer mixtures.[101]

1.5 Polymer Degradation Studies

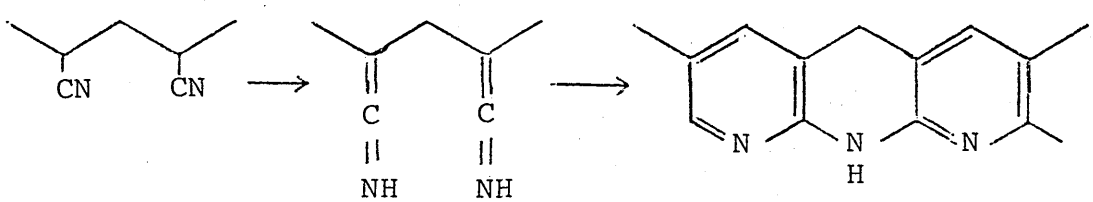
One method by which the general properties of polymers may be improved is by the study of the way polymers degrade and determination of the degradation mechanisms involved.

Carbon fibre is manufactured by the thermal degradation of polyacrylonitrile; knowledge of the mechanisms involved here could enhance the efficiency of the manufacturing process. The thermal degradation of polyacrylonitrile labelled with a range of isotopes has been studied by Fourier Transform infra-red spectroscopy. Poly(α-deuteroacrylonitrile) was thermally degraded under reduced pressure and the infra-red spectrum of the product compared with that of the undeuterated polymer, the major difference between the two spectra occurring in the 1600 cm^{-1} region.[102] The mechanism was believed to be as follows (eqn 1.28):



-1.28

More comprehensive degradation studies[103] performed on polymers labelled with deuterium, carbon-13 or nitrogen-15 and in the presence of oxygen-18 suggest the following mechanism (eqn 1.29), since analysis of the polymer showed no oxygen to be present:

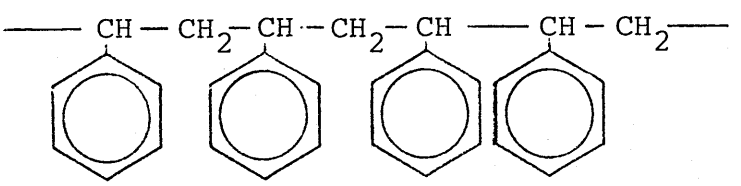


-1.29

The thermal degradation of polypropylene yields a range of volatile compounds including pentane, isobutylene, propene and propane.[104] Using poly([3-$^2H_1$]propylene) for thermal degradation studies and analysis of the products by mass spectrometry, nuclear magnetic resonance spectroscopy and infra-red spectroscopy, has allowed mechanisms to be suggested for their formation.

The thermal degradation of polystyrene is characterised by an initial rapid decrease in molecular weight;[105] this suggests the presence of thermally unstable groups within the polymer chains breaking early on in the degradation process. Were the structures of the links to be determined, their formation may be inhibited and the thermal stability of polystyrene improved. It was speculated that these

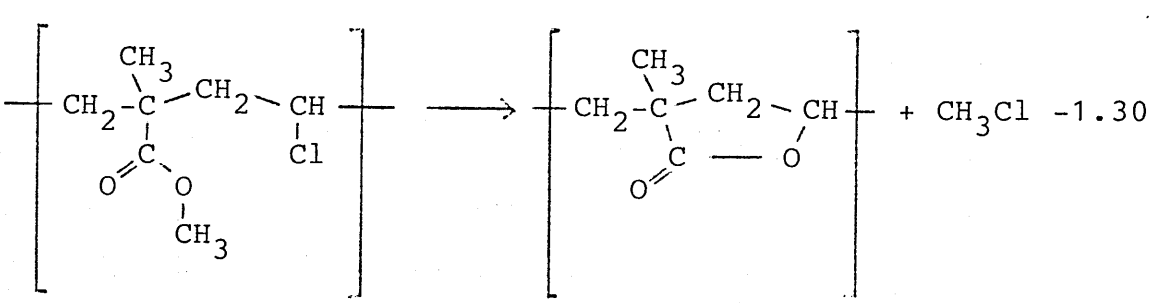
weak links were due to the formation of head to head linkages in the chain (VII) during the polymerisation process.[106]

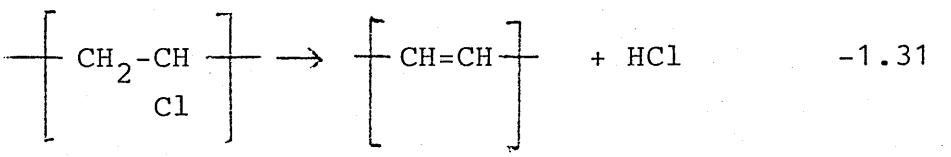


VII

To test the theory, 'weak links' were artifically produced by the co-polymerisation of styrene and stilbene to enhance any initial molecular weight decrease. [^{3}H] Stilbene was used in the preparation to allow accurate compositional analysis of the copolymer.

The thermal degradation of a poly(vinyl chloride)/ polymethylmethacrylate copolymer involves two competing reactions, lactonization of the copolymer unit (eqn 1.30) and dehydrochlorination of the vinyl chloride unit (eqn 1.31):





-1.31

The reactions were studied by the use of a chlorine-36 labelled copolymer.[107] A combination of thermal volatilasation techniques and radiochemical assay allowed the two reactions to be distinguished and followed.

A problem that can occur when using radioisotopes is a radiation induced degradation, the degree of which is dependent on the specific activity of the compound and its susceptibility to damage by radiation. The effects of β-particle radiation from the decay of tritium on β-tritiated polystyrene have been studied.[108,109] Analysis of the polymer by gel permeation chromatography reveals a gradual increase in molecular weight combined with slight changes in the UV spectrum and a slight discolouration of the polymer. Also observed during the degradation was the formation of traces of water, benzaldehyde, formaldehyde, styrene and hydrogen. [^{3}H]Methyl methacrylate and styrene, polymerised with carbon-14 labelled AIBN, have been shown to undergo an increase and broadening of the molecular weight distribution on standing in a liquid scintillator solution for some length of time.[110] The level of radioactivity of the polymer was however

extremely low and it was suggested that the degradation was not radiation induced but caused by photochemical degradation from the fluorescence of the scintillator.

1.6 Applications of Labelled Polymers

The particular advantages available when using radioisotopes, e.g. sensitivity to detection, makes radiolabelled polymers extremely useful for biochemical studies. Polymeric materials have been used in macromolecular drugs and pesticides; so, to aid the necessary safety tests and determine their metabolic fate, a range of these compounds have been labelled with carbon-14. The compounds include polymeric nitroaniline dyes and azo dyes for use in studies involving their metabolism in the intestine,[111] and a polymeric drug used to deliver an antiulcer drug to the colon.[112]

Compounds such as food antioxidants should ideally not be absorbed by the body as their job is to protect the food from spoiling before it is consumed, and if absorbed may cause toxicity problems. A range of phenolic polymeric food antioxidants have been labelled with carbon-14

for use in tracer studies to determine if in fact these compounds are absorbed by the body.

The recent development of ion-beam scattering techniques has opened up new possibilities for the study of the various physical properties of polymers. The technique involves the bombardment of a sample by an ion-beam either perpendicular to the sample,[113] where backscattered ions can be analysed, or at an angle[114] such that ions recoil from the surface and are then analysed. Such techniques allow for example a depth profile for deuterium in a hydrogen containing matrix to be obtained; hence, using deuterium labelled polymers and additives, polymer blends, membranes and coatings may be studied; these techniques may also be used to study additive migration, water sorption and drug release.

The carbon-deuterium bond is significantly stronger than the carbon-hydrogen bond and this can alter the various properties of polymeric materials markedly. Polymers with improved oxidation resistance,[115] thermostability[116] and higher optical transmittance[117] have been prepared. Also deuterated plastics can absorb X-ray radiation more efficiently and so produce higher neutron emission yields when used as neutron emission targets.[118]

1.7 Summary

With so much money tied up in the plastics market, the hunt will always be on to develop better polymers with improved properties and longer lifetimes. In polymer research isotopes can offer a range of advantages over the more established techniques, for example sensitivity to detection etc. as well as offering an alternative way of looking at a particular problem.

Isotopes have been used to study most types of polymerisation reactions particularly those involving radical initiation and Ziegler-Natta type catalysts as these are used for the most economically important polymers, polystyrene, polymethylmethacrylate and polypropylene. Much of the earlier work was done on the radical initiation of styrene and methylmethacrylate using labelled initiators (also a facile method for end-labelling polymers) to determine polymerisation mechanisms and kinetics. More modern polymerisation methods using butyl lithium as the initiator to prepare stereoregular polymers have been studied using deuterated monomers. The expensive catalysts involved in Ziegler-Natta polymerisations made it imperative that the mechanisms involved and the position of the active sites on the catalysts be improved to cut down on costs.

Difficulties did arise when studying the aqueous polymerisation systems and obtaining reliable results proved difficult; however this was more a feature of the reaction conditions (often more reliable results were obtained when a detergent was added to the system) than a fault of the isotope techniques.

The chain transfer studies were very useful in obtaining enough information on the kinetics of these reactions to enable accelerators and retarders to be used to control polymer molecular weights.

The analysis of copolymers has always been difficult, particularly in the case of very similar co-monomers; the use of labelled monomers has simplified this process and also allowed the calibration of other more routine analytical techniques.

Infra-red spectroscopy, nuclear magnetic resonance spectroscopy, mass spectrometry and small angle neutron scattering techniques have been able to take advantage of the way isotopes can be used to label a particular part of a polymer. Conformational studies and end-group analysis using these labelled polymers have helped to tie up the relationship between the chemical structure of a polymer and its physical properties.

However, little work has been done in the polymer degradation field using isotopes. With the advantages isotopes offer, it was felt that more information could be obtained from the various degradation studies if isotopically labelled polymers were used in conjunction with some of the more recently developed techniques such as radio-gas chromatography and radio-high performance liquid chromatography were employed. Most of the isotope labelling work has centred around polystyrene and polymethylmethacrylate as the most popular polymers and so it was felt that a range of specifically labelled polymers should be prepared and their potential usefulness in degradation studies demonstrated.

1.8 References

1. European Plastics News, 14, 15, (1987).
2. Encyl. Mat. Sci. Eng. (1st Ed.), 1, 504, (1982), Pergammon Press, Oxford.
3. Willenberg, W., Makromol. Chem. 177, 3625, (1976).
4. Ayrey, G., and Moore, C.G., J. Polymer Sci. 36, 41, (1959).
5. Pearson, R.G., and Frost, A.A., Kinetics and Mechanism (2nd Ed.), J. Wiley, London, (1961).
6. Arnett, L.M., J. Am. Chem. Soc. 74, 2027, (1952).
7. Bradbury, J.H., Bevington, J.C., and Burnett, G.M., J. Polymer Sci. 12, 469, (1954).
8. Koton, M.M., Kisheva, T.M., and Bessenov, M.I., Zh. Fiz. Khim. 28, 2137, (1954).
9. Bevington, J.C., and Lewis, T.D., Trans. Faraday Soc. 54, 1340, (1958).
10. Smith, W.V., J. Am. Chem. Soc. 71, 4077, (1949).
11. Kolthoff, I.M., O'Conner, P.R., and Hansen, J.L., J. Polymer Sci. 15, 459, (1955).
12. Hatada, K., Kityama, T., Fujikawa, K., Ohta, K., and Yuki, H., Polymer Bull. 1, 103, (1978).
13. Hatada, K., Kityama, T., Fumikawa, K., Ohta, K., and Yuki, H., Am. Chem. Soc. Sym. Ser. 166, 327, (1981).

14. Hatada, K., Kityama, T., Okahata, S., and Yuki, H., Polymer J. 13, 1045, (1981).

15. Hatada, K., Kityama,T., and Yuki, H., Makromol. Chem. Rapid Commun. 1, 51, (1980).

16. Hatada, K., Kityama, T., and Yuki, H., Polymer Bull. 2, 15, (1980).

17. Hatada, K., Kityama, T., Okahata, S., and Yuki, H., Polymer J. (Jap) 14, 971, (1982).

18. Pasquoi, I., J. Polymer Sci. 60, S47, (1962).

19. Burfield, D.R., and Savariar, C.M., Macromolecules, 12, 243, (1979).

20. Kohn, E., Schuurmans, H.J.L., Cavender, J.V., and Mendelson, R.A., J. Polymer Sci. 58, 681, (1962).

21. Burfield, D.R., and Tait, P.J.T., Polymer, 13, 243, (1979).

22. Feldman, C.F., and Perry, E., J. Polymer Sci. 46, 217, (1960).

23. Chumaevskii, N.B., Zakharov, V.A., Bukatov, G.D., Kutznetzova, G.I., and Yemakov, Y.I., Makromol. Chem. 177, 747, (1976).

24. Bukatov, G.D., Chumaevskii, N.B., Zakharov, V.A., Kuznetzova, G.I., and Yemakov, Y.I., Makromol. Chem. 178, 953, (1977).

25. Rodriguez, L.A.M., and van Looy, H.M., J. Polymer Sci. (A1)4, 1951, (1966).

26. Baulin, A.A., Sokolov, V.N., Semenova, A.S., Chirkov, N.M., and Shalayeva, L.F., Polymer Sci. (USSR) 17, 51, (1975).

27. Ayrey, G., and Mazza, R.J., Makromol. Chem. 176, 3353, (1975).

28. Chien, J.C.W., J. Polymer Sci. (A)1, 425, (1963).

29. Mayo, F.R., J. Am. Chem. Soc. 75, 6133, (1953).

30. Hammond, G.S., and Kopecky, K.R., J.Polymer Sci. 60, S54, (1962).

31. Kirchner, R., Makromol. Chem. 96, 179, (1966).

32. Kopecky, K.r., and Evani, S., Can. J. Chem. 47, 4049, (1969).

33. Schuerch, C., Fowells, W., Yamada, A., Bovey, F.A., Hood, F.P., and Anderson, E.W., J. Am. Chem. Soc. 86, 4481, (1961).

34. Hatada, K., Ute, K., Tanaka, K., Kityama, T., and Okamoto, Y., Polymer J. (Jap) 17, 977, (1985).

35. Yoshino, T., Koniyama, J., and Shinomiya, M., J. Am. Chem. Soc. 86, 4482, (1964).

36. Price, C.C., and Spector, R., J. Am. Chem. Soc. 88, 4171, (1966).

37. Yokoyama, M., Ochi, H., Tadokoro, H., and Price, C.C., Macromolecules, 5, 690, (1972).

38. Kolthoff, I.M., and Harris, W.E., J. Polymer Sci. 2, 41, (1947).

39. Mochel, W.E., and Peterson, J.H., J. Am. Chem. Soc. 71, 1426, (1949).

40. Wheeler, O.L., Lavin, E., and Crozier, R.N., J. Polymer Sci. 9, 157, (1952).

41. Litt, M.H., and Chang, K.H.S., Org. Coat. Plast. Chem. 43, 716, (1980).

Lamante, J.N., and Tirpak, G.A., J. Polymer Sci. A2, 705, (1964).

43. Blackley, D.C., and Melville, H.W., Makromol. Chem. 18, 16, (1956).

44. Allen, J.K., and Bevington, J.C., Trans. Faraday. Soc. 56, 1762, (1960).

45. Wiley, R.H., and Davis, B., J. Polymer Sci. 62, 8132, (1962).

46. Wiley, R.H., and Sale, E.E., J. Polymer Sci. 42, 479, (1960).

47. Wall, L.A., Brown, D.W., and Hart, V.E., J. Polymer Sci. 15, 157, (1955).

48. Wiley, R.H., and Davis, B.J., J. Polymer Sci. 62, S140, (1962).

49. McGuchan, R., and McNeill, I.C., J. Polymer Sci. (A1)4, 2051, (1966).

50. Bevington, J.C., Guzmann, G.M., and Melville, H.W., Proc. Roy. Soc. A221, 453, (1954).

51. Bevington, J.C., and Baines, F.C., Eur. Polym. J. 3, 593, (1967).

52. Matsushita, Y., Furuhashi, H., Choshi, H., Noda, I., Nagasawa, M., and Fujimoto, T., Polymer J. (Jap) 14, 489, (1982).

53. Ohtani, H., Tsuge, S., Matsushita, Y., and Nagasawa, M., Polymer J. (Jap) 14, 495, (1982).

54. Ohtani, H., Tsuge, S., Matsushita, Y., and Nagasawa, M., Polymer J. (Jap) 16, 727, (1984).

55. Lewis, J.E., Deviney, M.L., and Whittington, L.E., Rubber Chem. Tech. 42, 892, (1969).

56. Park, G.S., and Hoang, T.V., Eur. Polym. J. 14, 817, (1979).

57. Figge, K., and Rudolph, F., Die Angew Makromol. Chem. 78, 157, (1979).

58. Vink, P., and Van Veen, Th. J., Eur. Polym. J. 14, 533, (1978).

59. Dubin, P.L., Hale, R., Kronstadt, M., Read, A.R., and de Keczer, S., Polym. Preprints, 18, 3, (1977).

60. Kulicke, W.M., and Siesler, H.W., J. Polymer Sci. Polym. Phys. Ed. 20, 553, (1982).

61. Cumberbirch, R.J.E., and Jefferies, R., J. Appl. Polym. Sci. 11, 2083, (1967).

62. Koshino, A., J. Appl. Polym. Sci. 9, 55, (1965).

63. Koshino, A., J. Appl. Polym. Sci. 9, 81, (1965).

64. Liang, C.Y., Lytton, M.R., and Boone, C.J., J. Polymer Sci. 44, 549, (1960).

65. Shirakawa, H., and Ikeda, S., Polymer J. 2, 231, (1971).

66. Liang, C.Y., Pearson, F.G., and Marschessault, R.H., Spectrochim. Acta, 17, 568, (1961).

67. Dirilikov, S., Makromol. Chem. 180, 2971, (1979).

68. Nagai, H., J. Appl. Polym. Sci. 1, 1697, (1963).

69. Nagai, H., Watanabe, H., and Nishioka, A., J. Polymer Sci. 62, S95, (1962).

70. Cockburn, W.F., and Hubley, C.E., Appl. Spectrosc. 11, 188, (1957).

71. Mihailov, M., Dirlikov, S., Peeva, N., and Georgiova, Z., Makromol. Chem. 176, 789, (1975).

72. Schneider, B., Stokr, J., Schmidt, P., Mihailov, M., Dirlikov, S., and Peeva, N., Polymer, 20, 705, (1979).

73. O'Reilley, J.M., Teergarden, D.M., and Mosher, R.A., Macromolecules, 14, 1693, (1984).

74. Sillescu, H., Pure and Appl. Chem. 54, 619, (1982).

75. Willenberg, B., and Sillescu, H., Makromol. Chem. 178, 2401, (1977).

76. Lindeur, P., Rössler, E., and Sillescu, H., Makromol. Chem. 182, 3653, (1981).

77. Ziliox, M., Spegt, P., Mathis, C., Francois, B., and Weill, G., Solid State Commun. 51, 393, (1984).

78. Hentschel, D., Sillescu, H., and Speiss, H.W., Makromol. Chem. 180, 241, (1979).

79. Humphreys, J., Duckett, R.A., and Ward, I.M., Polymer, 25, 1227, (1984).

80. Mueller, K., Hisgen, B., Rungsdorf, H., Lenz, R.W., and Kothe, G., Proc. Eur. Sci. Found. Polym. Workshop, 6th, (1983).

81. Hentschel, R., Sillescu, H., and Speiss, H.W., Polymer, 22, 1516, (1981).

82. Suzuki, T., Koshiro, S., and Takegani, Y., J. Polym. Sci. Polym. Lett. Ed. 10, 829, (1972).

83. Grandjcan, J., Sillescu, H., and Willenberg, B., Makromol. Chem. 178, 1445, (1977).

84. Blum, F.D., Durairaj, B., and Padmanbhan, A., Polym. Preprints, 25, 143, (1984).

85. Zimm, B.H., J. Chem. Phys. 16, 1093, (1948).

86. Strool, G.R., Schneider, M.J., and Voight-Martin, I.G., J. Polym. Sci. Polym. Phys. 18, 1361, (1980).

87. Cotton, J.P., Farnoux, B., and Jannik, G., J. Chem. Phys. 57, 290, (1972).

88. Duval, M., Duplessix, R., Picot, C., Decker, D., Rempp, P., Benoit, H., Cotton, J.P., Jannik, G., Farnoux, B., and Ober, R., J. Polym. Sci. Polym. Lett. Ed. 14, 585, (1976).

89. Cotton, J.P., Farnoux, B., Jannik, G., Picot, C., and Summerfield, G.C., J. Polym. Sci. Polym. Symp. 42, 807, (1973).

90. Wignall, G.D., Ballard, D.G.H., Schelten, J. Eur. Polym. J. 10, 861, (1974).

91. Daoud, M., Cotton, J.P., Farnoux, B., Jannik, G., Sarma, G., Benoit, H., Duplessix, R., Picot, C., and de Gennes, P.G., Macromolecules, 8, 804, (1975).

92. Duplessix, R., Cotton, J.P., Benoit, H., and Picot, C., Polymer, 20, 1181, (1979).

93. Tangari, C., Summerfield, G.C., King, J.S., Berhiner, R., and Mildner, D.F.R., Macromolecules, 13, 1546, (1980).

94. Akcasu, A.Z., Summerfield, G.C., Han, C.C., Kim, C.Y., and Yu, H., J. Polym. Sci. Polym. Phys, Ed. 18, 863, (1980).

95. Cotton, J.P., Decker, D., Benoit, H., Farnoux, B., Higgins, J., Jannik, G., Ober, R., Picot, C., and des Cloizeaux, J., Macromolecules, 7, 863, (1974).

96. Crist, B., Graessley, W.W., and Wignall, G.D., Polymer, 23, 1561, (1982).

97. Tanzer, T.D., Bartels, C.R., and Crist, B., Macromolecules, 17, 2768, (1984).

98. Schelten, J., Wignall, G.D., Ballard, D.G.H., and Longman, G.W., Polymer. 18, 1111, (1977).

99. Buckingham, A.D., and Hentschel, H.G.E., J. Polym. Sci. Polym. Phys. Ed. 17, 165, (1978).

100. Fernandez, A.M., Widmaier, J.M., Wignall, G.D., and Sperling, L.H., Org. Coat. Applic. Polym. Sci. 48, 327, (1983).

101. Bartels, C., Crist, B., and Graessley, W.W., Macromolecules, 17, 708, (1984).

102. Petcavich, R.J., Painter, P.C., and Coleman, M.M., J. Polym. Sci. Polym. Phys. Ed. 17, 165, (1979).

103. Rafalko, J.J., J. Polym. Sci. Polym. Phys. Ed. 22, 1211, (1984).

104. Bailey, W.J., and Statz, R.J., Polym. Preprints, 11, 244, (1970).

105. Cameron, G.G., Meyer, J.M., and McWalter, I.T., Macromolecules, 11, 696, (1978).

106. Cameron, G.G., and Grassie, N., Makromol. Chem. 51, 130, (1962).

107. McNeill, I.C., and Straiton, T., Eur. Polym. J. 15, 1043, (1979).

108. Wier, N.A., Radiation Effects, 11, 23, (1971).

109. Wier, N.A., J. Macromol. Sci. Chem. A6, 125, (1972).

110. Norris, J.F., and Peaker, F.W., Int. J. Appl. Rad. Isotop. 25, 143, (1974).

111. Brown, J.P., Appl. Environ. Microbiology, 41, 1283, (1981).

112. Parkinson, T.M., Brown, J.P., and Wingard, R.E., U.S. Pat. 4 190 176 (1980).

113. Mills, P.J., Palmstron, C.J., and Kramer, E.J., J. Mat. Sci. 21, 1457, (1986).

114. Mills, P.J., Green, P.F., Palmstrom, C.J., Mayer, J.W., and Kramer, E.J., Appl. Phys. Lett. 45, 958, (1984).

115. Tranzeddel, R., and Hubner, H., Isotopenpraxis, 1, 12, (1971).

116. Rummel, S., and Hubner, H., Isotopenpraxis, 1, 462, (1971).

117. Mattor, C., Peraldo, M., and Farina, M., U.S. Pat. 3 303 177 (1967).

118. Halpern, G.M., and Kim. H., U.S. Pat. 4 092 381 (1978).

CHAPTER TWO

The Preparation and Analysis of Tritium Labelled Monomers and Polymers

2.1 Introduction

2.1.1 Choice of Isotope

The properties of the four most common radioisotopes used in polymer chemistry are listed in Table 2.1. The choice of which isotope to use for labelling experiments can easily be narrowed down to two as the use of chlorine is limited to only a few polymers and sulphur is usually only found in accelerators and retarders used in elastomer chemistry. Tritium and carbon-14 are the most common isotopes for labelling studies and the choice between these two isotopes is dependent on the uses to which the labelled compound is to be put as they possess different properties and so are suitable for different applications.

To label a compound with carbon-14 generally requires a relatively complex synthetic route[1] but this usually leads to incorporation at a specific and stable site. Carbon-14 has a nuclear spin I of zero so can not be studied by nuclear magnetic resonance (NMR) spectroscopy, therefore the position of the label has to be determined by the degradation of the compound; however the labelling techniques used for this isotope generally mean that the position of the label is specific and unequivocal.

Table 2.1 Properties of Common Radioisotopes

Isotope	Mass	Radiation	Maximum Energy MeV	Half Life Years	Maximum Specific Activity Ci/mmol	Common Specific Activity mCi/mmol	Nuclear Spin I	Production Process
Hydrogen	3	β^-	0·018	12·44	29·12	10^2-10^5	$\frac{1}{2}$	$^6Li(n,\alpha)^3H$
Carbon	14	β^-	0·159	5730	0·062	1-10^2	0	$^{14}N(n,p)^{14}C$
Chlorine	36	β^-	0·709	301000	0·001	10^{-3}-10^{-1}	0	$^{35}Cl(n,\gamma)^{36}Cl$
Sulphur	35	β^-	0·167	0·24	1500	1-10^2	0	$^{35}Cl(n,p)^{35}S$ $^{34}S(n,\gamma)^{35}S$

Carbon-14 has the conveniently long half life of 5730 years; however, although there would be no need therefore to make any corrections for the natural decay of the radionuclide during an experiment, the maximum specific activity of a carbon-14 labelled compound is relatively low at 62 mCi/mmol per site.

Tritium has a shorter half life of 12·44 years which means that the maximum specific activity attainable is 2912 Ci/mmol per site, but the half life is still long enough to avoid the need for any correction for natural decay during an experiment becoming necessary. Several simple techniques are available for the labelling of a compound with tritium[2]; however, as the isotope is not part of the backbone of the molecule, the stability of the site can not always be guaranteed and the labelling pattern is not always regiospecific. The triton, like the proton has a nuclear spin of $\frac{1}{2}$ so, using tritium (^3H) NMR spectroscopy, the labelling pattern can be unequivocally confirmed.[3]

Carbon-14 is often used for biochemical research where it is important to have a stable site and the low specific activity of the compound is often an advantage by decreasing the likelihood of radiation induced damage. However, the advantages offered by tritium, ease of labelling,

analysis by NMR spectroscopy and the fact that tritium is significantly cheaper per curie than carbon-14 suggest that this isotope would be the more suitable isotope for this study.

2.1.2 Properties of Tritium

Tritium has a natural abundance of $\sim 10^{-16}$% (Table 2.2) and is formed in the upper atmosphere as a result of reactions brought about by cosmic radiation. Tritium is generally produced by the bombardment of lithium-6 with neutrons in a nuclear reactor (eqn 2.1).

$$^{6}Li\ (n,\alpha)\ ^{3}H \qquad -2.1$$

Tritium is commercially available in a range of forms, as tritium gas, isotopically enriched water, as metal tritides or as a range of tritiated compounds e.g. [1-^{3}H]acetic acid and [^{3}H]methyl iodide. The labelling techniques available for tritium can be divided into two main categories, isotope exchange reactions and direct chemical synthesis. Isotope exchange reactions provide an easy method of labelling complex molecules and is the most widely used technique. Exchange into labile groups such as thiols, alcohols and amines etc. occurs almost instantaenously; however, these reactions

are reversible and the label is easily lost. Isotope exchange into more stable positions requires the use of a catalyst be it simple acid/base catalysis, freshly reduced platinum dioxide or a tritiated phosphoric acid-boron trifluoride catalyst. The major drawback of this type of technique is that the specificity of labelling can not be guaranteed. Direct chemical synthesis generally involves the reduction of unsaturated groups such as alkenes/alkynes, aldehydes and ketones with tritium gas, tritiated water or metal tritides. Another alternative method is the catalytic replacement of halogens with tritium using a hydrogenation catalyst; these types of reactions are slightly more difficult to perform but produce a specific labelling pattern. Therefore by the use of these techniques a wide range of compounds can be labelled.

One of the major advantages of using tritium as a radioisotope is the availability of tritium NMR spectroscopy as a routine analytical technique for establishing tritium labelling patterns. The triton is well suited to study by NMR spectroscopy, it has a larger magnetic moment than the proton (Table 2.2) hence a larger magnetogyric constant than the proton and so is more sensitive to study than any other nucleus. This enhanced sensitivity to detection is necessary

Table 2.2 The Nuclear Properties of Hydrogen and Tritium

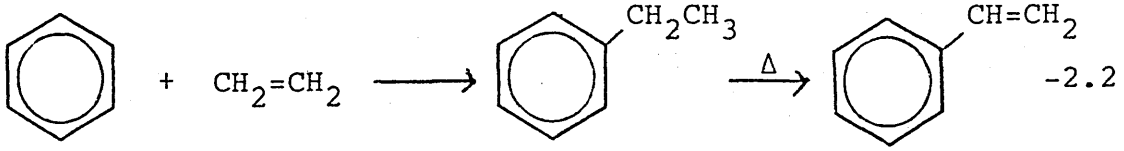
	Hydrogen	Tritium
Relative Mass	1	3
Natural Abundance	99•98%	$\sim 10^{-16}$%
Nuclear Spin	$\frac{1}{2}$	$\frac{1}{2}$
Magnetic Moment (μ/μ_N)	4•837	5•159
Magnetogyric Constant ($\gamma/10^7$ rad $T^{-1}s^{-1}$)	26•752	28•534
Resonance Frequency (MHz at 2•11T)	90•0	96•0
Relative Sensitivity (for equal numbers of nuclei at constant field)	1•0	1•21

as the concentration of tritium in a labelled compound is normally of the order of 0·1-0·0035%, equivalent to 30-0·1 mCi/mmol per labelled site. Another advantage of the triton is that its NMR frequency is slightly higher than that of the proton so spectral dispersity is lower and there is a larger chemical shift with respect to frequency. As tritium is an isotope of hydrogen, the chemical shifts in parts per million are almost exactly the same, so a wealth of chemical shift information is available. The frequencies of the shifts are converted from proton to triton by multiplication by the Larmor ratio (1·06663974).[4]

2.1.3 Monomers and Polymers

The usefulness of the above mentioned techniques have been illustrated by the preparation of the following labelled monomers and polymers.

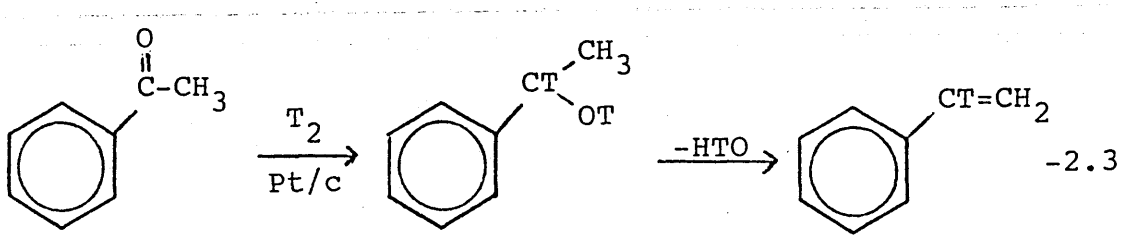
Polystyrene was first prepared as a clear polymer in 1845.[5] The monomer is prepared industrially from benzene and ethylene, the ethyl benzene thus formed dehydrogenated (eqn 2.2).



-2.2

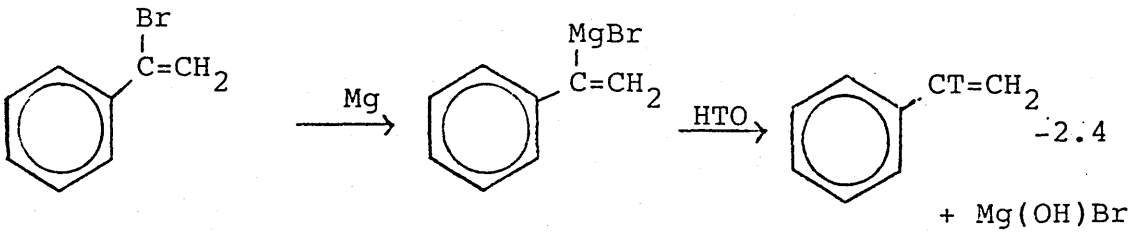
The monomer can be polymerised by a range of techniques[6]; the polymer thus formed has a high electrical resistance and scratch and mar resistance; however it is attacked by solvents and discolours on exposure to UV light.

A range of techniques have previously been used to label styrene with tritium in a number of positions; [α-^{3}H]-styrene may be prepared by the reduction of acetophenone with tritium gas (eqn 2.3)[7]



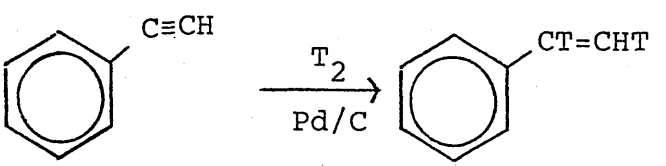
-2.3

or by decomposition of the relevant styryl magnesium bromide with tritiated water (eqn 2.4)[8].



-2.4

[β-^{3}H] Styrene may be prepared by the same method.[9] [α,β-$^3H_2$] Styrene may be prepared by the catalytic reduction of phenylacetylene (eqn 2.5).[2]



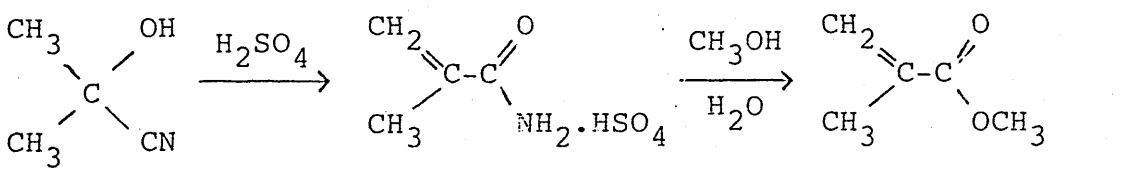
-2.5

A technique has been suggested for generally labelling a range of monomers using a P_2O_5 catalyst,[10] but this method was unsuccessful in the case of styrene as a competing polymerisation reaction was observed.

α-Methylstyrene is produced by a similar method to styrene with propylene and benzene.[5] The α-methyl group decreases the reactivity of the monomer to polymerisation so an aluminium trichloride catalyst is necessary. The monomer is usually co-polymerised with

butadiene to form synthetic rubbers or as a synthetic lacquer resin finish.

Methylmethacrylate is produced by the reaction between acetone cyanohydrin and concentrated sulphuric acid followed by methanol hydrolysis (eqn 2.6).[5]



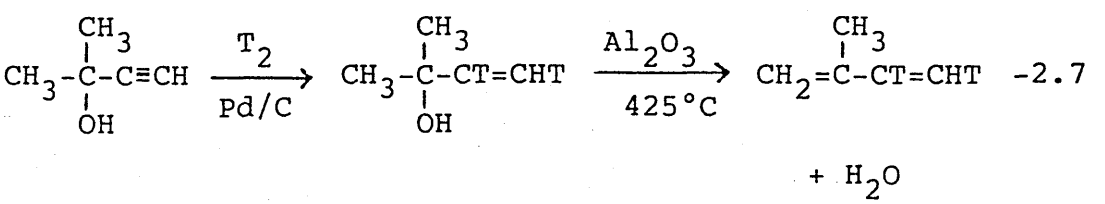
$$+ NH_4HSO_4 \quad -2.6$$

The monomer is generally polymerised by thermal or UV initiation producing a polymer suitable for casting when its viscosity reaches a consistency of syrup.

The addition of diazomethane to methacrylic acid labelled with tritium enables methylmethacrylate to be prepared, labelled in the methyl ester group.[11,18] The monomer has also been sucessfully labelled at low specific activity by heating the polymer with tritiated water and P_2O_5 catalyst, followed by depolymerisation to yield the monomer.[10]

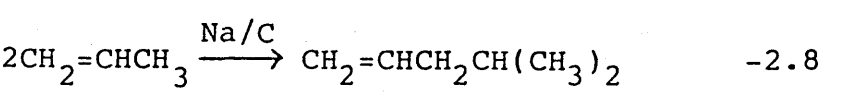
Butylmethacrylate is prepared by the esterification of methacrylic acid with butanol or the alcoholysis of methylmethacrylate and polymerised by radical initiation.[5] The polymer has useful elastomeric properties and is used for modifiers in lubricating oils, optical and other special adhesives, textile and leather finishes.[6]

Isoprene is prepared by the pyrolysis of natural rubber and is co-polymerised with styrene by radical or thermal initiation to form synthetic rubbers. [3,4-$^3H_2$] Isoprene has been prepared by the catalytic reduction of 3-methyl-3-butynol with tritium gas and a palladium catalyst partially deactivated with quinoline. The resulting alcohol was then dehydrated to yield the product (eqn 2.7).[12]



-2.7

4-Methyl-1-pentene is produced by the dimerisation of propylene by a sodium on charcoal catalyst (eqn 2.8).[7]



-2.8

Polymerisation is performed using a Ziegler-Natta catalyst to form a polymer with very low density, good high temperature resistance and optical density. The polymer has been used for light fittings and items of medical apparatus but is very susceptible to UV light and oxidation.

2.2 Materials and Equipment

The reagents were commercially available and were either purified prior to use or their purity checked by standard procedures. Tritiated water (50 Ci/ml) was obtained from Amersham International. The specific activities of the prepared compounds were determined by the use of a Beckman Liquid Scintillation Counter LS 1800. The ^{3}H-NMR spectra were obtained at 25 °C on a Bruker WH 90 pulse spectrometer operating at 96 MHz. (90 MHz for ^{1}H spectra) with quadrature detection. The flip angle was 30°, the repetition interval 1·6 seconds and, depending on the amount of radioactivity present, between 100 and $2{\cdot}5 \times 10^{5}$ transients were acquired. The data were stored in 4K channels and Fourier transformed to provide spectral display widths of up to 13 ppm. Referencing was to a ghost reference generated from the proton resonance frequency of the internal standard (measured at 90 MHz) by multiplying by the Larmor ratio

1·06663974. Samples for analysis were sealed in 3 mm diameter combination tubes (Wilmad SK1374A) with deuteriated chloroform as the solvent and tetramethylsilane as the internal standard.

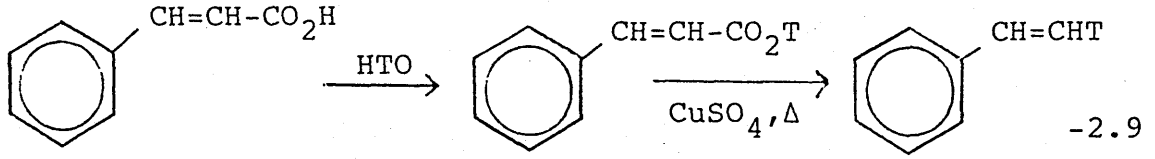
2.3 Synthesis of ^{3}H-Labelled Monomers

2.3.1 Preparation of Reduced Platinum Dioxide Catalyst

Platinum dioxide (50 mg) was mixed with water (10 ml), sodium borohydride (250 mg) was added in small stages then the mixture heated to 70 °C to complete the reaction. The liquid was decanted and the solid washed several times with water and then acetone which was removed by evaporation.

2.3.2 Preparation of [β-^{3}H] Styrene

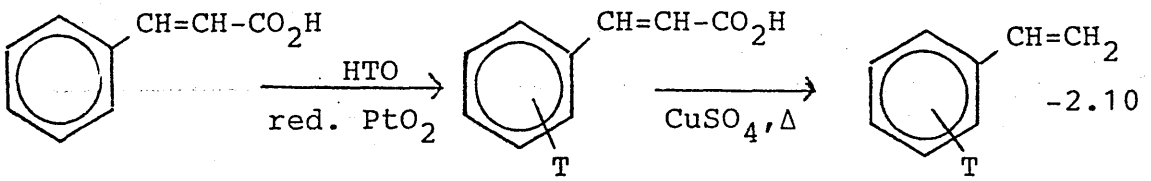
Cinnamic acid (0·5 g) was dissolved in a minimum amount of 1,4-dioxan (ca. 2 ml) and mixed with tritiated water (3 μl). After 72 hours, the solvent was removed and the acid mixed with quinoline (2 ml) and anhydrous copper sulphate (0·01 g). The mixture was refluxed for one hour, 6M hydrochloric acid (30 ml) added and the product obtained by steam distillation.



-2.9

2.3.3 Preparation of [Ar-^{3}H] Styrene

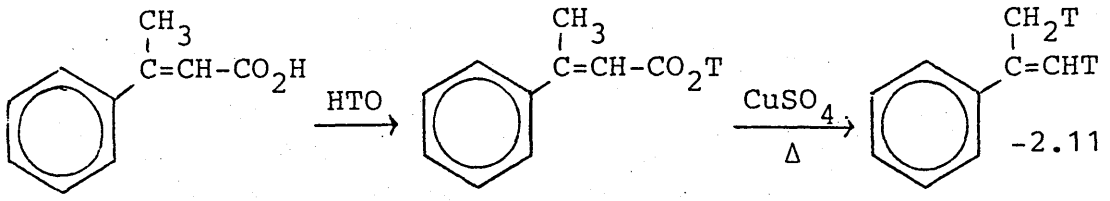
Cinnamic acid (0·5 g) was mixed with freshly reduced platinum dioxide (20 mg) and tritiated water (3 μl) and sealed in a glass vial. The mixture was heated at 150 °C for 24 hours and then decarboxylated with quinoline as described above.



-2.10

2.3.4 Preparation of [β,Me-$^3H_2$] α-Methylstyrene

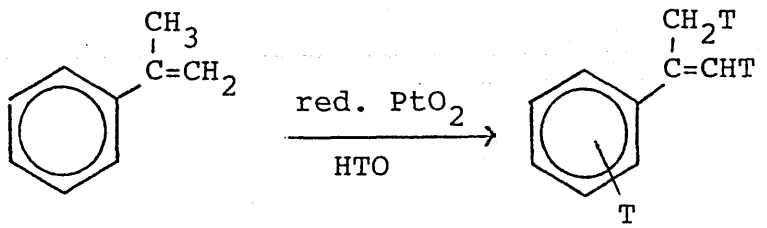
β-Methylcinnamic acid was prepared as described in the literature[13] and then treated in the same way as for cinnamic acid (sect. 2.3.2).



-2.11

2.3.5 Preparation of [G-^{3}H] α-Methylstyrene

α-Methylstyrene (0·5 g) was sealed in a glass vial with freshly reduced platinum dioxide (20 mg) and tritiated water (3 μl). The mixture was heated at 110 °C for 24 hours, the product filtered to remove the catalyst and dried over anhydrous sodium sulphate.

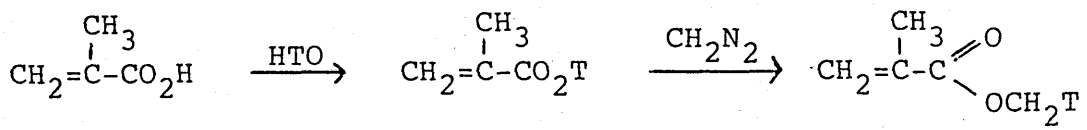


-2.12

2.3.6 Preparation of [1-^{3}H] Methylmethacrylate

Methacrylic acid (0·5 g) was mixed with tritiated water (3 μl) and allowed to stand for 20 minutes. Diazomethane in ether was added dropwise until the yellow colour of diazomethane persisted for five minutes. The

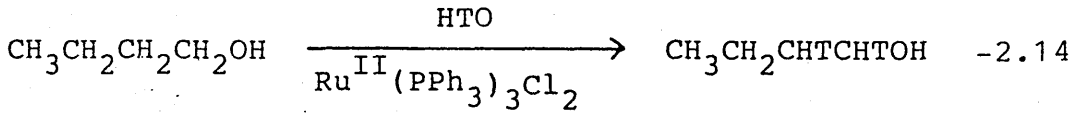
solvent was removed by evaporation.



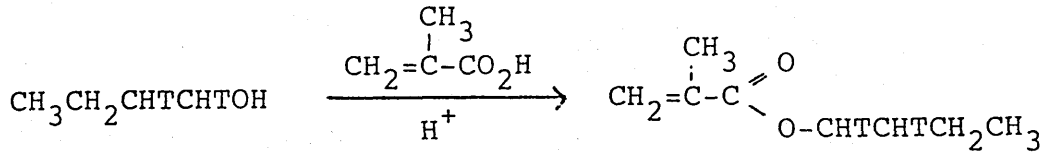
-2.13

2.3.7 Preparation of [G-^{3}H]Butylmethacrylate

Butanol (0·5 ml), dichlorotris(triphenylphosphine)-ruthenium(II), (10 mg) and tritiated water (2 μl) were sealed in a glass vial under nitrogen and heated at 180-200 °C for three hours. The contents of the vial were taken up in ether (20 ml) and washed with water(1 ml) and dried over anhydrous sodium sulphate. The ether was removed by evaporation and the alcohol mixed with methacrylic acid (0·5 ml), dilute sulphuric acid (150 μl) and a small quantity of hydroquinone. The mixture was sealed in a glass tube and heated at 95 °C for one hour, washed with dilute aqueous sodium hydroxide, water and then dried over anhydrous sodium sulphate.



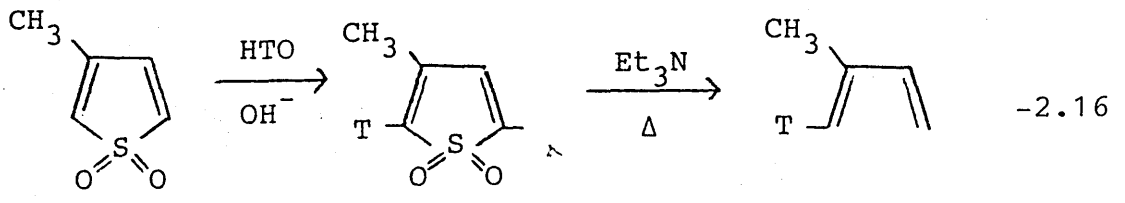
-2.14



-2.15

2.3.8 Preparation of [1-^{3}H] Isoprene

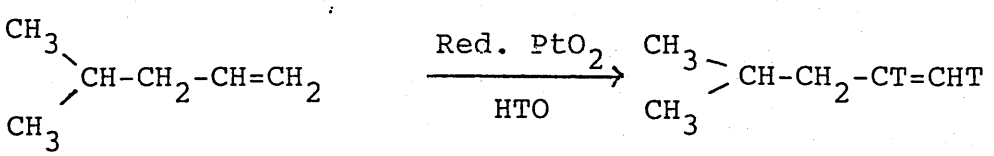
3-Methyl-3-sulpholene (0·5 g) was dissolved in the minimum volume of 1,4-dioxan, a pellet of sodium hydroxide was added followed by tritiated water (3 µl). After 24 hours the compound was taken up in chloroform (2 ml), washed twice with distilled water (5 ml) and the solvent removed. The compound was sealed in a glass vial with triethylamine (5 ml) and heated at 130 °C for two hours. The product was taken up in deuterated chloroform (200 µl), washed with water and dried over anhydrous sodium sulphate.



-2.16

2.3.9 Preparation of [G-^{3}H] 4-Methyl-1-pentene

4-Methyl-1-pentene (0·5 ml) was sealed in a glass vial with freshly reduced platinum dioxide (10 mg) and tritiated water (3 µl). The mixture was heated at 110 °C for 24 hours, then, on cooling, filtered, washed with water and dried over anhydrous sodium sulphate.



-2.17

2.4 Preparation of ^{3}H-Labelled Polymers

2.4.1 Preparation of Poly([1-^{3}H]methylmethacrylate)

[1-^{3}H] Methylmethacrylate (0·5 ml) was sealed in a glass vial under vacuum and heated at 110 °C for 24 hours. The resultant polymer was dissolved in toluene (5 ml) and precipitated with methanol (50 ml), filtered and air dried.

2.4.2 Preparation of Poly([G-^{3}H]butylmethacrylate)

[G-^{3}H] Butylmethacrylate (0·5 ml) was sealed in a glass vial under a vacuum with α,α'-azobisisobutyronitrile

(100 μg) and heated at 100 °C for 24 hours. The polymer was purified as above.

2.4.3 Preparation of Poly([G-^{3}H] α-methylstyrene)

[G-^{3}H] α-Methylstyrene (0·5 mg) was dissolved in dichloromethane (2 ml) and cooled to -78 °C with a dry ice/acetone mixture. Concentrated sulphuric acid (100 μl) was added and the mixture stirred for two hours. The polymer was purified as described as above.

2.4.4 Preparation of Poly([G-^{3}H]4-methyl-1-pentene)

Aluminium sesquichloride (200 μl) was added to a solution of titanium (IV) chloride (300 μl) in petroleum spirit (100-120°)(2 ml) under dry nitrogen. The mixture was allowed to stand for three hours to allow for the formation of the catalyst, a titanium (III) aluminium alkyl complex indicated by the formation of purple crystals.[19] [G-^{3}H]4-Methyl-1-pentene (0·5 ml) was added to the catalyst mixture and the vessel shaken in an oil bath at 60 °C for 24 hours. The resultant suspension was dissolved in chloroform (5 ml) and reprecipitated with methanol (50 ml), the polymer filtered off and air dried.

2.5 Results

2.5.1 Specific Activities of Labelled Monomers

To determine the specific activities of the monomers a known amount of each compound was dissolved in a solvent containing the appropriate scintillator and counted. If the counts were excessive, the solutions were diluted further as necessary and from these results the specific activity was calculated. The specific activities of the labelled monomers are given in Table 2.3.

Table 2.3 Specific Activities of Labelled Monomers

Monomer	Specific Activity mCi/mmol
[1-^{3}H]Styrene	2·6
[Ar-^{3}H]Styrene	4·2
[1,Me-^{3}H] α-Methylstyrene	6·5
[G-^{3}H] α-Methylstyrene	13·0
[1-^{3}H]Methylmethacrylate	7·5
[G-^{3}H]Butylmethacryate	2·2
[1-^{3}H]Isoprene	1·9
[G-^{3}H]4-Methyl-1-pentene	9·5

2.5.2 Analysis of NMR Spectra

The NMR spectra of [CO_2-^{3}H]cinnamic acid (fig 2.1) show the tritium located as expected entirely in the carboxylic acid group (signal at δ11·4 ppm). Decarboxylation of the acid yielded [β-^{3}H]styrene (fig 2.2), the two singlets at δ5·2 and δ5·7 in the ^{3}H-NMR spectrum correspond to the cis and trans configurations. Comparisons between the ^{1}H-NMR spectra of the labelled and unlabelled compounds show that the tritiated product is as pure as the unlabelled material.

The tritiation of cinnamic acid with reduced platinum dioxide labels the compound specifically in the aromatic ring (fig 2.3) and thermal decomposition yields [Ar-^{3}H]-styrene (fig 2.4).

β-Methyl cinnamic acid labelled in the carboxylic acid group (fig 2.5) decomposes to form [β,Me-^{3}H]α-methyl-styrene (fig 2.6). Unlike styrene, α-methylstyrene does not polymerise by thermal initiation, so it can be labelled directly with reduced platinum dioxide. The ^{3}H-NMR (fig 2.7) shows the tritium to be present in all positions, the signal at δ2·1 corresponds to the methyl group, the two singlets at δ5·4 and δ5·1 are the cis and trans positions in the methylene group and the signals between δ7·2 and δ7·5

Fig 2.1a ^{3}H-NMR (^{1}H-decoupled) of [CO_2-^{3}H]cinnamic acid

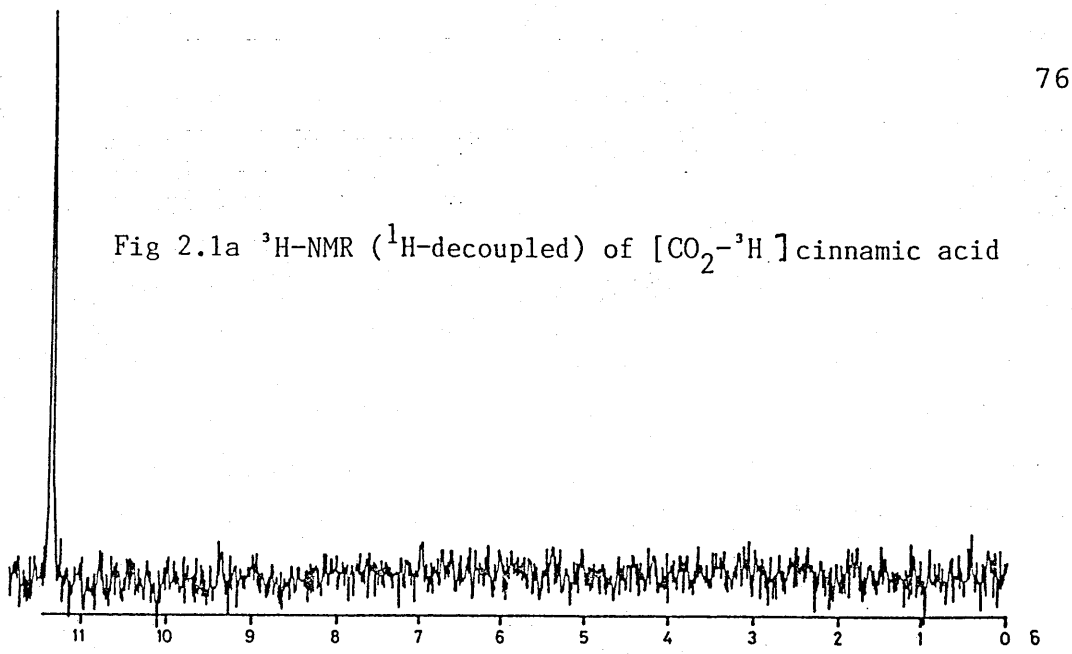


Fig 2.1b ^{1}H-NMR of [CO_2-^{3}H]cinnamic acid

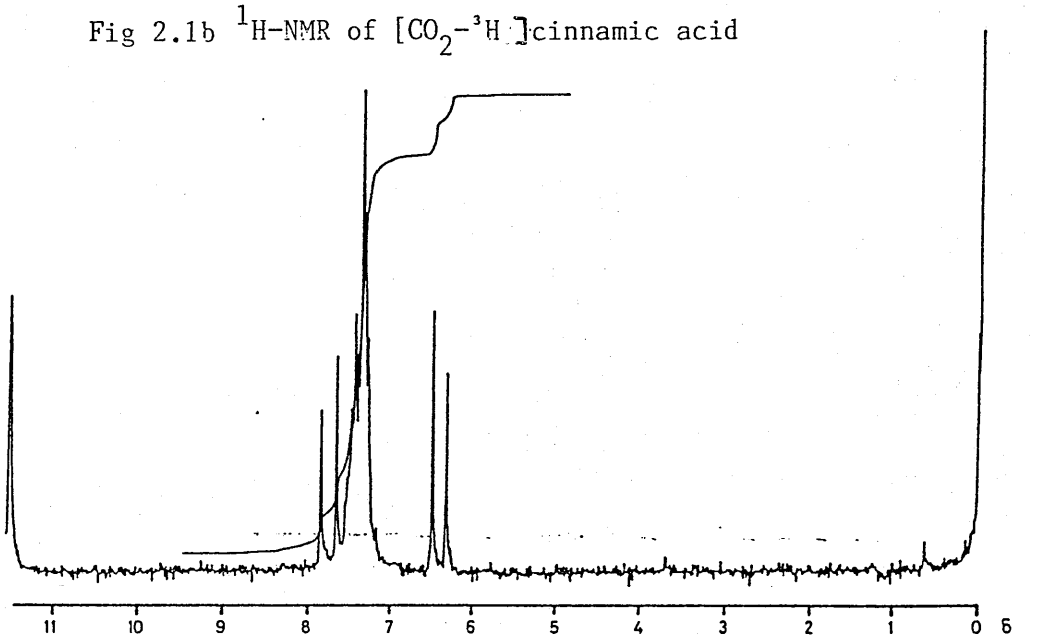


Fig 2.1c ^{1}H-NMR of cinnamic acid

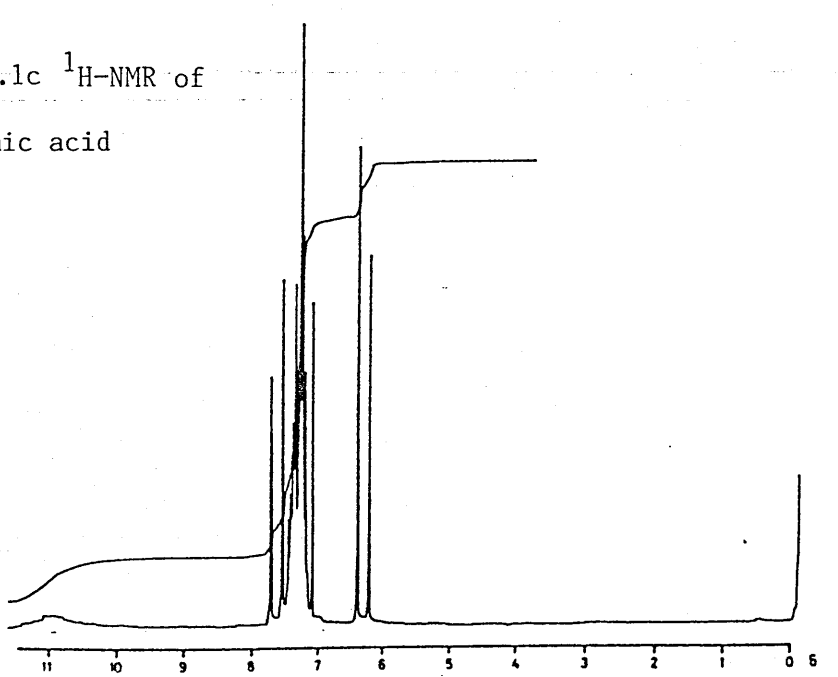


Fig 2.2a ^{3}H-NMR (^{1}H-decoupled) of [β-^{3}H]styrene

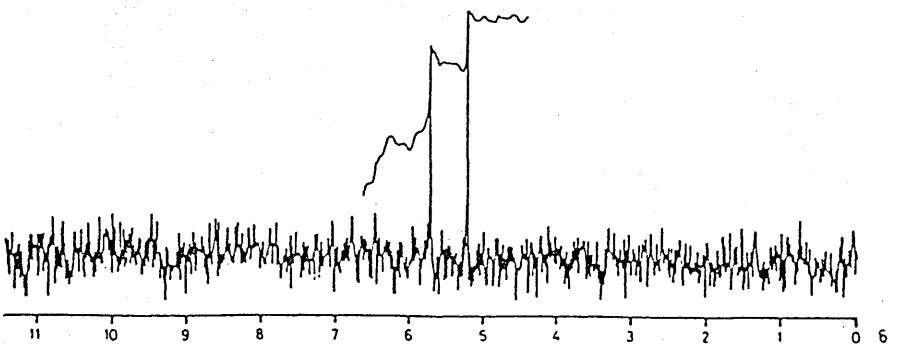


Fig 2.2c ^{1}H-NMR of [β-^{3}H]styrene

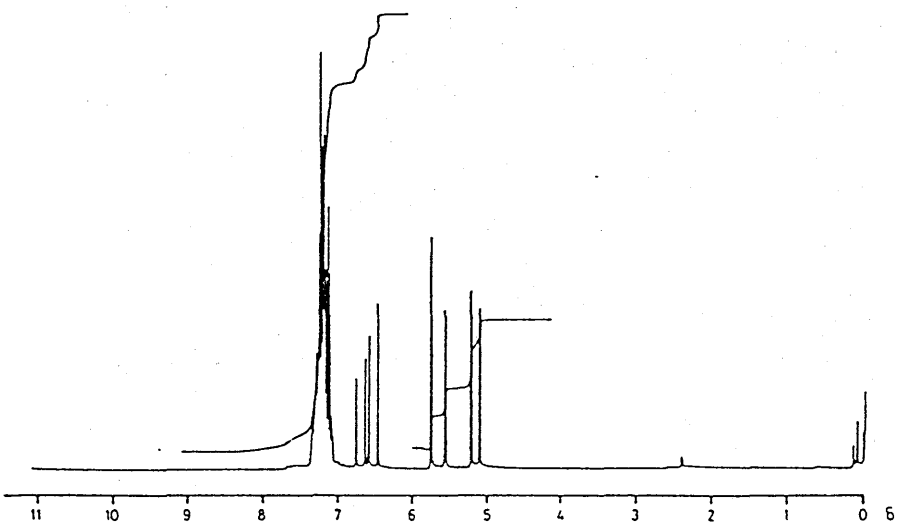


Fig 2.2c ^{1}H-NMR of styrene

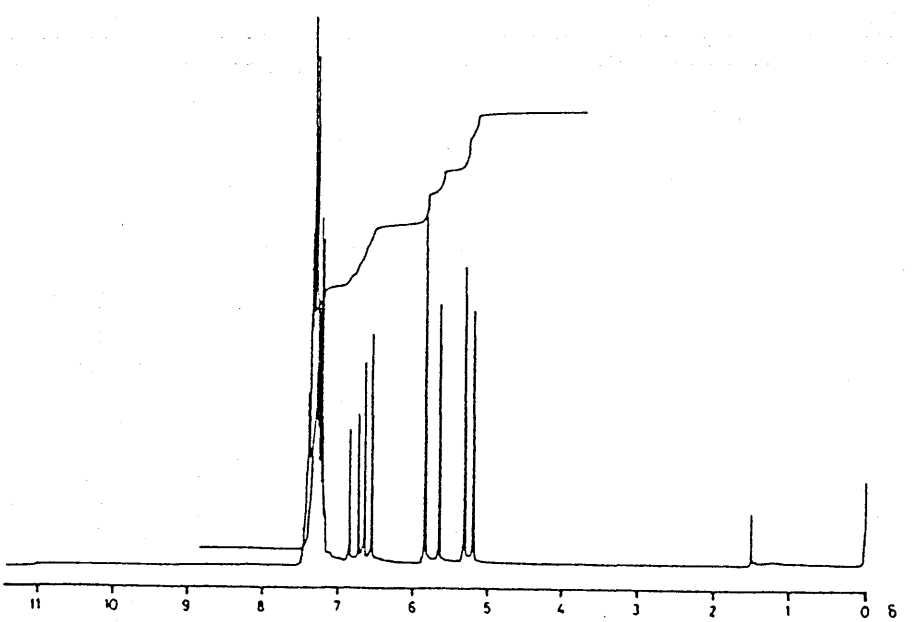


Fig 2.3 ^{3}H-NMR (^{1}H-decoupled) of [Ar-^{3}H]cinnamic acid

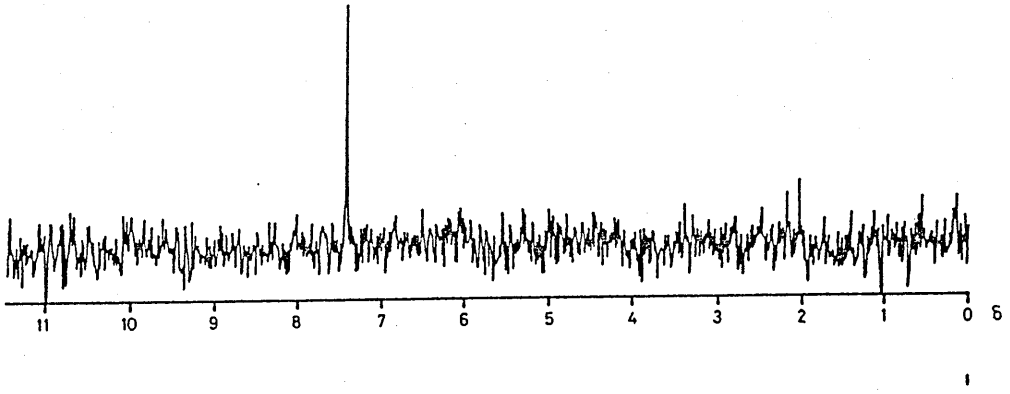


Fig 2.4 ^{3}H-NMR (^{1}H-decoupled) of [Ar-^{3}H]styrene

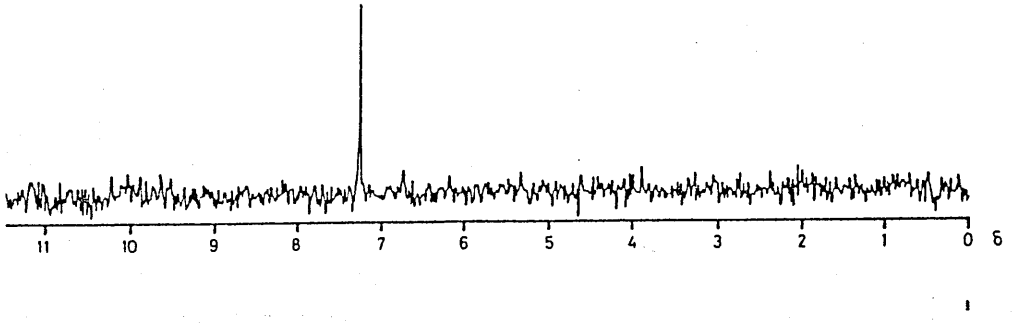


Fig 2.5a ^{3}H-NMR (^{1}H-decoupled) of [CO_2-^{3}H] β-methylcinnamic acid

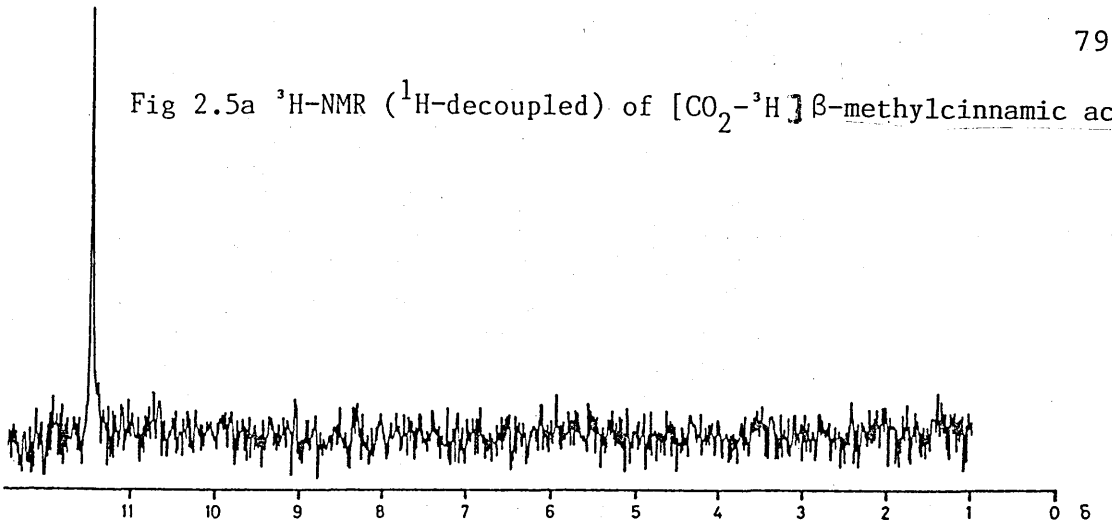


Fig 2.5b ^{1}H-NMR of [CO_2-^{3}H] β-methylcinnamic acid

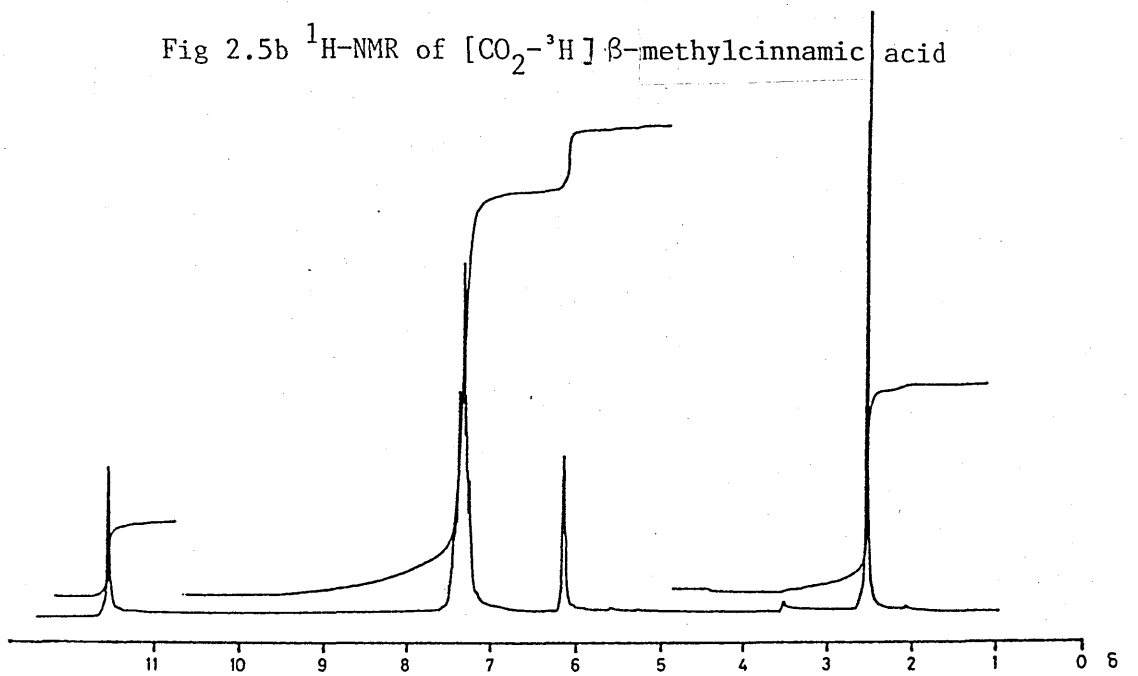


Fig 2.5c ^{1}H-NMR of β-methylcinnamic acid

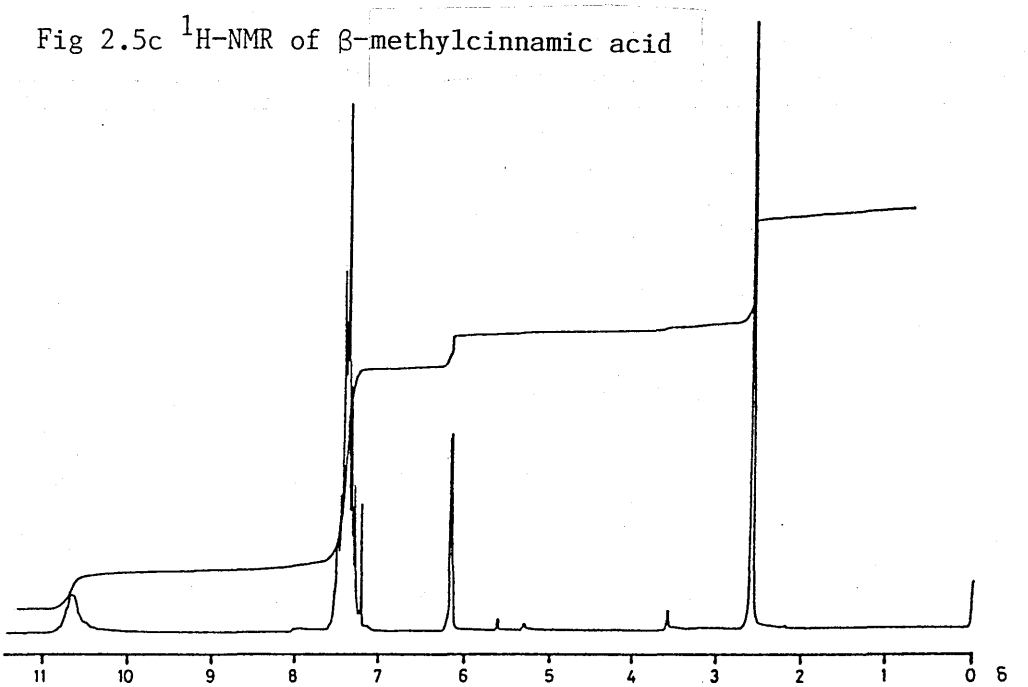


Fig 2.6a ^{3}H-NMR (^{1}H-decoupled) of [β,Me-^{3}H]α-methyl styrene

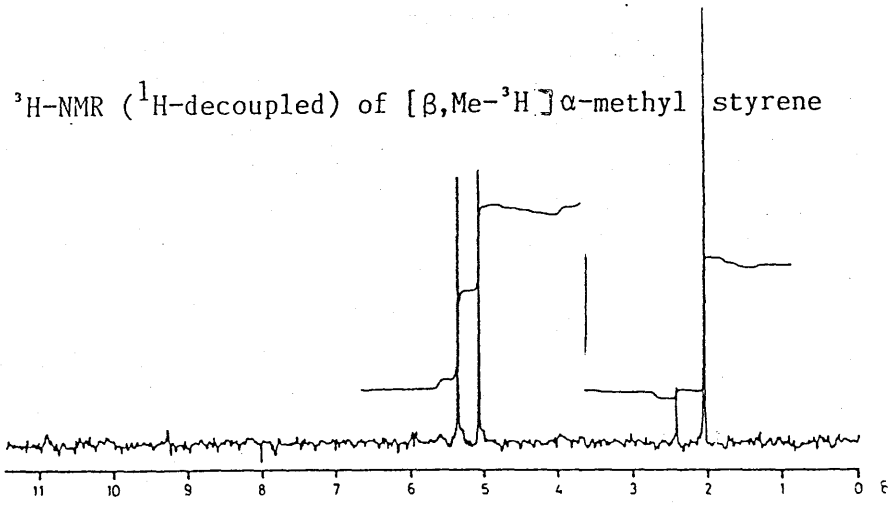


Fig 2.6b ^{1}H-NMR of [β,Me-^{3}H]α-methylstyrene

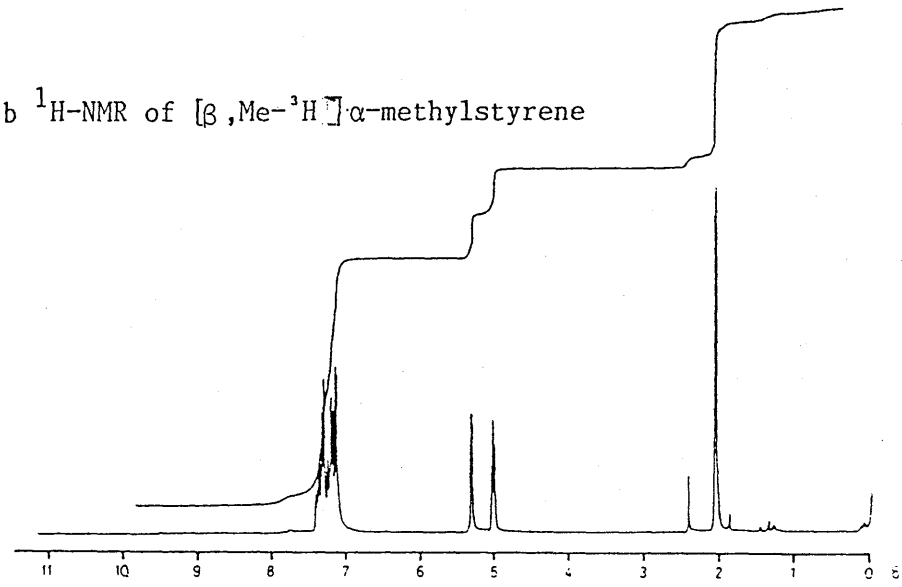


Fig 2.6c ^{1}H-NMR of α-methylstyrene

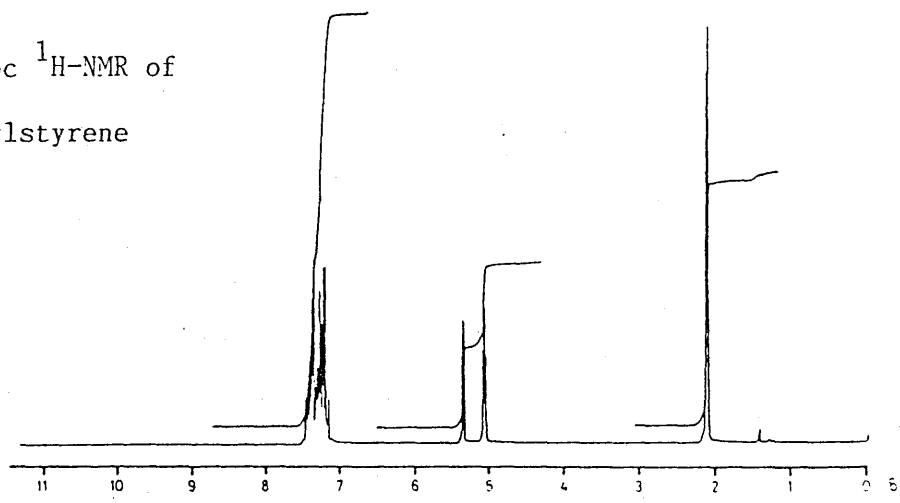


Fig 2.7a ^{3}H-NMR (^{1}H-decoupled) of [G-^{3}H] α-methylstyrene

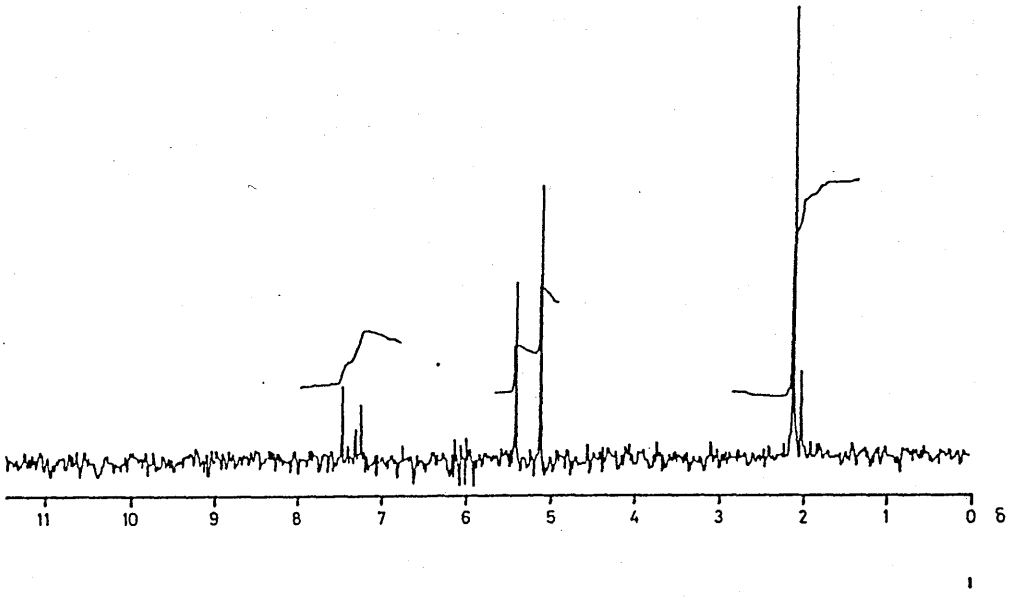
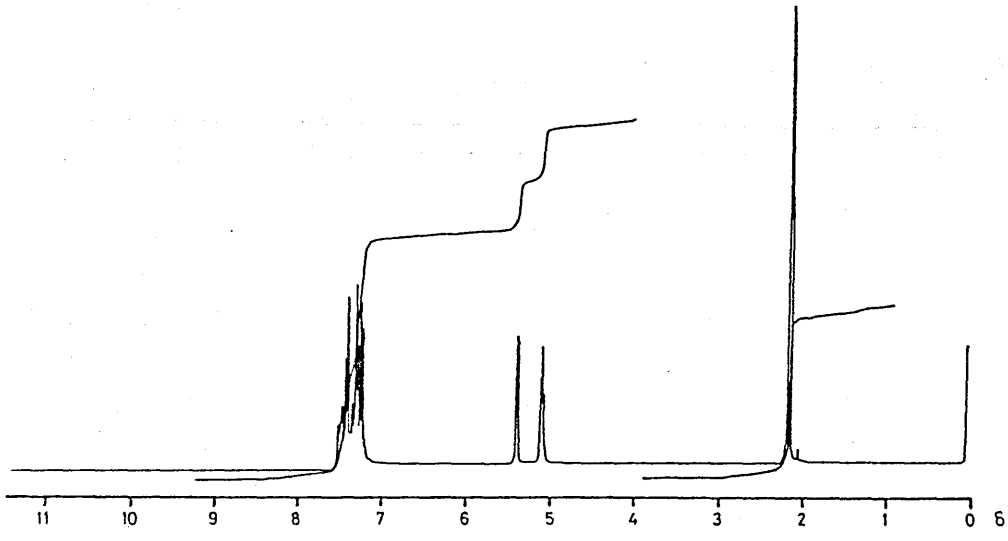


Fig 2.7b ^{1}H-NMR of [G-^{3}H] α-methylstyrene



are for the aromatic hydrogens.

The ^{3}H-NMR spectrum of [1-^{3}H]methylmethacrylate (fig 2.8a) shows as expected a singlet at δ3·8 corresponding to the methyl ester group. A large radiochemical impurity is present at δ3·9 accounting for some 30 % of the radioactivity. The impurity manifests itself in the ^{1}H-NMR spectrum of the labelled compound (fig 2.8b) as a broad signal underneath the ester signal. Also visible in the ^{1}H-NMR spectrum is a triplet at δ1·2 and a quartet at δ3·6 due to the presence of residual diethylether solvent.

The ^{3}H-NMR spectrum of butanol (fig 2.9a) shows the alcohol to be labelled mainly in the α-position (70 %) at δ3·6, with the remainder of the label incorporated in the β-position (>25 %) at δ1·5. Esterification to yield the ester (fig 2.10) does not lead to any scrambling of the label as the two main signals are retained in the final product.

3-Methyl-3-sulpholene has been labelled in the two methylene groups (fig 2.11), predominately in the 2-position (signal at δ3·6). Thermal degradation yields isoprene (fig 2.12) labelled specifically in the 1-position as represented by the doublet for the cis and trans positions at δ5·0.

Fig 2.8a ^{3}H-NMR (^{1}H-decoupled) of [1-^{3}H]methylmethacrylate

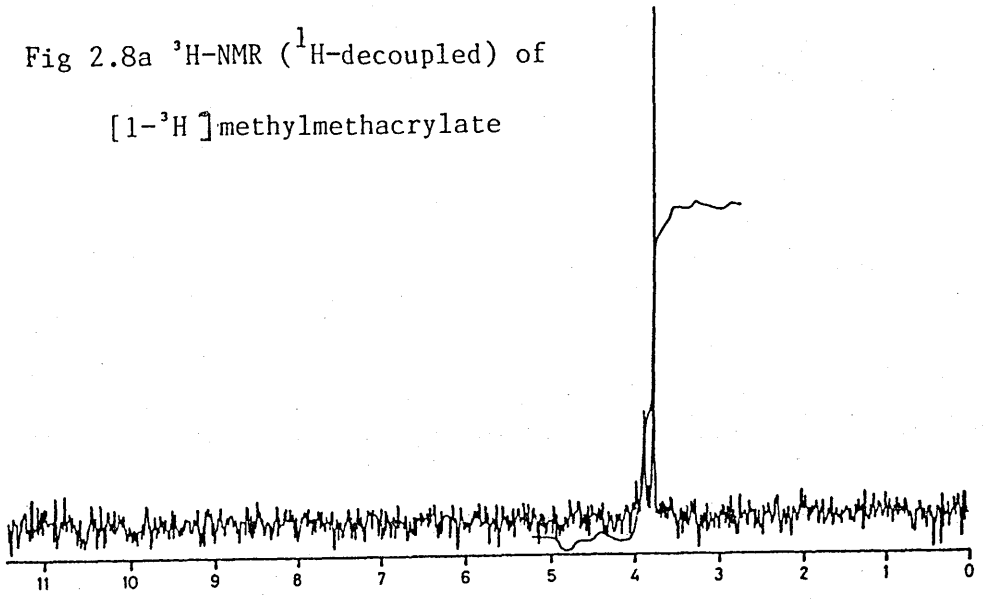


Fig 2.8b ^{1}H-NMR of [1-^{3}H]methylmethacrylate

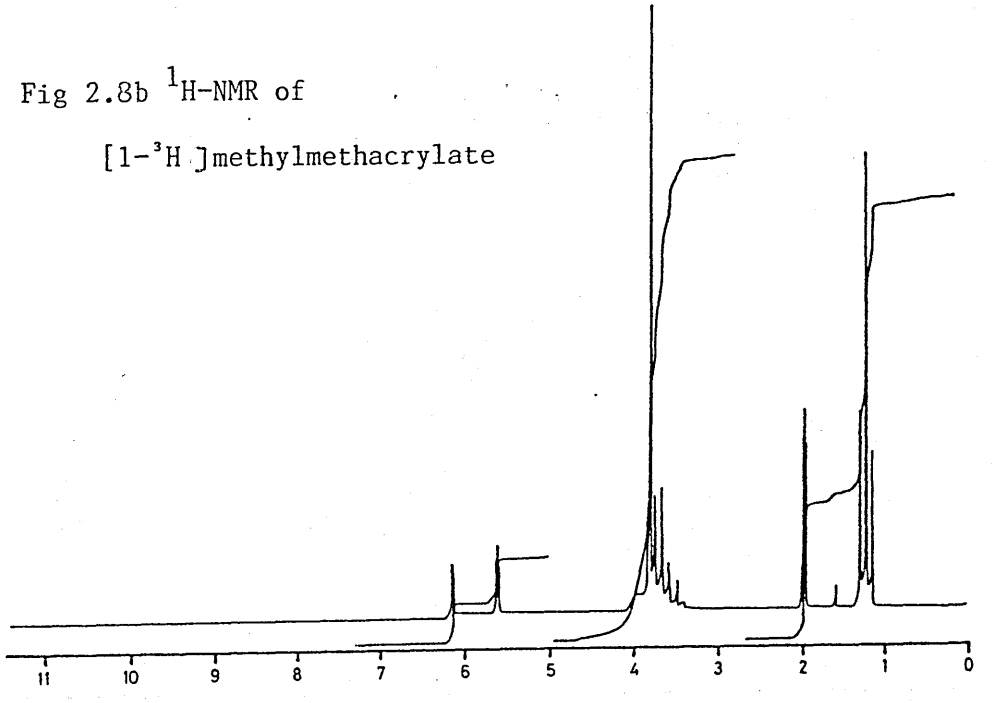


Fig 2.8c ^{1}H-NMR of methylmethacrylate

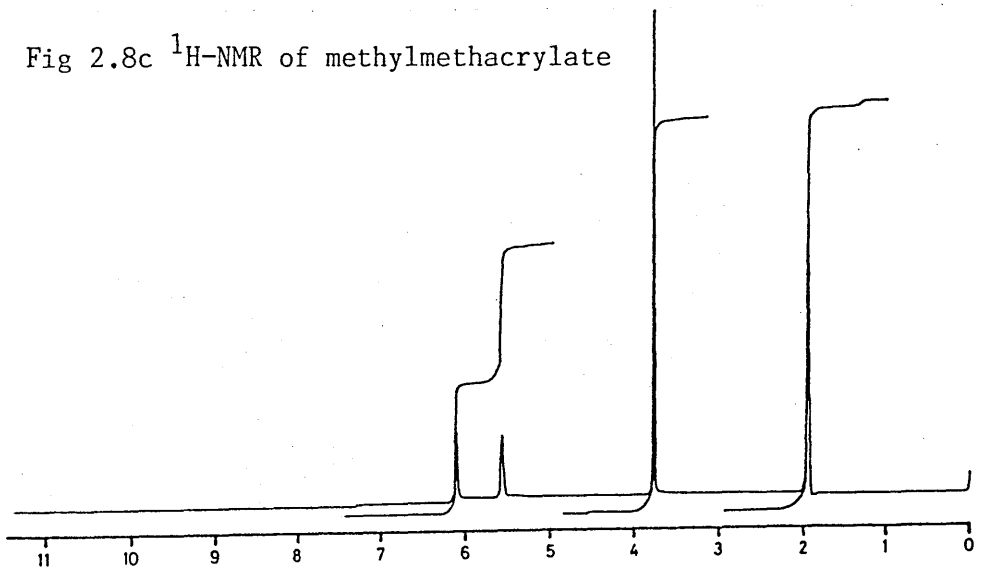


Fig 2.9a ^{3}H-NMR (^{1}H-decoupled) of [α,β-^{3}H]-butanol

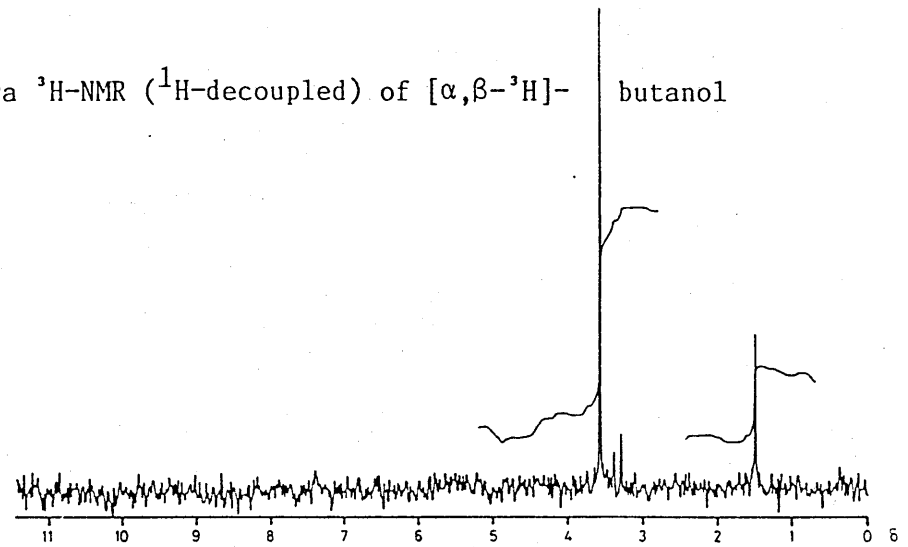


Fig 2.9b ^{1}H-NMR of [α,β-^{3}H]butanol

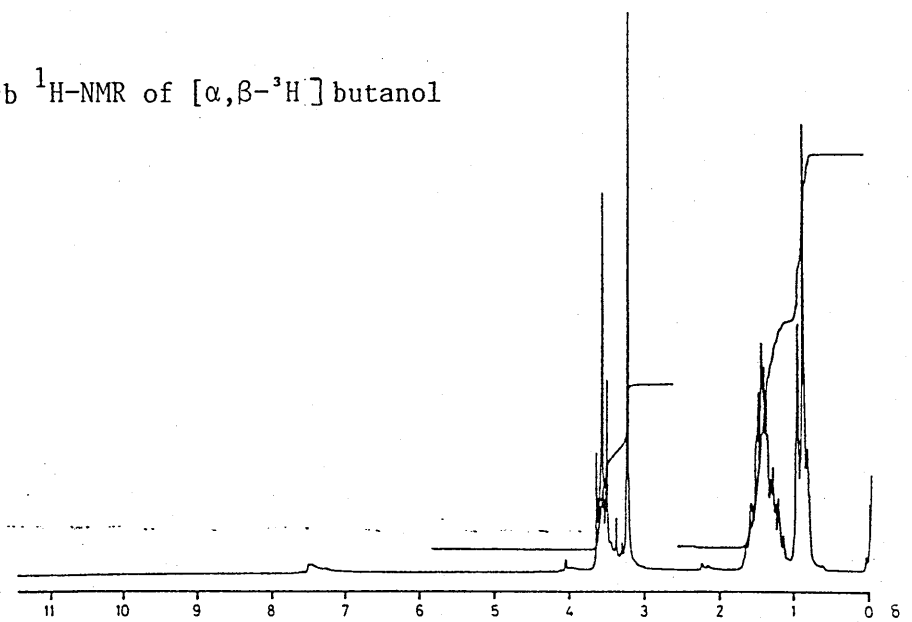


Fig 2.9c ^{1}H-NMR of butanol

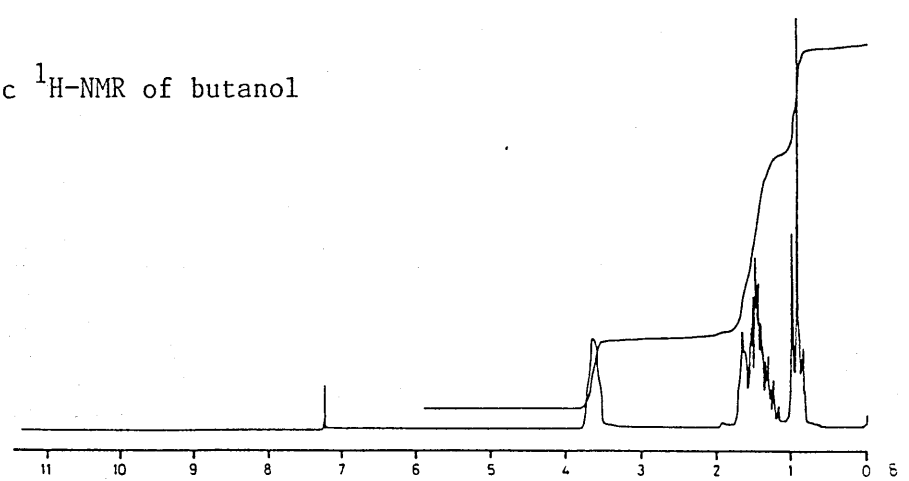


Fig 2.10a ^{3}H-NMR (^{1}H-decoupled) of [G-^{3}H]butylmethacrylate

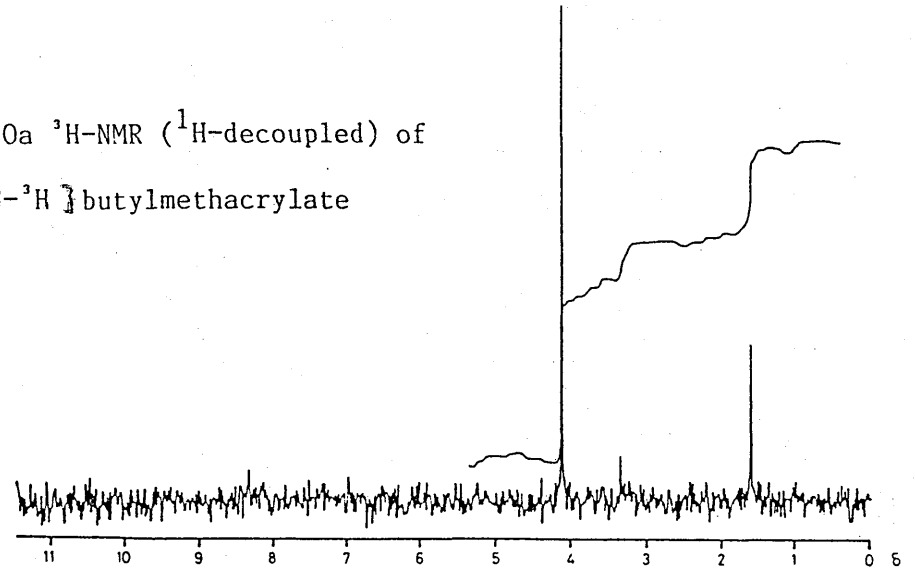


Fig 2.10b ^{1}H-NMR of [G-^{3}H]butylmethacrylate

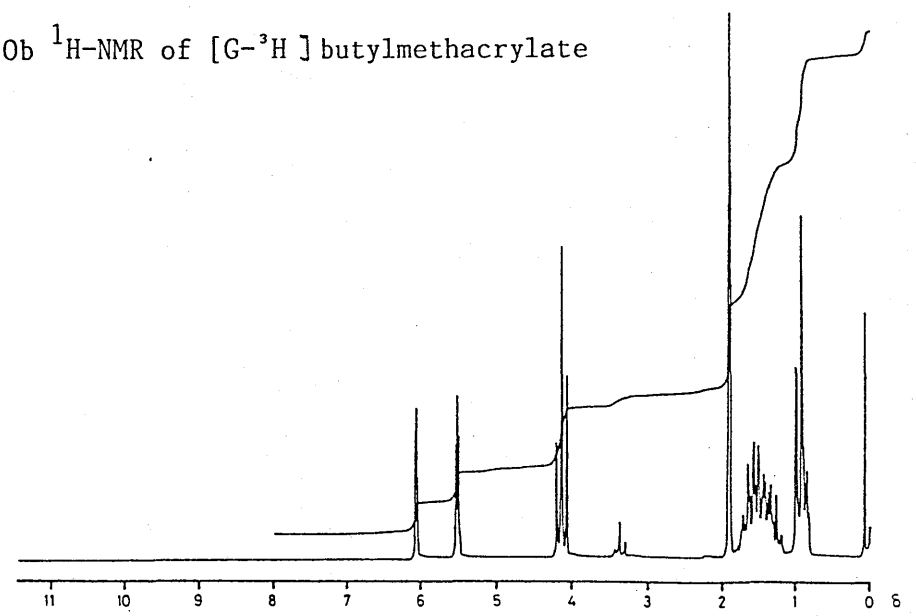


Fig 2.10c ^{1}H-NMR of butylmethacrylate

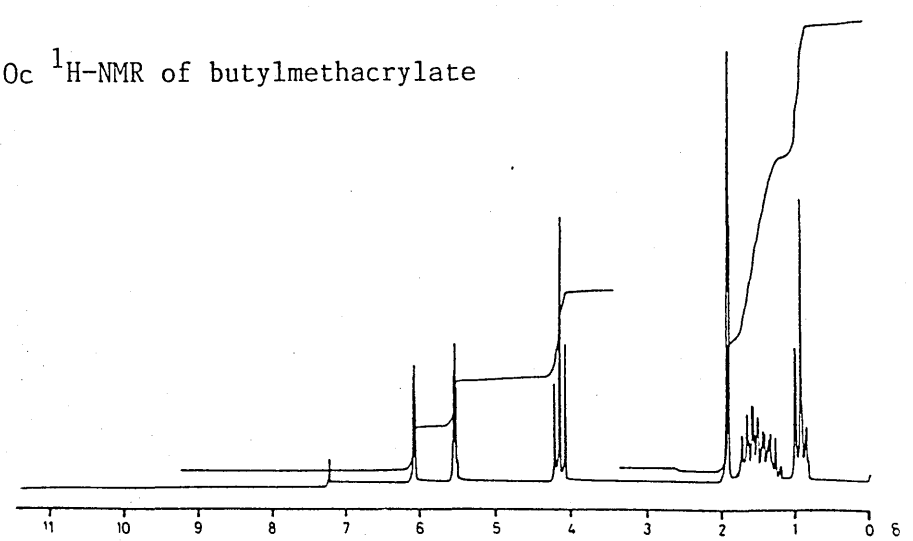


Fig 2.11a ^{3}H-NMR (^{1}H-decoupled) of [2,5-^{3}H] 3-methyl-3-sulpholene

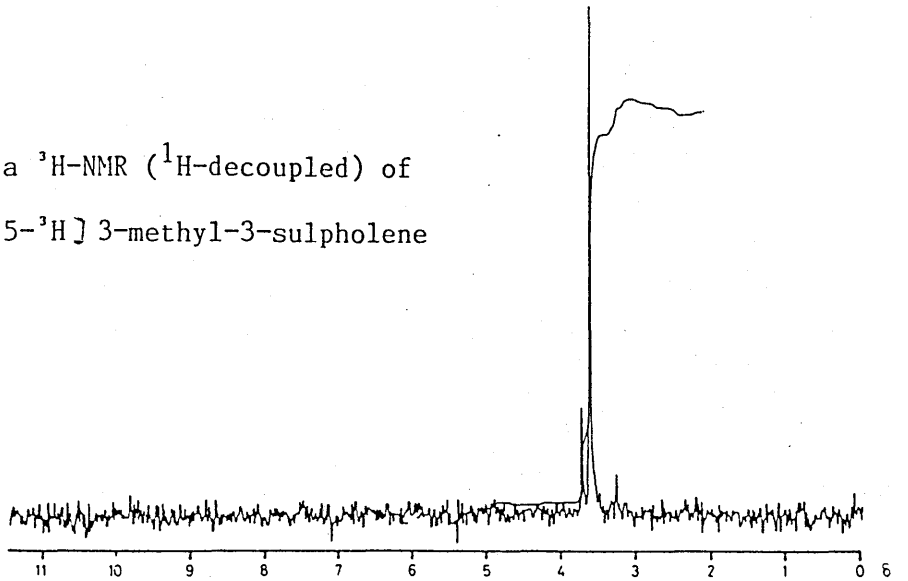


Fig 2.11b ^{1}H-NMR of [2,5-^{3}H] 3-methyl-3-sulpholene

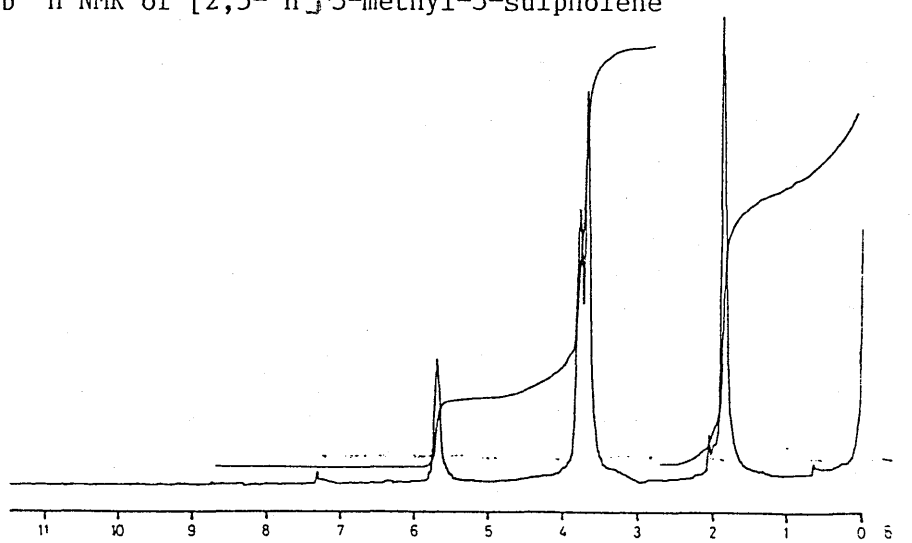


Fig 2.11c ^{1}H-NMR of 3-methyl-3-sulpholene

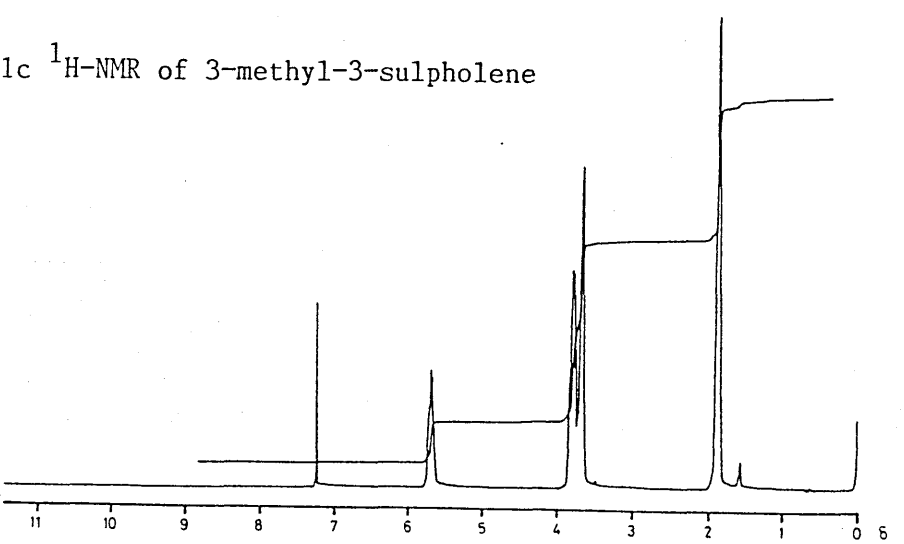


Fig 2.12a ^{3}H-NMR (^{1}H-decoupled) of [1-^{3}H] isoprene

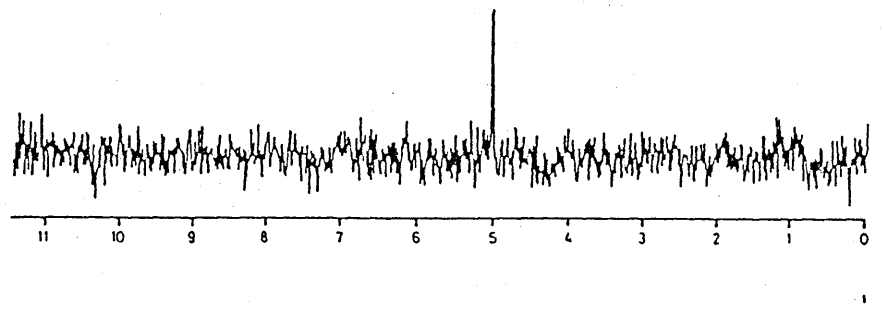


Fig 2.12b ^{1}H-NMR of [1-^{3}H] isoprene

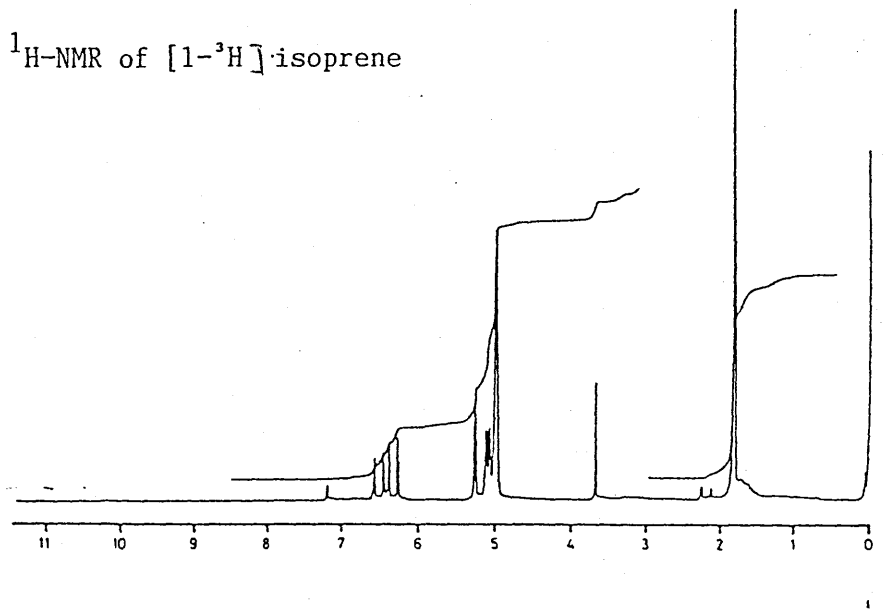
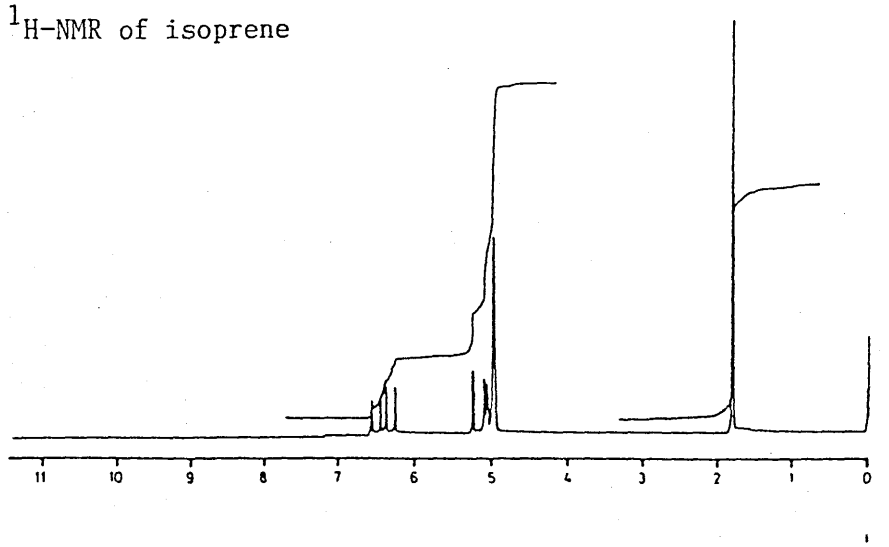
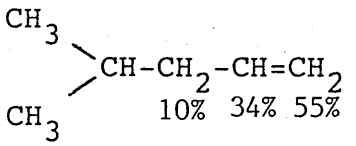


Fig 2.12c ^{1}H-NMR of isoprene



4-Methyl-1-pentene has been labelled generally with the tritium distribution as follows (fig 2.13):-



with some 1% associated with the other positions.

Polymerisation of [1-^{3}H] methylmethacrylate has not scrambled the labelling; as can be seen from the ^{3}H-NMR (fig 2.14a) the label is entirely in the methyl ester group (signal at δ3·6) as expected.

The ^{3}H-NMR of poly([G-^{3}H] butylmethacrylate) (fig 2.15a) shows the label to be only in the α-position of the butyl ester group (signal at δ4·0); no signal is visible in the δ1-2 ppm region where the signals for the remaining methylene protons appear (fig 2.15b).

The labels have remained in position for the polymerisation of [G-^{3}H] α-methylstyrene (fig 2.16) and the integral ratios are approximately the same for monomer and polymer.

The NMR spectrum of poly([G-^{3}H] 4-methyl-1-pentene) (fig 2.17) shows the label to be in approximately the same

Fig 2.13a ^{3}H-NMR (^{1}H-decoupled) of [G-^{3}H]4-methyl-1-pentene

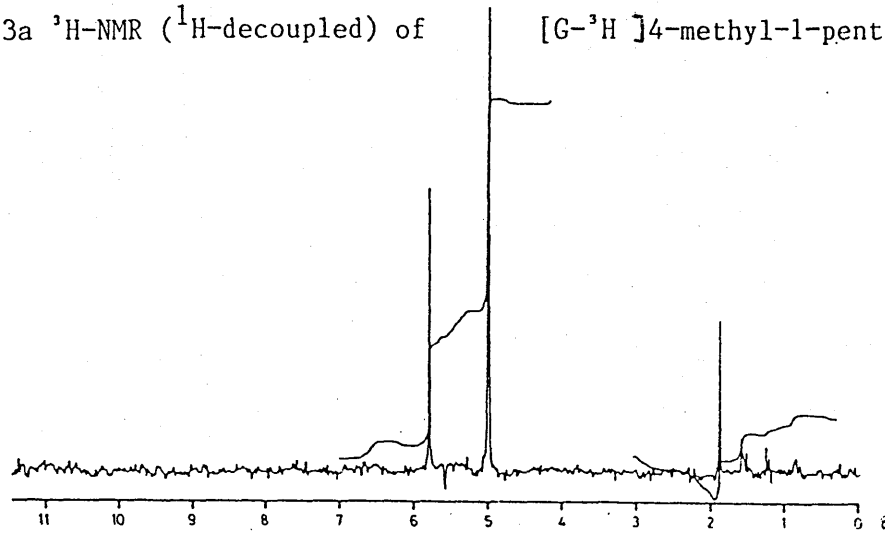


Fig 2.13b ^{1}H-NMR of [G-^{3}H]4-methyl-1-pentene

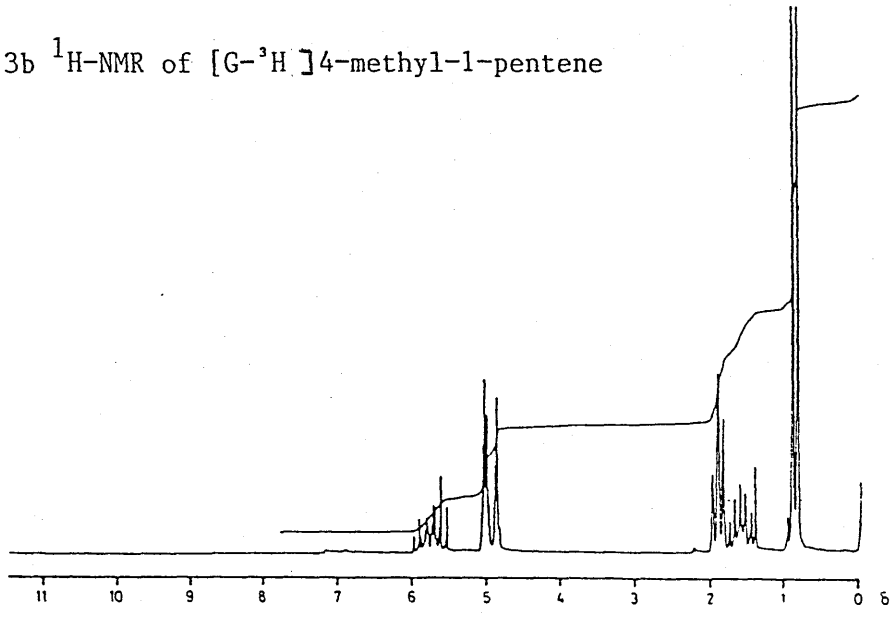


Fig 2.13c ^{1}H-NMR of 4-methyl-1-pentene

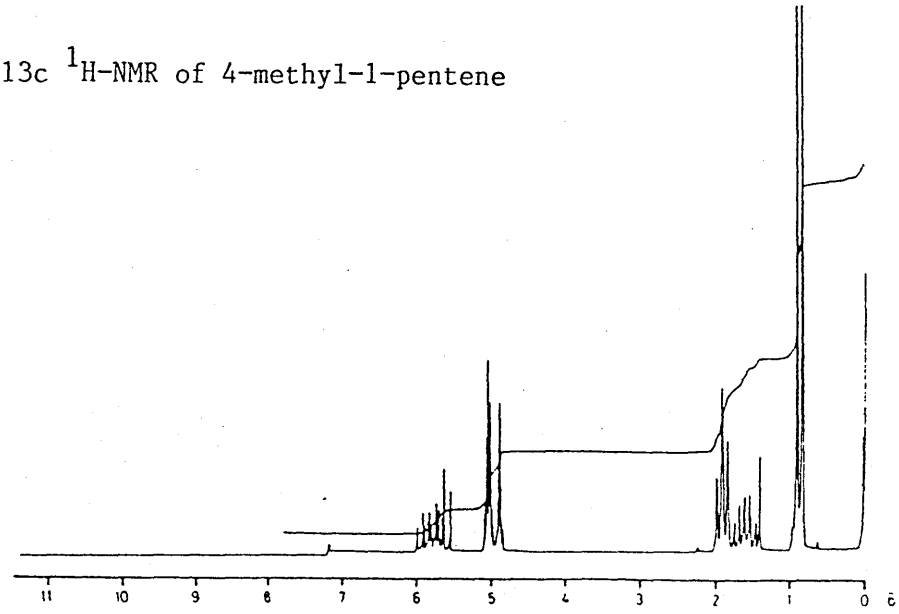


Fig 2.14a ^{3}H-NMR (^{1}H-decoupled) of poly([1-^{3}H]methylmethacrylate)

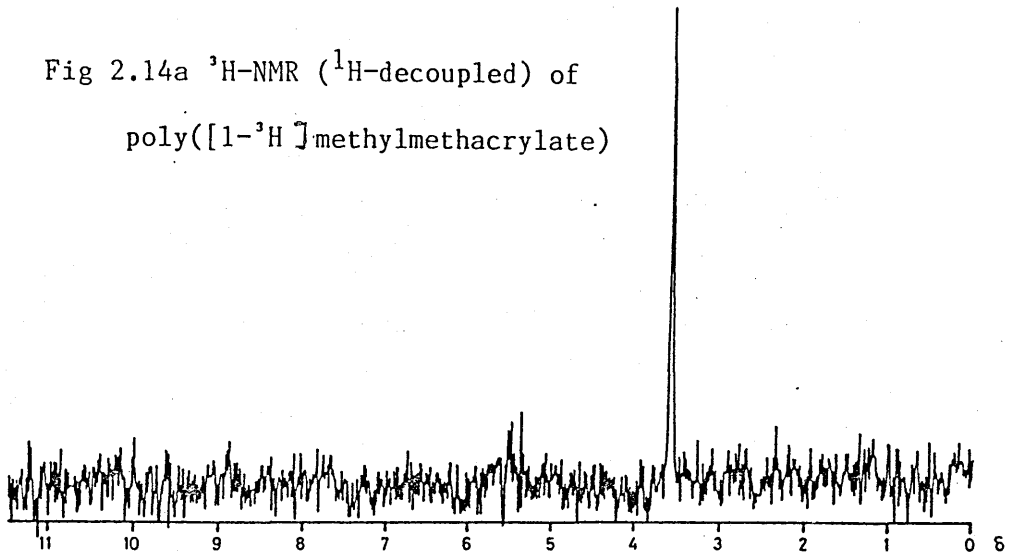


Fig 2.14b ^{1}H-NMR of poly([1-^{3}H]methylmethacrylate)

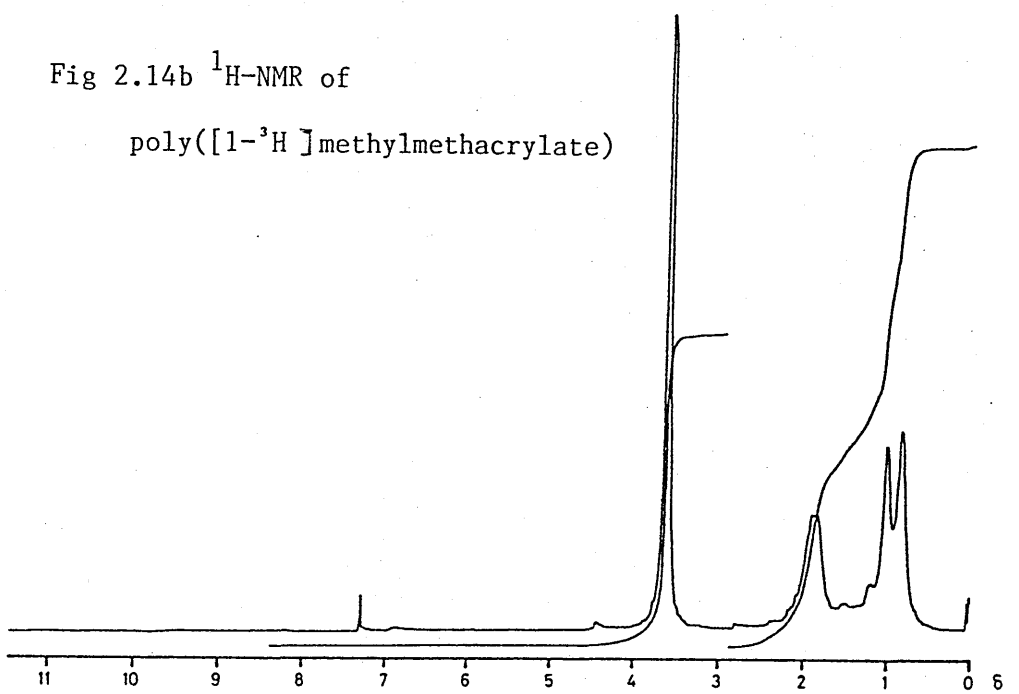


Fig 2.14c ^{1}H-NMR of polymethylmethacrylate

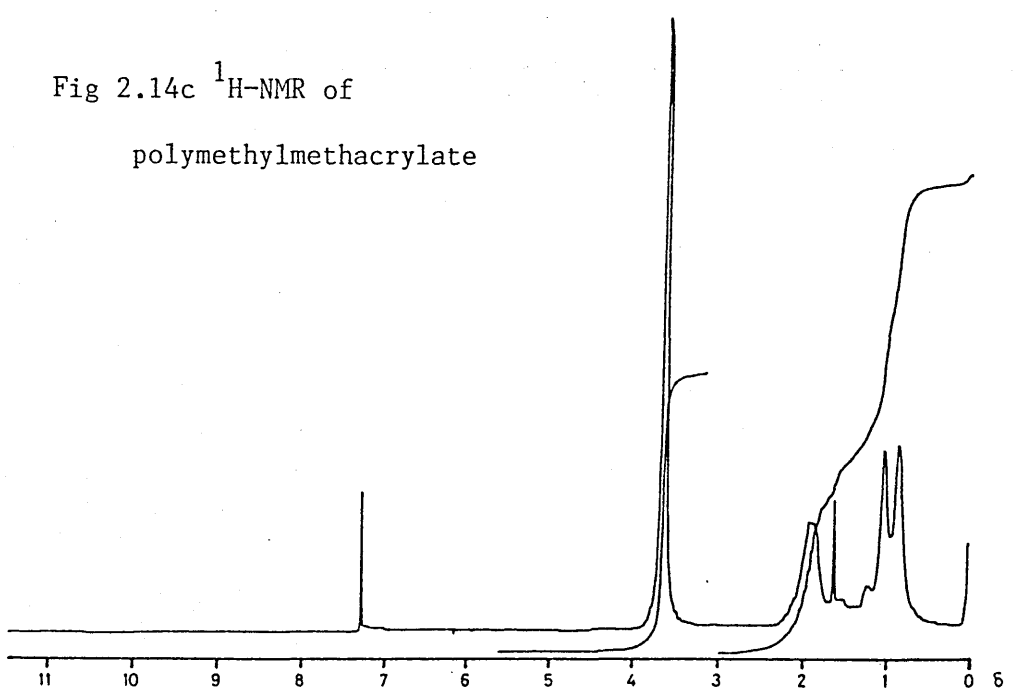


Fig 2.15a ^{3}H-NMR (^{1}H-decoupled) of poly([G-^{3}H]butylmethacrylate)

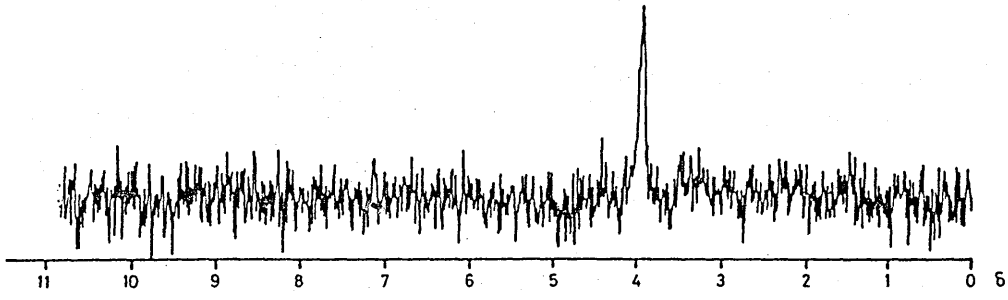


Fig 2.15b ^{1}H-NMR of poly([G-^{3}H]butylmethacrylate)

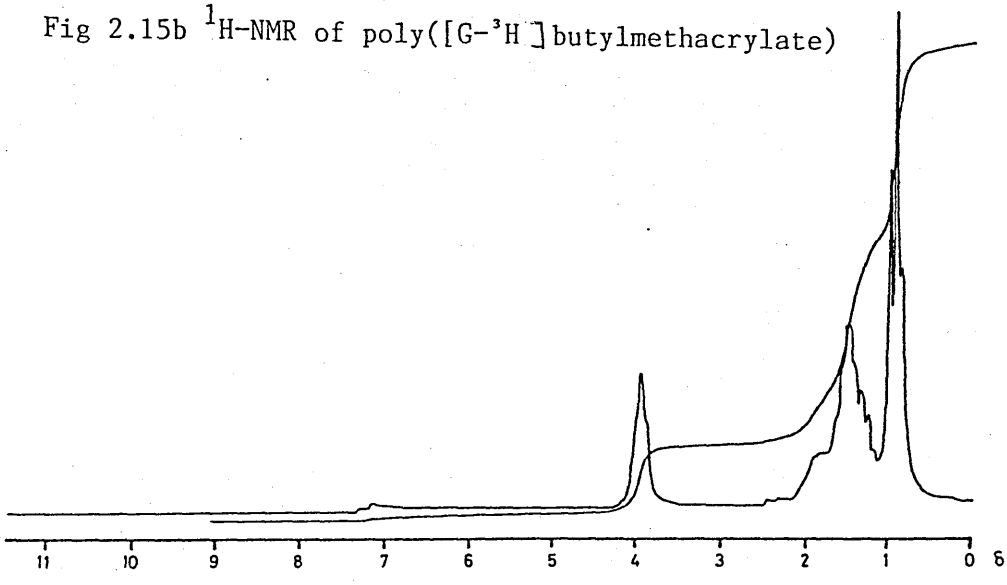


Fig 2.15c ^{1}H-NMR of polybutylmethacrylate

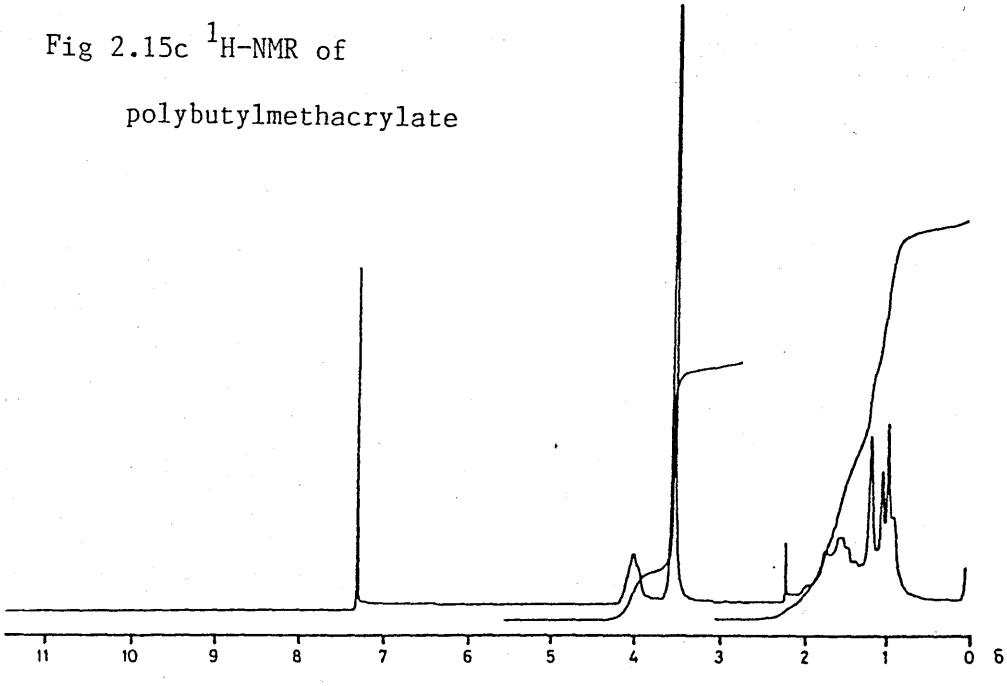


Fig 2.16a ^{3}H-NMR (^{1}H-decoupled) of poly([G-^{3}H]α-methylstyrene)

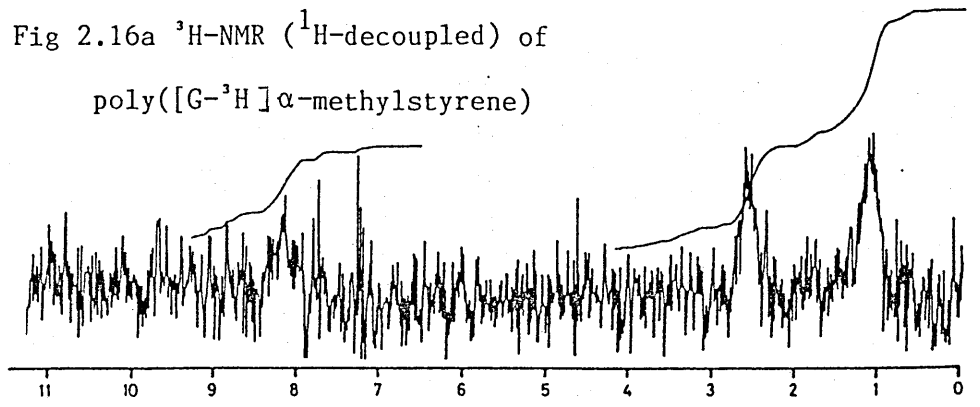


Fig 2.16b ^{1}H-NMR of poly([G-^{3}H]α-methylstyrene

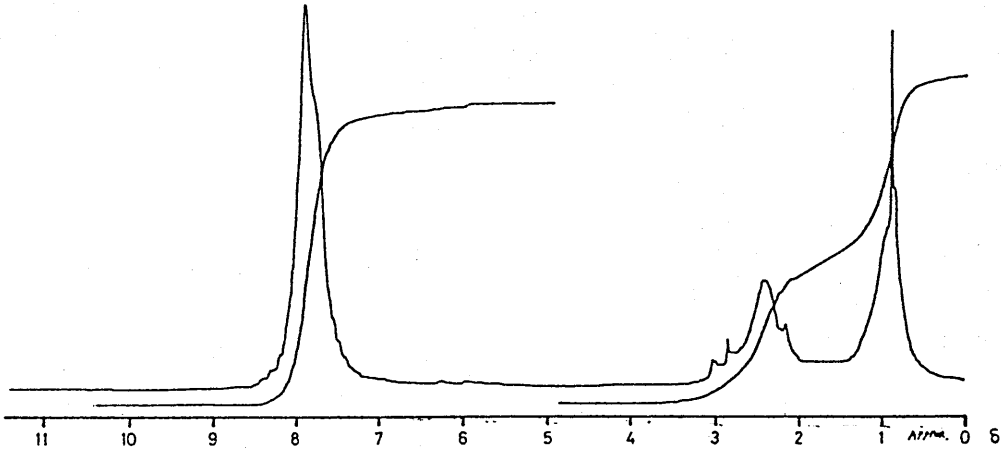


Fig 2.16c ^{1}H-NMR of poly(α-methylstyrene)

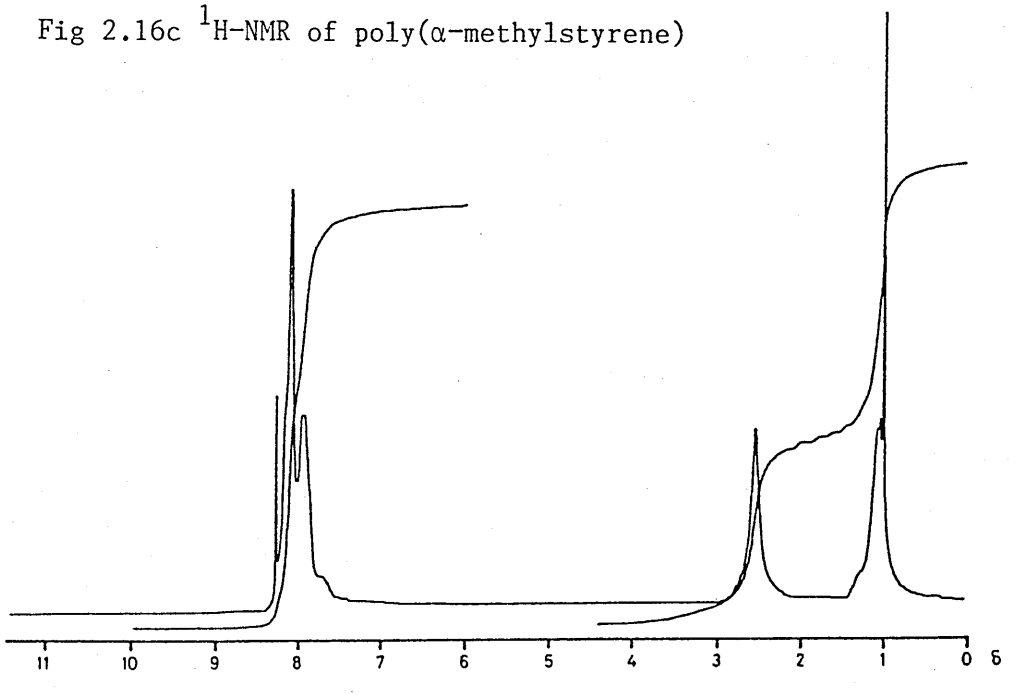


Fig 2.17a ^{3}H-NMR (^{1}H-decoupled) of poly([G-^{3}H]4-methyl-1-pentene)

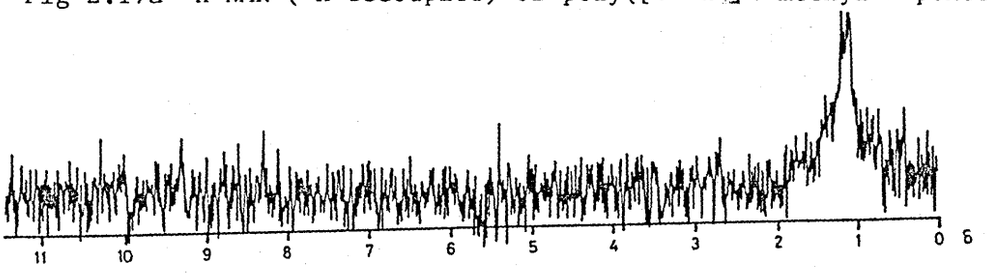


Fig 2.17b ^{1}H-NMR of poly([G-^{3}H]4-methyl-1-pentene)

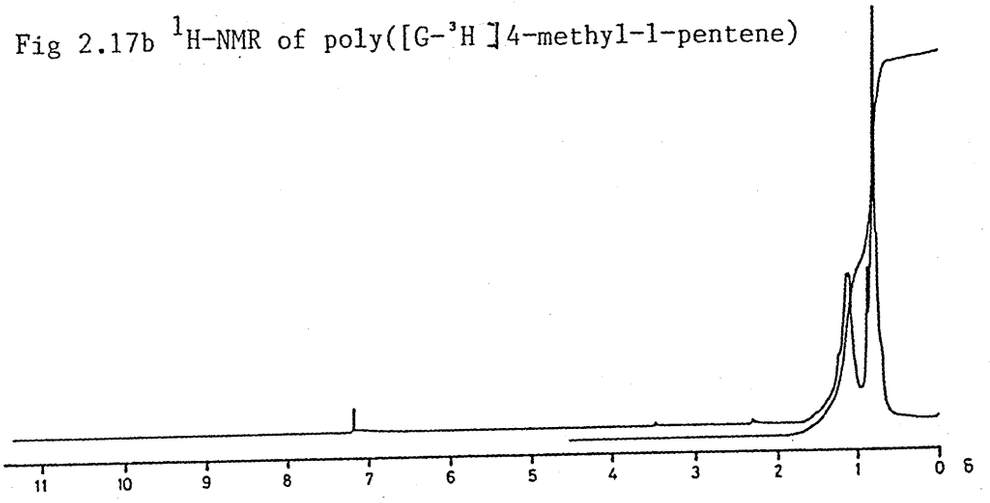
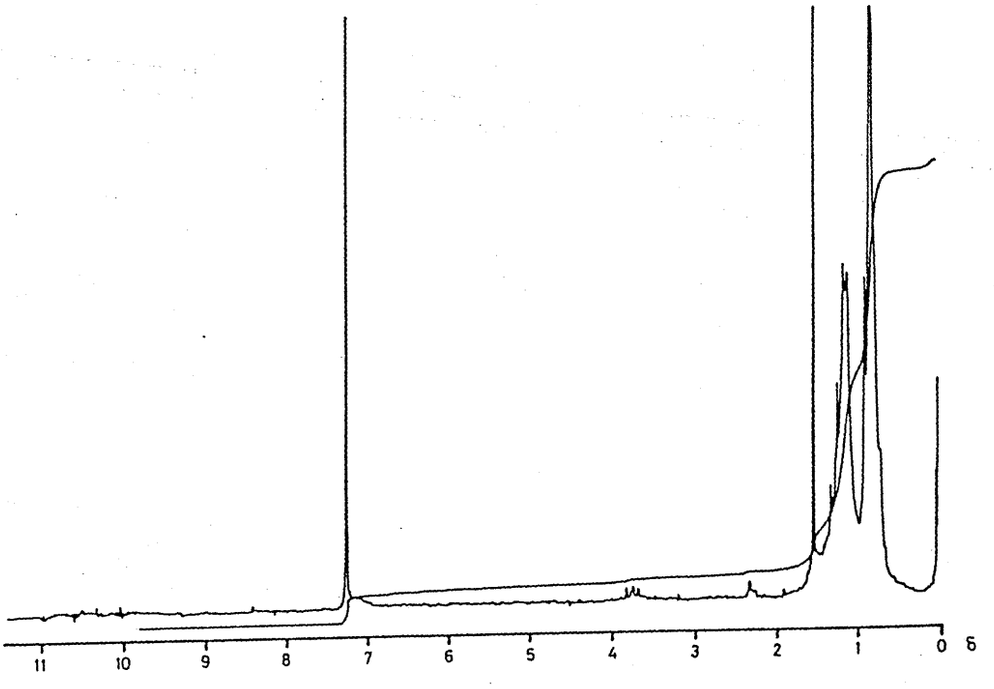


Fig 2.17c ^{1}H-NMR of poly(4-methyl-1-pentene)



positions as the monomer and have not migrated to the terminal methyl groups.

2. 6 Discussion

The area of a peak in an NMR spectrum is proportional to the number of nuclei contributing to it in the sample. As the concentration of tritium atoms in a labelled compound is of the order of fractions of a percent, the 'detectability' of a signal becomes dependent on the peak shape.[4] Hence for a compound labelled at one site, under conditions that would give a single sharp line in the NMR spectrum, a radioactivity of 0·1 mCi usually requires 35 000 accumulations (approximately 16 hours) to give a signal to noise ratio of 4:1. However, for a polymer in solution, intermolecular interactions brought about by the restricted motion of the polymer molecules gives rise to severe line splitting and so produces peak broadening.[14] This broadening effect decreases the 'detectability' of a tritium signal and so a radioacitvity of at least 5 mCi per site is required for the signal to be observed.

It is partly for the reasons explained above that it was not possible to obtain a ^{3}H-NMR spectrum of tritiated polystyrene. Styrene has been prepared sucessfully labelled

in both the vinyl hydrogens and the aromatic ring. The radioactivity of the [β-^{3}H]styrene was 20 mCi/g sufficient to obtain a ^{3}H-NMR spectrum; however, on polymerisation, the radioactivity of the polymer was found to be only 5 mCi/g, insufficient to obtain a ^{3}H-NMR spectrum; the remaining radioactivity remained in solution during purification as a low molecular weight fraction. The reason for this is not known and was tentatively put down to a kinetic isotope effect inhibiting the formation of the initiating radical. However this is now not believed to be the case as it has been shown that the rate of polymerisation of [β-^{2}H]styrene is some 28 %higher than that of styrene,[15] and it would therefore be expected that, with tritium in this position, any kinetic isotope effect observed would increase the rate of polymerisation producing a well labelled polymer.

The polymerisation of [Ar-^{3}H]styrene produced a polymer of significantly higher specific activity than the [β-^{3}H]-styrene but was observed to undergo radiation induced cross-linking and precipitated out of solution, hence it was not possible to obtain a ^{3}H-NMR spectrum of the polymer.

On thermal decarboxylation of [CO_2-^{3}H]β-methylcinnamic acid, extensive labelling of the methyl group was observed to occur; these rearrangements in α,β-unsaturated acids have been observed before.[16] On polymerisation, the same

decrease in radioactivity was observed as that shown with [β-^{3}H]styrene. The presence of the α-methyl group on the molecule while decreasing the reactivity of the monomer to polymerisation also inhibits any tendency to undergo cross-linking; hence when the monomer was labelled in the aromatic ring and polymerised, the polymer produced was stable enough to allow a ^{3}H-NMR spectrum to be obtained.

One of the drawbacks of using radioisotopes is the possibility of radiation induced reactions such as cross-linking. Another example of this problem occurred when trying to prepare [1-^{3}H]methylmethacrylate for the first time; on addition of diazomethane to esterify the acid, the monomer was observed to polymerise out of solution as the polymer is not soluble in diethyl ether. However, on repeating the experiment using a smaller amount of tritiated water in the presence of an inhibitor, it was possible to stabilise the monomer sufficiently to obtain a ^{3}H-NMR spectrum of the monomer.

The monomers were generally purified by passing over activated charcoal and then washing with distilled water and drying over anhydrous sodium sulphate to remove any remaining tritiated water. However, these techniques were not sufficient in the case of methylmethacrylate as a large radiochemical impurity can be observed in the NMR spectrum

(signal at δ2·0). Because of the small quantities involved, to purify this compound further would require either a preparative radio-high performance liquid chromatography apparatus, of the dilution of the product with unradioactive material (decreasing its specific activity), and fractional distillation.

The use of dichlorotris(triphenylphosphine)ruthenium(II) as a catalyst provides an efficient method of labelling aliphatic alcohols.[18] By reducing the heating time, it would probably be possible to restrict the label to the α-position in butanol. Although 30 % of the label in [G-^{3}H]butyl-methacrylate is in the β-position of the butyl ester, on polymerisation no signal can be observed in the polymer ^{3}H-NMR spectrum for this position. It is believed that rather than the label migrating to the α-position of the group or being removed from the molecule altogether, the peak for that signal has broadened significantly enough for the signal to be no longer 'detectable', as previously described. The signal at δ3·6 in the ^{1}H-NMR spectrum of the unlabelled polymer (fig 2.15c) is believed to be due to residual methanol from the polymer purification process.

The acidity of the methylene hydrogens in 3-methyl-3-sulpholene has enabled these positions to be labelled by base catalysed exchange. The integrals for the signals

in the ^{3}H-NMR spectrum (fig 2.11a) are in the ratio 85:15 indicating that the methyl group has had the effect of reducing the acidity of one position relative to the other. Thermal degradation to produce isoprene has introduced an impurity to the sample (signal at δ3·6 in the ^{1}H-NMR spectrum) (fig 2.12b); however the product is radiochemically pure. Triethylamine was added to the reaction mixture to form a stable complex with the sulphur dioxide produced during the reaction and so favouring the reaction.

The preparation of [G-^{3}H]4-methyl-1-pentene illustrates the effectiveness of the reduced platinum dioxide catalyst and its potential to label a variety of aliphatic and aromatic compounds.

2.7 Conclusions

A series of monomers and polymers have been successfully labelled with tritium via a range of synthetic routes and their labelling patterns analysed by ^{3}H-NMR spectroscopy.

2.8 References

1. Catch, J.R., Carbon-14 Compounds, Butterworths, London, (1961).
2. Evans, E.A., Tritium and its Compounds, 2nd Ed. Butterworths, London, (1974).
3. Elvidge, J.A., Evans, E.A., Jones, J.R., and Warrell, D.C., Handbook of Tritium NMR Spectroscopy and Applications, Wiley and Sons, Chichester, (1985).
4. Bloxsidge, J.P., and Elvidge, J.A., Progress in NMR Spectroscopy, 16, 99, (1983).
5. Schildknecht, C.E., Vinyl and Related Polymers, Wiley and Sons, New York, (1952).
6. Encyclopaedia of Polymer Science and Technology, Ed. Mark, H.F., Gaylord, N.G., and Bikales, N.M., Wiley and Sons, New York, (1967).
7. Bernstein, I.A., Bennett, W., and Fields, M., J. Am. Chem. Soc. 74, 5763, (1952).
8. Pryor, W.A., Henderson, R.W., Patsiga, R.A., and Carrol, N., J. Am. Chem. Soc. 88, 1199, (1966).
9. Lenz, H., Buckel, W., Wunderwald, P., Biedermann, G., Buschoneier, V., Eggerer, H., Cornforth, J.W., Redmond, J.W., and Mallaby, R., Eur. J. Biochem. 24, 207, (1971).
10. Burfield, D.R., and Sarvariar, C.M., Eur. Polym. J. 20, 343, (1984).

11. Diamond, R.J., Jones, J.R., and Wright, W.W., Eur. Polym. J. 22, 601, (1986).

12. Lewis, J.E., Mercer, H.N., Deviney, M.L., Hughes, L., Jewell, J.E., 'Autoradiographic Electron Microscopy Studies on Elastomer Systems I' Paper presented to Div. of Rubber Chem. Am. Chem. Soc. 98th meeting, Chicago, Ill. 20/10/1970.

13. Lipkin, F., and Stewart, T.D., J. Am. Chem.Soc. 61, 3295, (1935).

14. Bovey, F.A., High Resolution NMR of Macromolecules, Academic Press, New York, (1972).

15. Kopecky, K.R., and Evani, S., Can. J. Chem. 47, 4049, (1969).

16. Elvidge, J.A., Jones, J.R., Mane, R.B., and Saljoughian, M., J. Chem. Soc. Perkin Trans. I, 1191, (1978).

17. Regen, S.L., J. Org. Chem. 39, 260, (1974).

18. Weiner, V.K.E., and Eckert, H.G., Chem Ztg. 103, 69, (1979).

19. Clark, K.J., British Pat. 942 297, (1963).

CHAPTER THREE

The Preparation and Analysis of Deuterium Labelled Monomers and Polymers

3.1 Introduction

Developments in analytical equipment e.g. Fourier transform infrared spectroscopy, capillary gas chromatography and high performance liquid chromatography etc. have led to considerable improvements in sensitivity to detection of many isotopes and opened up opportunities for using stable isotopes in mechanistic studies. Stable isotopes have some considerable advantages over radioisotopes; they present no problems with radiation induced damage to the labelled compound and its environment, an aspect that is particularly important in clinical studies; they are safer to handle than radioactive materials and are frequently cheaper. One further advantage, particularly with deuterium, is the wide range of partially and wholly labelled reagents available commercially that can simplify the preparation of the required labelled compounds.

The advantages of using deuterium as an isotope tracer in polymer studies over carbon isotopes, are similar to those of tritium, ease of labelling, cost etc. However, until now, the major problem with using deuterium was a difficulty in determining the pattern of labelling in a compound, although the extent of labelling can be found simply from mass spectrometry. Developments in Fourier

transform nuclear magnetic resonance (FTNMR) spectroscopy and the advent of superconducting high field magnets has increased the sensitivity of NMR spectroscopy to such a level that natural abundance deuterium spectra can be obtained relatively easily. These advances have simplified the analysis of deuterium labelled compounds to the extent that the isotope has become an alternative to tritium for hydrogen tracer studies.

Although the methods used to label compounds with deuterium and tritium are usually the same (with the exception of radiation induced methods such as the Wilzbach method) there are important differences. Thus deuterium labelled compounds are prepared on a larger scale and are purified by customary chemical methods e.g. distillation, recrystallisation and preparative HPLC whereas tritium labelled compounds are dependent on their radioactivity for their purification. The degree of isotopic incorporation is also usually different e.g. in labelling acetophenone. In the methyl group the products are $C_6H_5COCD_3$ and $C_6H_5COCH_2T$. Finally there is no radiation induced degradation so that regular repurification is unnecessary.

The preparation of tritium labelled methylmethacrylate as reported in the previous chapter presented some difficulty

due to radiation induced polymerisation. Similarly, it was not possible to obtain a ^{3}H-NMR spectrum of labelled polystyrene as cross linking reactions led to precipitation of the polymer from solution. The presence of these reactions suggested that it would be wise if parallel deuteration studies were carried out so offsetting these problems. It was therefore decided to label the range of monomers and polymers with deuterium and analyse their labelling patterns by ^{2}H-NMR spectroscopy.

3.2 Properties of Deuterium

Deuterium is a stable isotope of hydrogen, present at a natural abundance of approximately 0·0156 % (the natural abundance levels vary and have been used to identify the source of the compound) in all hydrogen containing compounds.[1] The isotope is concentrated by the electrolysis of water and is available commercially in the form of labelled compounds of different structures as well as deuterium gas and isotopically enriched water.

As a nucleus for detection by NMR spectroscopy, deuterium has some major disadvantages, but, with modern apparatus however, these can be overcome. The deuterium nucleus has a low NMR frequency of 13·8 MHz (in a 2·11 T magnetic field) which decreases the spectral dispersity

by approximately a factor of six compared to the proton.[2] To achieve an equivalent spectral dispersion to the proton therefore requires a six fold increase in applied magnetic field, the development of superconducting materials which enables the manufacture of 8-9 T magnets has greatly assisted this requirement. The low NMR frequency also means that coupling constants are smaller and multiplicity in the spectrum is decreased, therefore compounds with closely similar chemical shifts can be difficult to analyse. Although the chemical shifts expressed as frequency changes are smaller, as deuterium is a hydrogen isotope the shifts when expressed as parts per million (ppm) are almost exactly the same allowing access to the wealth of ^{1}H-NMR data.

The deuterium nucleus has a low magnetogyric constant of $6{\cdot}54 \times 10^{6}$ $Hz T^{-1}$ and is less sensitive to detection than the proton by a factor of 100. Developments in instrumentation have overcome this problem, since, although theoretically a thousand scans of a deuterium spectrum are required to obtain a signal to noise ratio equivalent to one scan of a proton spectrum, improved electronic circuitry has allowed much lower signal to noise ratios to be accepted. In addition, the use of wide bore samples which allow more nuclei within the area of the detector coil provide further compensation.

The deuteron is a quadrupolar nucleus of spin I=1. The spin of unity implies that the nuclear charge distribution is aspherical, hence, as it spins, the nucleus produces a fluctuating electric field. Interaction occurs with the molecular electric field gradient which shortens relaxation times by allowing a loss of upper spin state energies to the lattice and broadening the NMR lines. This effect makes the spectra more difficult to analyse but through spin-lattice relaxation time measurements and wide line deuterium NMR studies of labelled solids and liquid crystals studies of molecular dynamics and orientation can be made. Analysis of the spectrum can be simplified by magic angle spinning of the sample which averages the spatial orientation of the nuclei to zero, narrowing the spectral lines.[3]

3.3 Materials and Equipment

The deuterated water used for these labelling experiments was obtained form Aldrich Chemical Co. and was 99·8 % isotopically enriched.

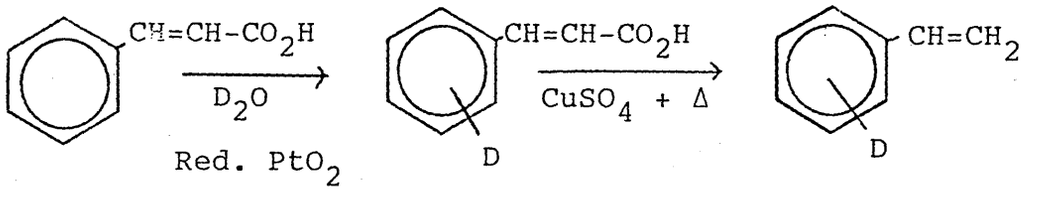
The deuterium NMR spectra were obtained at 25 °C on a Brucker WH500 spectrometer (University of Oxford) operating at 500 MHz. The flip angle was 45° and the repetition interval 0·7 seconds; between 16 and 100

transients were acquired. The samples were run as solutions in solvents such as benzene and the signals from the natural abundances of deuterium in the solvent were used for reference purposes.

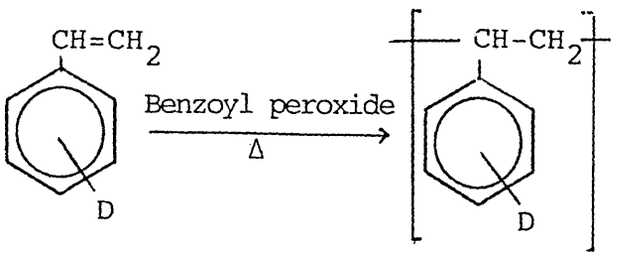
3.4 Synthesis of ^2H-Labelled Monomers and Polymers

3.4.1 Preparation of [Ar-^2H] Styrene and Poly([Ar-^2H]-styrene)

Cinnamic acid (0·5 g) was mixed with freshly reduced platinum dioxide (20 mg) prepared as described in section 2.3.1 and deuterated water (300 μl). The mixture was sealed in a glass vial and heated at 150 °C for 24 hours. After cooling, the acid was decarboxylated, purified and polymerised as described in the previous chapter.

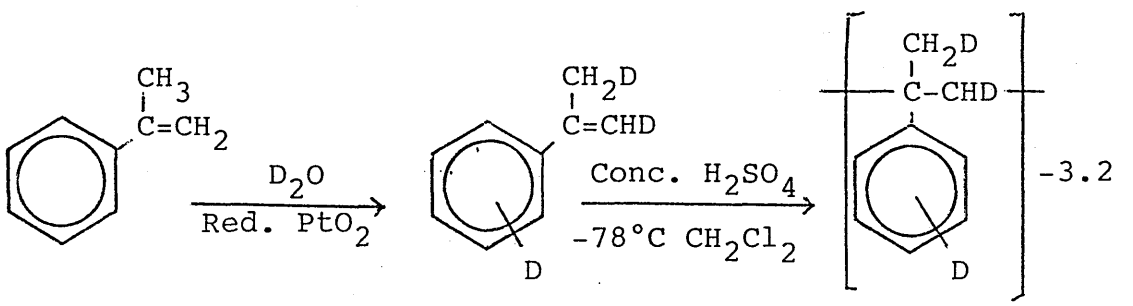


-3.1



3.4.2 Preparation of [G-^{2}H]α-Methylstyrene and Poly([G-^{2}H]α-methylstyrene)

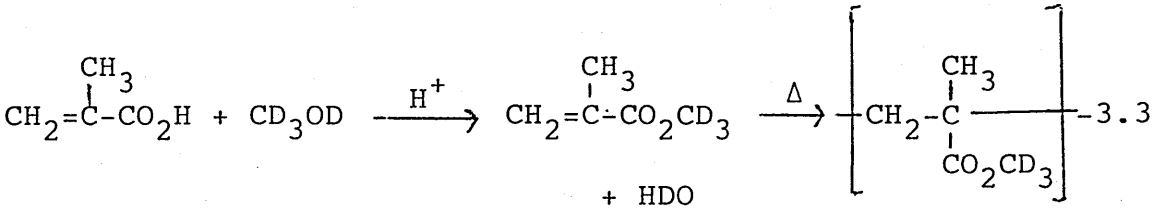
α-Methylstyrene (0·5 ml) was sealed in a glass vial with freshly reduced platinum dioxide (20 mg) and deuterated water (300 µl), and heated at 150 °C for 24 hours. The vial was cooled, opened and the contents filtered and washed with distilled water to remove any labile deuterium. After drying over anhydrous sodium sulphate, the monomer was polymerised as described in section 2.4.3.



3.4.3 Preparation of [1-^{2}H]Methylmethacrylate and Poly([1-^{2}H]methylmethacrylate)

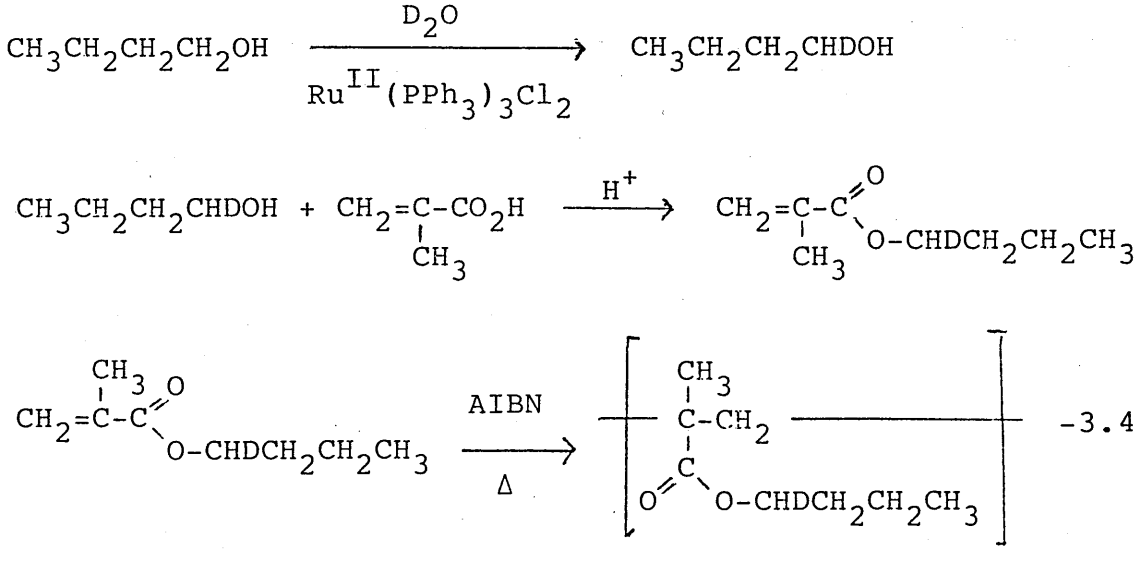
Methacrylic acid (0·5 ml) was esterified with perdeuterated methanol (0·3 ml) by heating the two compounds in a sealed glass vial with dilute sulphuric acid catalyst (10 µl) and a small quantity of hydroquinone inhibitor, at 110 °C for two hours. The vial was allowed to cool and opened, the contents washed with dilute sodium hydroxide (2 ml) and distilled water (10 ml) then dried over anhydrous

sodium sulphate. The polymerisation technique for the monomer was the same as that described in section 2.4.1.



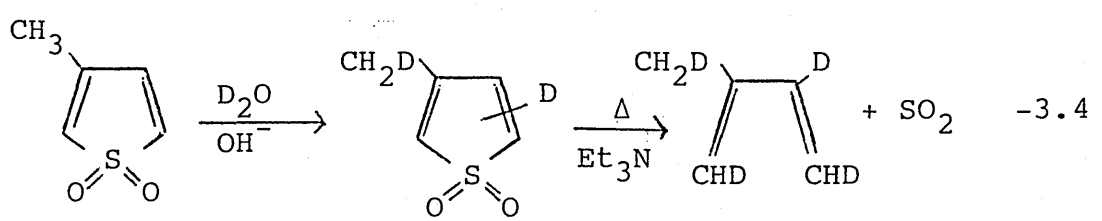
3.4.4 Preparation of [1-^{2}H]Butylmethacrylate and Poly([1-^{2}H]butylmethacrylate)

Butanol was labelled by the same procedure as that used for the preparation of [G-^{3}H]butanol (section 2.3.7), with deuterated water (300 μl) substituted for tritiated water. The monomer and polymer were prepared as described in sections 2.3.7 and 2.4.2.



3.4.5 Preparation of [G-^{2}H]Isoprene

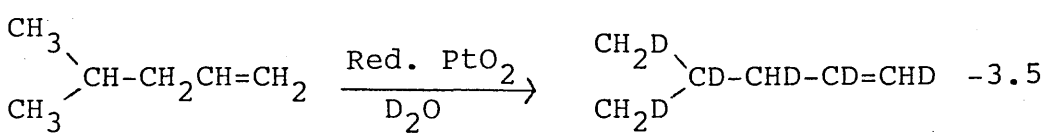
3-Methyl-3-sulpholene (0·8 g) was dissolved in a minimum quantity of 1,4-dioxan to which was added deuterated water (0·5 ml) and one pellet of sodium hydroxide. After three days the material was treated by the same procedure as that described in section 2.3.8 to yield [G-^{2}H]isoprene.



-3.4

3.4.6 Preparation of [G-^{2}H]4-Methyl-1-pentene

4-Methyl-1-pentene (1 ml) was sealed in a glass vial under vacuum with freshly reduced platinum dioxide (20 mg) and deuterated water (0·5 ml) and heated at 110 °C for five days. On cooling, the monomer was purified and resealed with fresh catalyst and deuterated water and heated for a further five days. The process was repeated a third time to increase further the incorporation of deuterium in the monomer.



-3.5

3.5 Analysis of ^{2}H-NMR Spectra

The deuterium NMR spectrum of [Ar-^{2}H]styrene (fig 3.1) has two signals at δ7·2 and δ4·8 ppm. The downfield signal represents the deuterium labels in the aromatic ring. The other signal in the spectrum may well belong to the methylene group, But is slightly too far upfield for this position. An alternative interpretation would be that it belongs to a deuterium labelled impurity.

The deuterium NMR spectrum of methylmethacrylate (fig 3.2) has as expected only one signal at δ3·3 ppm, from the fully deuterated methyl ester group. Similarly, only one signal is visible in the spectrum of [1-^{2}H]butyl-methacrylate at δ3·9 ppm (fig 3.3). This signal corresponds to the deuterium label present solely in the α-position of the butyl ester; there is no indication that, like [G-^{3}H]butylmethacrylate, the monomer is labelled in any other group.

[G-^{2}H]Isoprene (fig 3.4) has been labelled generally with the deuterium distribution as follows:-

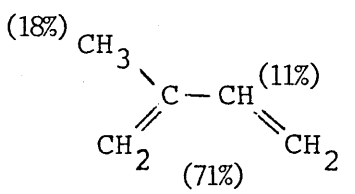


Fig 3.1 ^{2}H-NMR (^{1}H-decoupled) of [Ar-^{2}H]-styrene

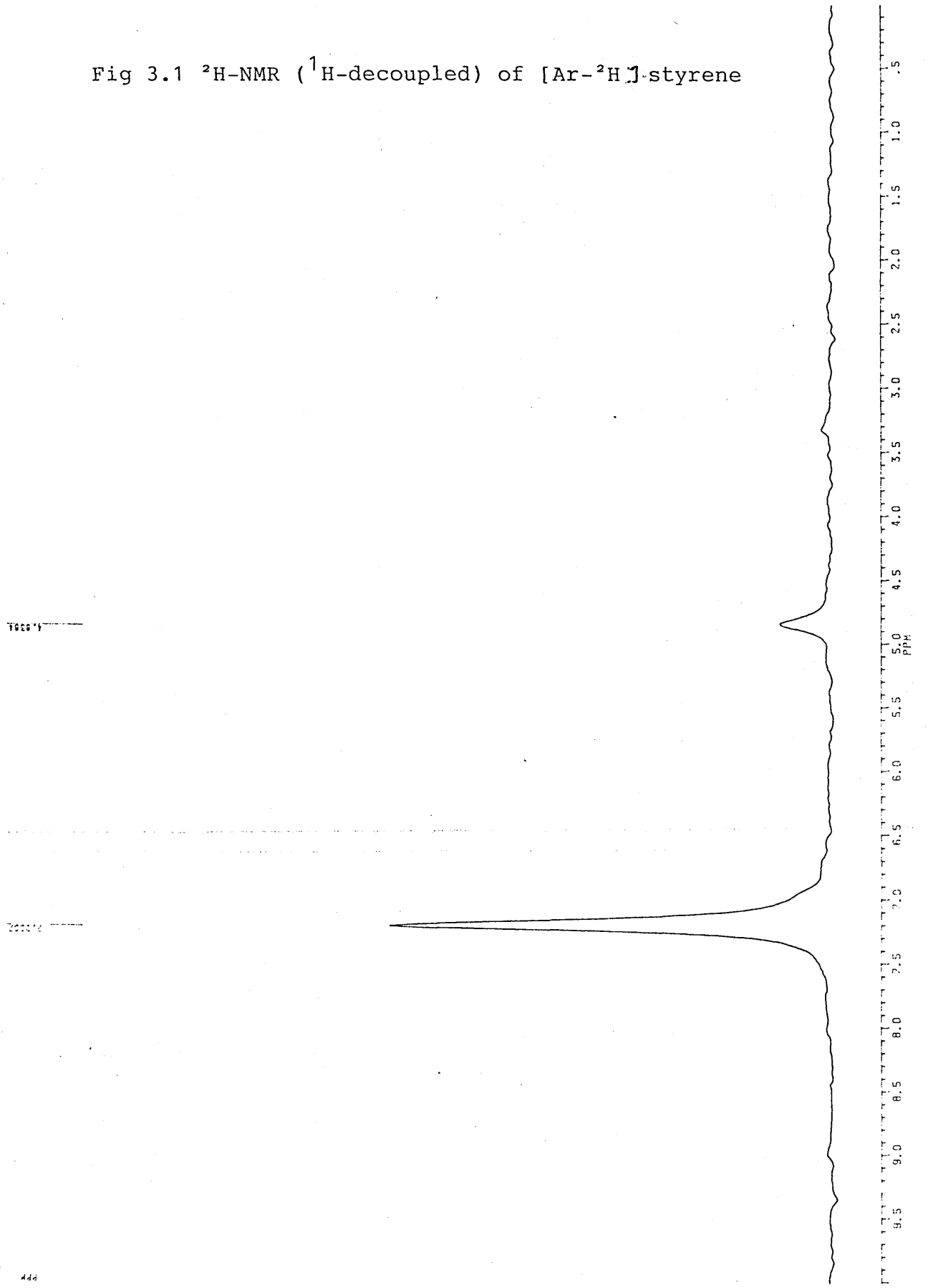


Fig 3.2 ^{2}H-NMR (^{1}H-decoupled) of [1-^{2}H]methylmethacrylate

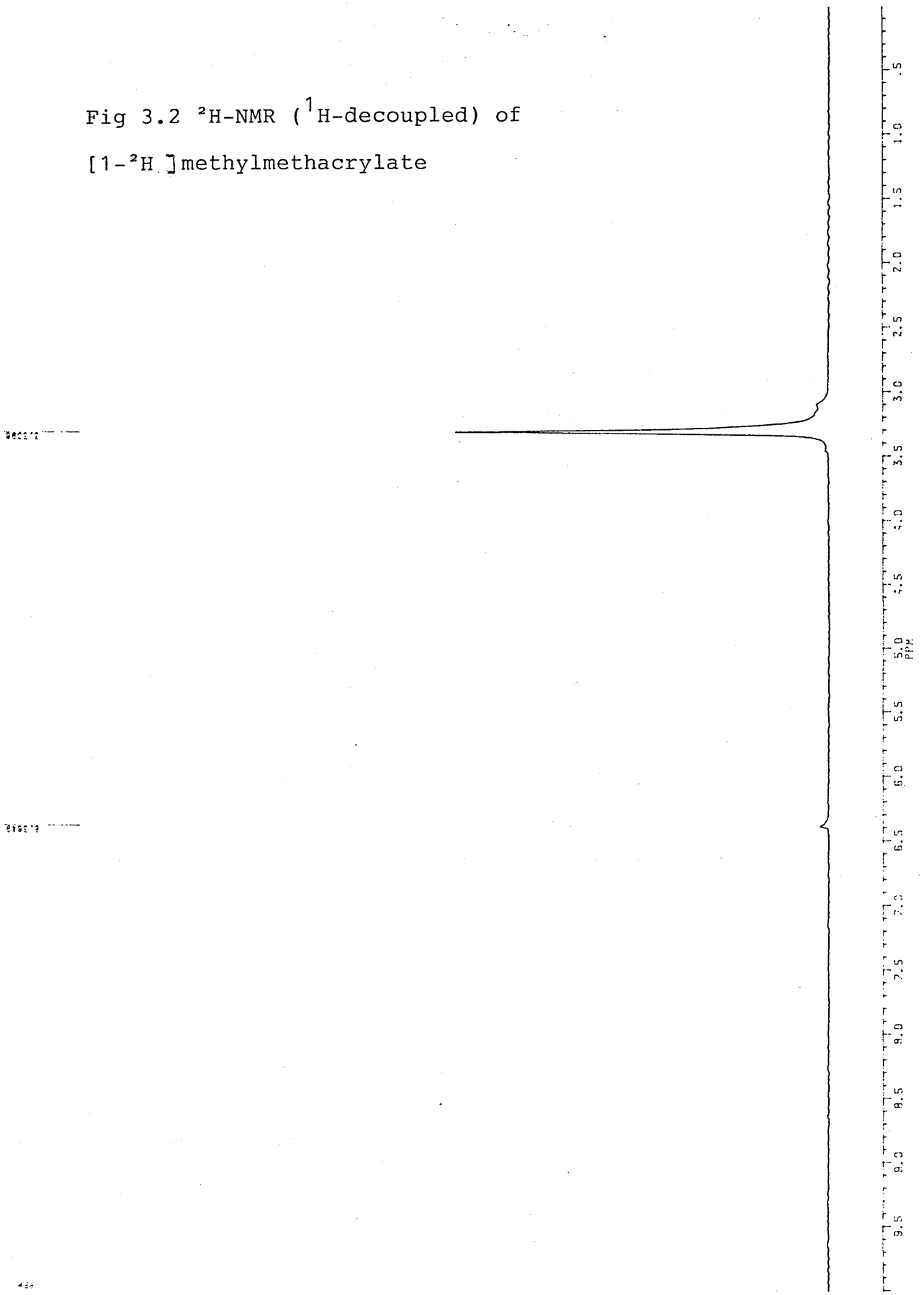
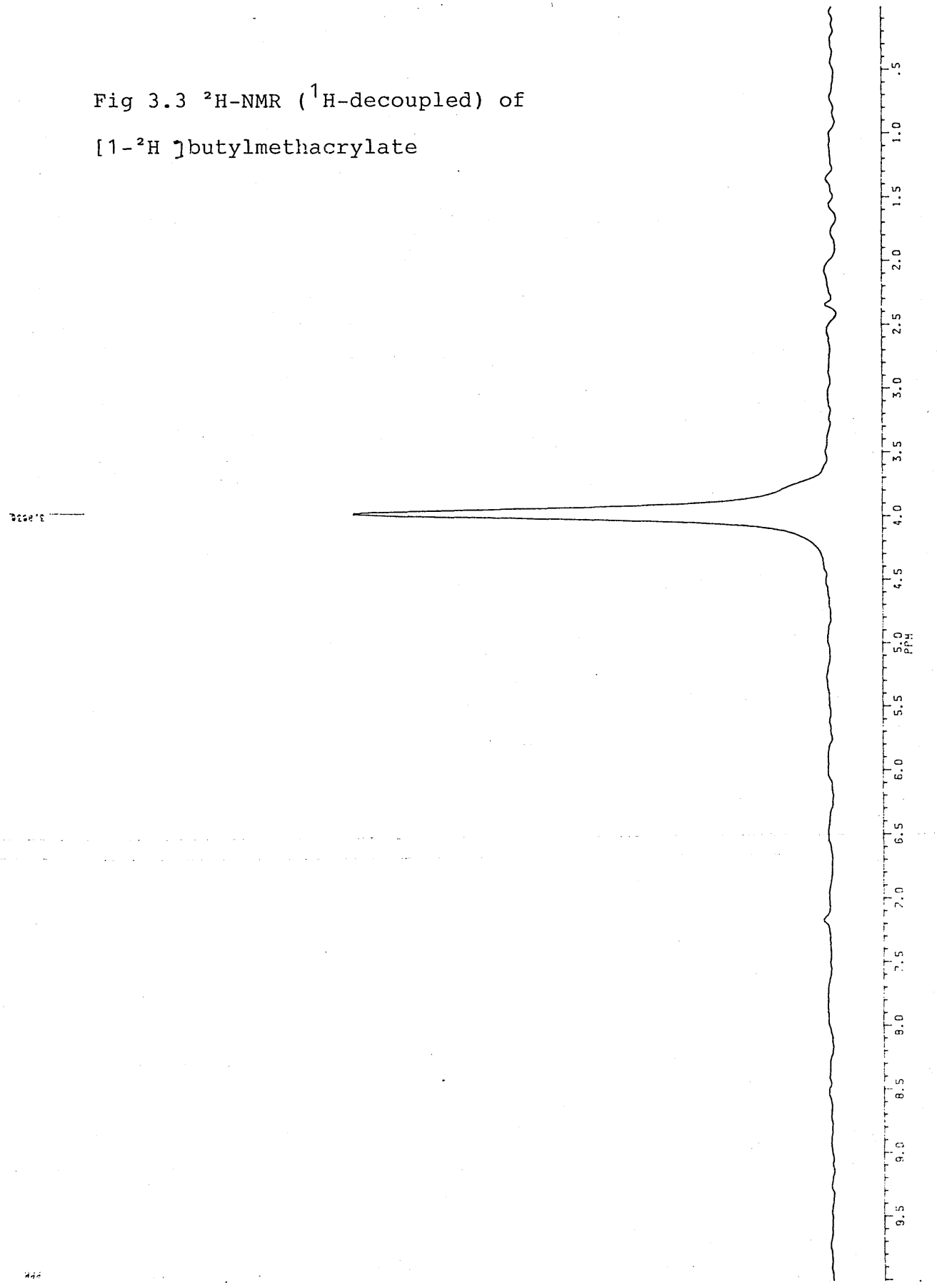


Fig 3.3 ^{2}H-NMR (^{1}H-decoupled) of [1-^{2}H]butylmethacrylate



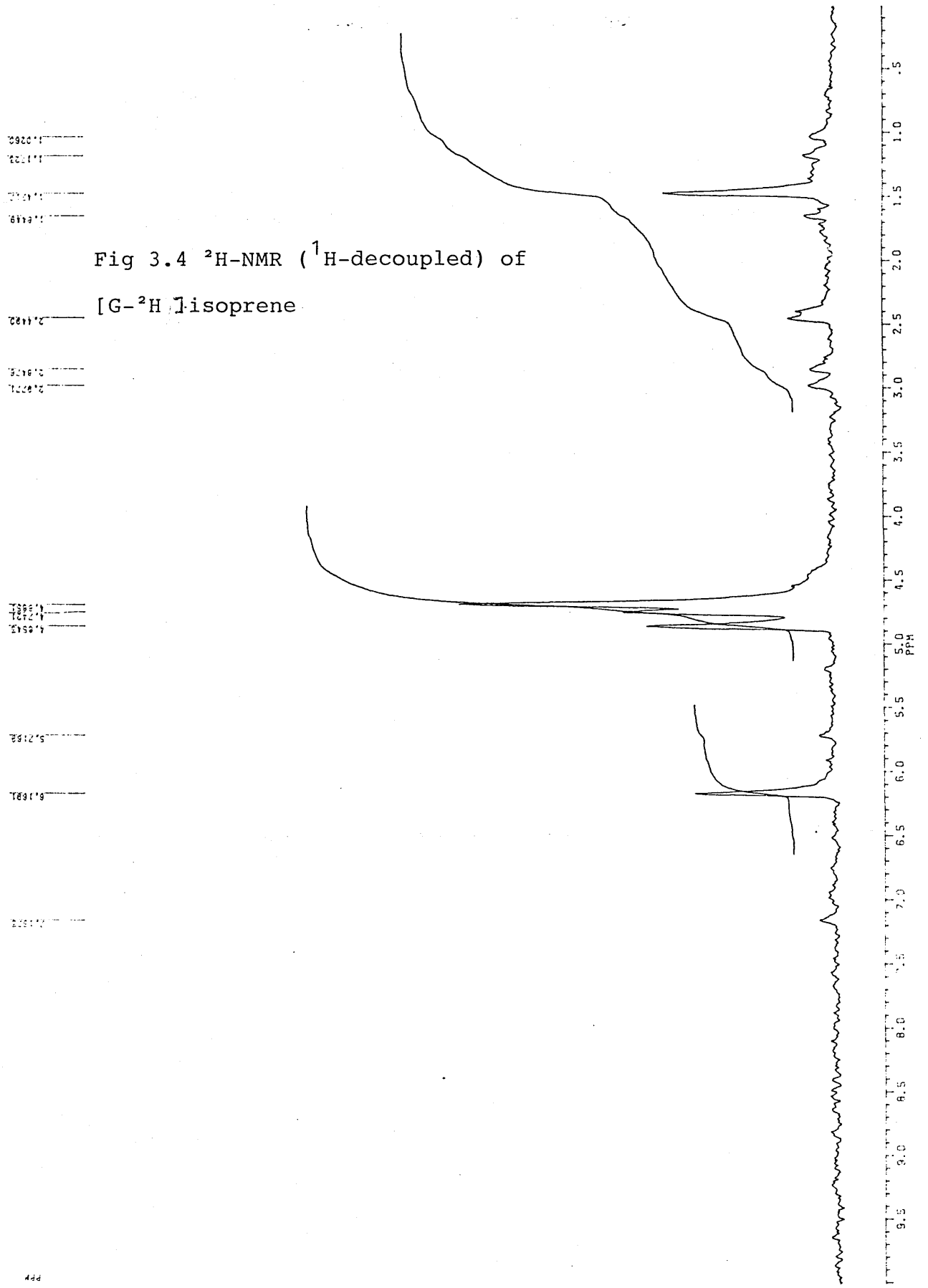
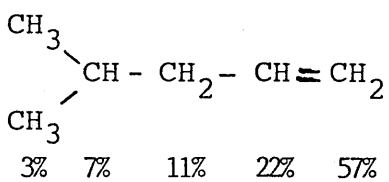


Fig 3.4 ^{2}H-NMR (^{1}H-decoupled) of [G-^{2}H$_{3}$]isoprene

Some deuterium labelled impurities are visible at δ2·4, 2·8 and 4·0 ppm.

4-Methyl-1-pentene has also been generally labelled (fig 3.5) and the deuterium distribution is as follows:-



some deuterium labelled impurity is visible at δ1·2 ppm.

The deuterium NMR spectrum of poly([Ar-^{2}H]styrene) (fig 3.6) consists of a broad signal at δ7·1 ppm over which is laid a sharp peak at δ7·4 ppm. The signals are both from the aromatic region, the broad resonance from the ortho- positions and the sharp signal from the meta- and para- positions. The relative areas of the two signals indicates that the labelling is predominantly in the ortho-positions; it is not possible however to determine the distribution.

The deuterium NMR spectrum of poly([G-^{2}H]α-methyl-styrene) (fig 3.7) has three signals at δ0·3, 1·4 and 7·3 ppm corresponding to the methyl, methylene and aromatic hydrogens respectively. The spectrum is extremely noisy,

Fig 3.5 ^{2}H-NMR (^{1}H-decoupled) of [G-^{2}H$_{n}$] 4-methyl-1-pentene

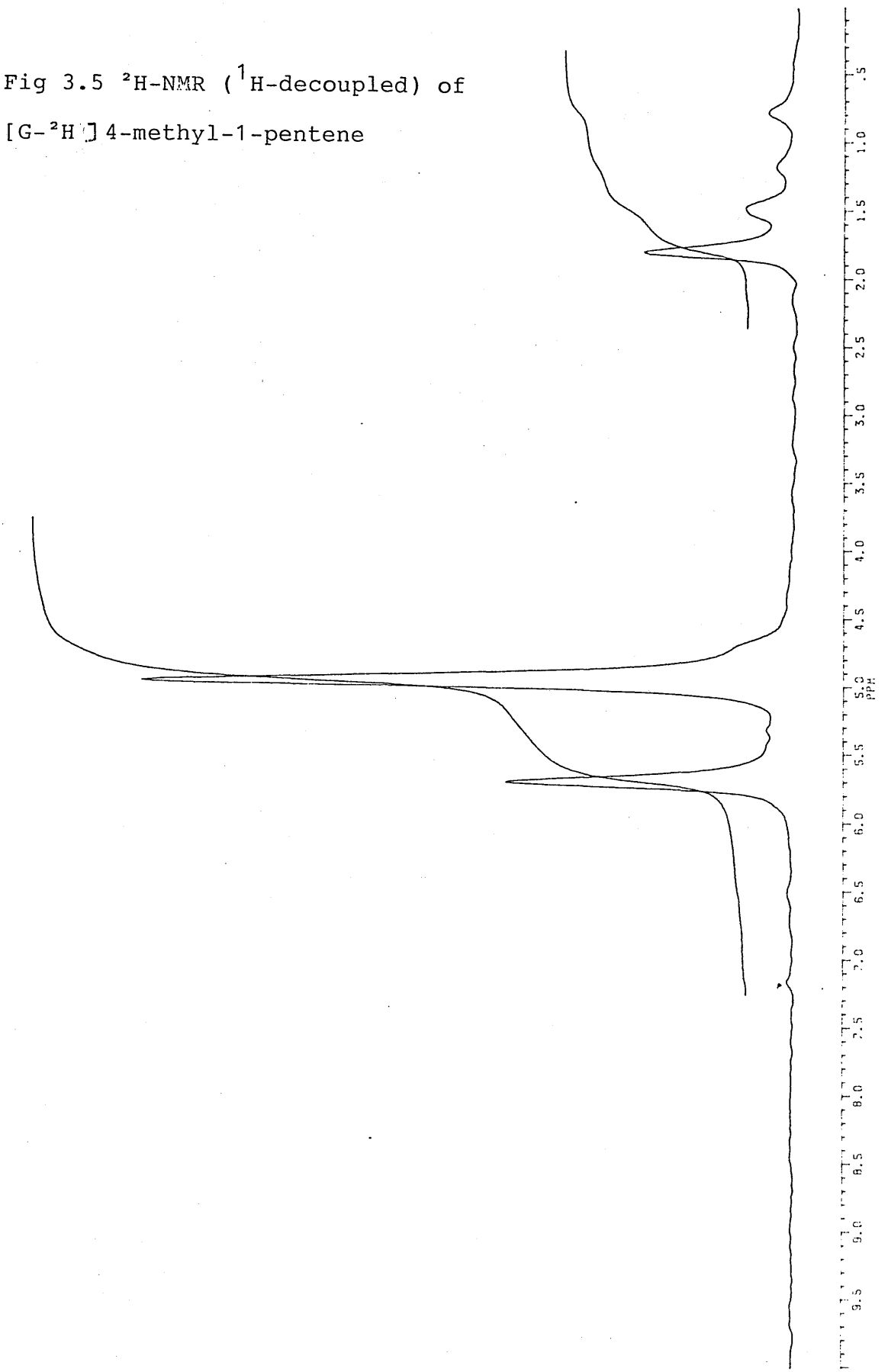
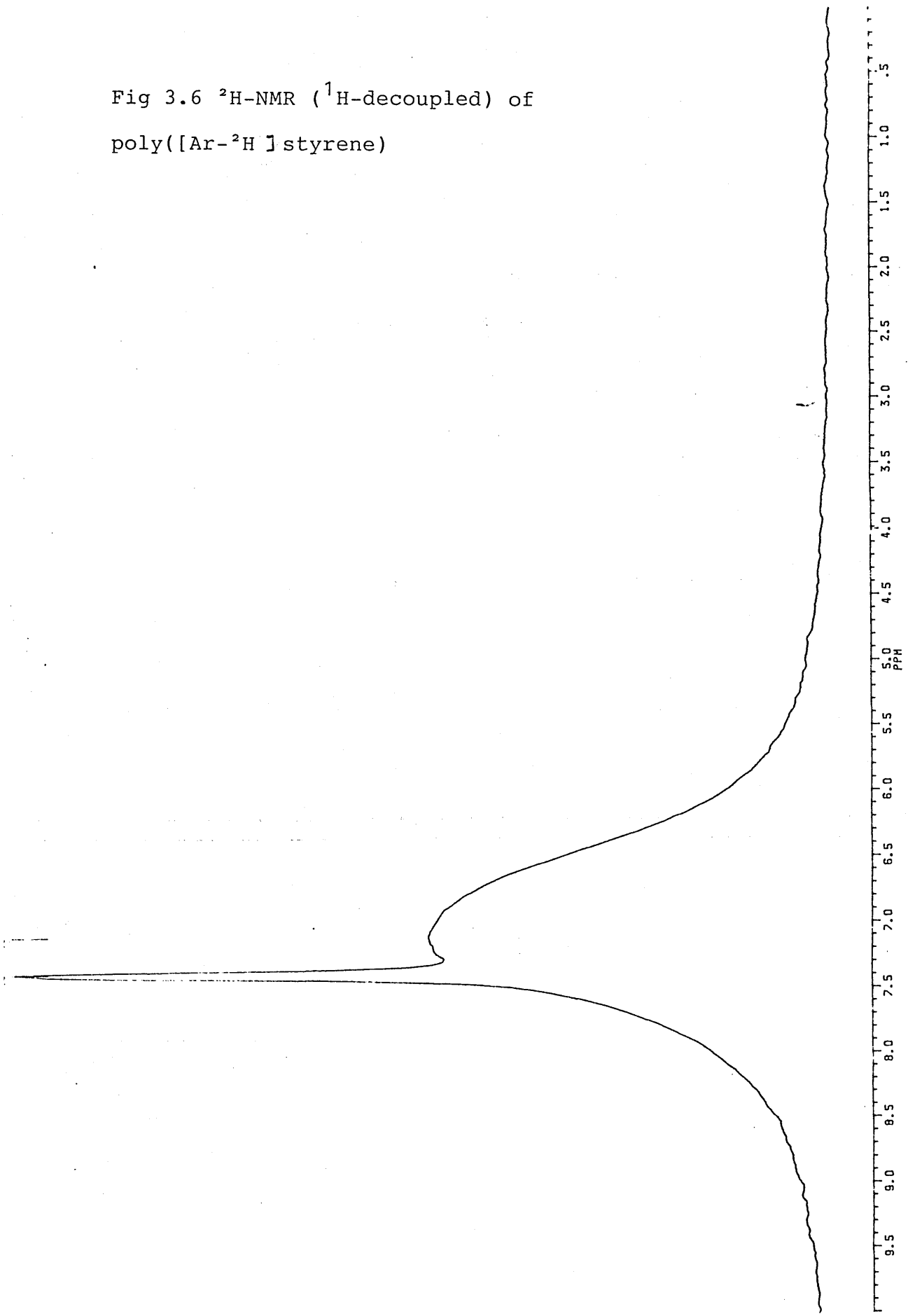


Fig 3.6 ^{2}H-NMR (^{1}H-decoupled) of poly([Ar-^{2}H]styrene)



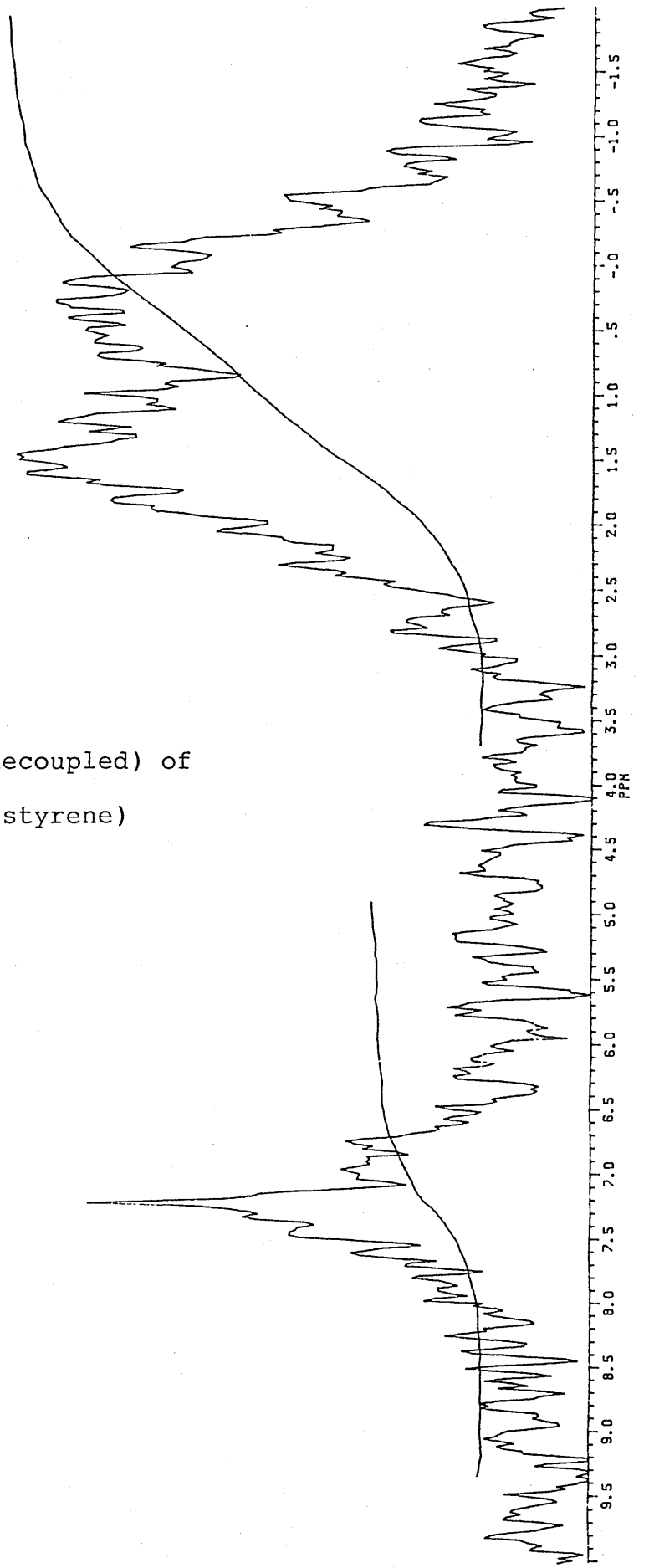


Fig 3.7 ^{2}H-NMR (^{1}H-decoupled) of poly([G-^{2}H$_3$]α-methylstyrene)

indicating a low level of deuterium incorporation of which 16 is in the aromatic ring and the remainder split equally between the two aliphatic sites.

The deuterium NMR spectrum of poly([1-^{2}H]methyl-methacrylate) (fig 3.8) has only one signal at δ3·2 ppm corresponding to the perdeuterated methyl ester group. This spectrum has a very high signal to noise ratio when compared with the previous spectrum indicating the high level of incorporation obtained by using perdeuterated starting material.

The deuterium NMR spectrum of poly([1-^{2}H]-butyl-methacrylate) (fig 3.9) has two signals at δ4·0 and δ7·2 ppm. The upfield signal is from the label in the butyl ester side chain, the signal at δ7·2 ppm may be a deuterium labelled impurity, but is probably the deuterium natural abundance signal from the solvent, $^1H_6$-benzene. Benzene was chosen as the NMR solvent precisely because any natural abundance signal would occur away from the regions of the expected signals while providing a reference frequency for the spectrum.

Fig 3.8 ^{2}H-NMR (^{1}H-decoupled) of poly([1-^{2}H]methylmethacrylate)

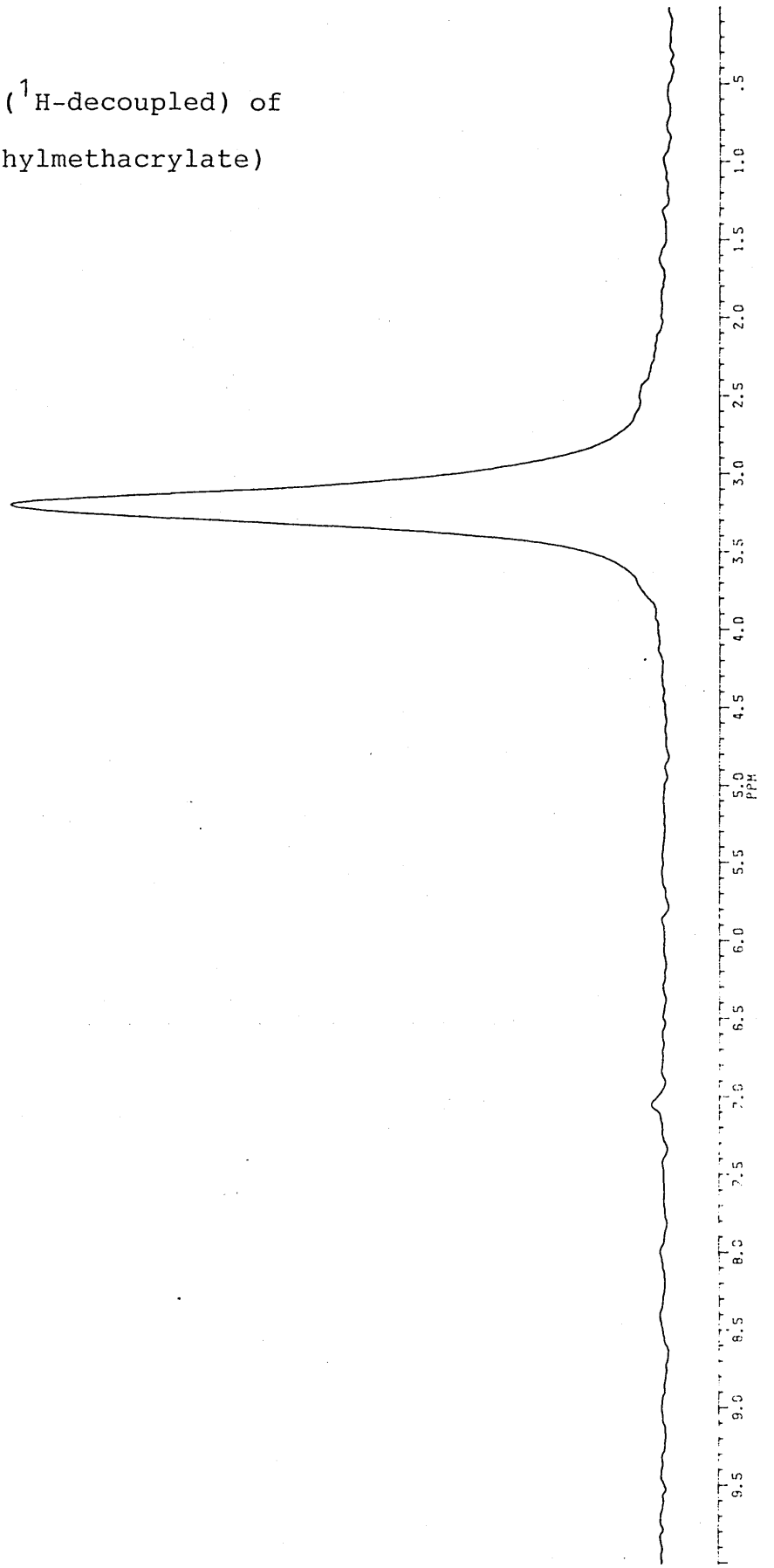
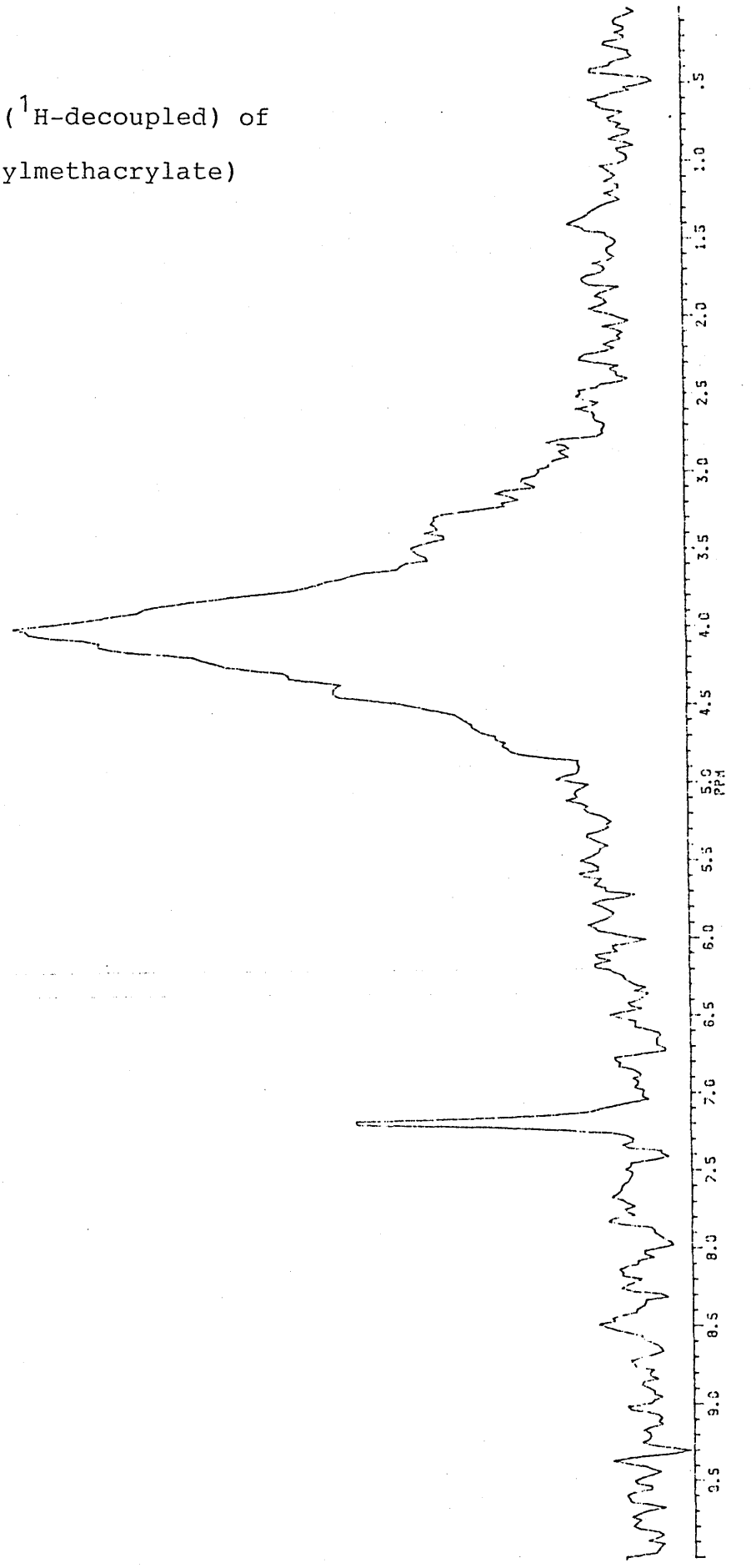


Fig 3.9 ^{2}H-NMR (^{1}H-decoupled) of poly([1-^{2}H]butylmethacrylate)



3.6 Discussion

The deuterium NMR spectra of the labelled monomers and polymers demonstrate that where the labelling reactions are the same as those used for tritium, so also are the labelling patterns. [Ar-^{2}H]Styrene has been labelled exclusively in the aromatic ring, as was found when this method was used in the tritium labelling of the monomer.

The deuterium NMR spectrum of poly([Ar-^{2}H]styrene) highlights one of the difficulties that can be encountered when using deuterium NMR spectroscopy. Deuterium quadrupole relaxation can broaden the linewidth when compared with the corresponding proton resonance lowering the resolution. This effect, when compounded with peak broadening from the restricted motion of the polymer chains, leads to spectra with very broad linewidths. The hydrogens on the aromatic ring are subject to different shielding effects and in a proton spectrum, the ortho- hydrogens can be clearly differentiated from the meta- and para- hydrogens if not completely separated.[4] In the deuterium NMR spectrum however, overlapping of these two signals has occurred to such a degree that it is not possible to determine the labelling distribution accurately, although the deuterium is obviously predominantly in the ortho- (upfield) position.

One of the most important advantages of carrying out labelling procedures using a stable isotope is the absence of any radiation induced reactions or damage. As noted in the previous chapter, the polymerisation of [Ar-^{3}H]styrene led to the formation of a polymer which gelled too rapidly for an NMR spectrum of the polymer solution to be obtained. When the reaction was repeated with deuterium, no such problem occurred and it was possible to obtain a ^{2}H-NMR spectrum of the labelled polymer. The absence of harmful radiation would be extremely important were these compounds to be used in food or drug experiments.

The deuterium NMR spectrum of poly([G-^{2}H]α-methylstyrene) has a very poor signal to noise ratio due to the low deuterium incorporation in the compound. The quality of the spectrum could be improved by repeating the labelling process as was done with 4-methyl-1-pentene, or by accumulating a greater number of transients for the spectrum.[5] However, the labelling pattern in the polymer can be clearly determined and, as was found with tritium, the labelling is predominantly in the aliphatic regions.

The availability of perdeuterated methanol much simplified the preparation of [1-^{2}H]methylmethacrylate leading to a product with a high incorporation of deuterium

in a single site. It is for this reason that the spectra of both the monomer and polymer have extremely high signal to noise ratios.

The labelling pattern of [1-^{2}H] butylmethacrylate does differ slightly from that of the tritiated monomer. The deuterium is situated entirely in the α-position of the butyl side chain and no migration to the β-position as found in [G-^{3}H] butylmethacrylate can be observed here. The labelling procedures used in both the deuterium and tritium experiments were the same apart from the use of extra deuterium which would be expected to decrease the specificity of the deuterium labelling pattern. Likewise the rate of tritiation would be expected to be lower than the rate of deuteration so some kinetic isotope effect would appear to be unlikely also. The difference in labelling pattern in the two monomers can therefore only be attributed to changes in the experimental conditions, believed to be due to the ruthenium catalyst which over the two year period between these two experiments may have lost some of its activity.

The use of greater quantities of deuterium for the base catalysed exchange reaction used in the preparation of deuterium labelled isoprene has led to a more general

labelling pattern than found with [1-^{3}H]isoprene. The tritiated water used for the tritiation experiments is 3 % isotopically enriched; therefore using 100 % deuterated water and 100 times the quantity increases the deuterium available for incorporation by a factor of 3000; this increases the liklihood of more general labelling patterns. The deuterium NMR spectrum shows the label to be present in every position in the molecule; the greater proportion of the label is present in the methylene groups, particularly the 1-position.

The deuterium labelling of 4-methyl-1-pentene is of a similar pattern to that of its tritium labelled counterpart. The main point of interest in this experiment has been the repeated labelling procedure which has led to a high deuterium incorporation (witnessed by the high signal to noise ratio of the signals). However, the label is still concentrated in the 1- and 2-positions at δ5·0 and δ5·7 ppm respectively.

A sample of poly([G-^{2}H]α-methylstyrene) was submitted for analysis by solid state magic angle spinning deuterium NMR spectroscopy. The results obtained from these experiments were disappointing as it appeared that the level of deuterium incorporation in the material was too

low for detection by this technique. Further work in this direction would require a higher level of incorporation which could simply be achieved by repeating the labelling process.

3.7 Conclusions

A range of deuterium labelled monomers and polymers have been prepared and the labelling patterns determined by solution deuterium NMR spectroscopy. Where the labelling techniques for both isotopes were the same, the deuterium and tritium labelling patterns were found to be similar. The efficiency of deuterium NMR spectroscopy brought about by recent developments in technology, has made possible the routine analysis of specifically labelled compounds, facilitating hydrogen tracer experiments without the problems associated with radioisotopes. An attempt to observe a deuterium NMR spectrum of a solid was unsuccessful.

3.8 References

1. Elvidge, J.A., and Jones, J.R., Isotopes-Essential Chemistry and Applications, Chem. Soc. London, (1980).
2. Mantsch, H.H., Saito, H., and Smith, I.C.P., Progress in NMR Spectroscopy, 11, 211, (1977).
3. Fyfe, C.A., Solid State NMR for Chemists, C.F.C. Press, Ontario, (1983).
4. Simons, W.W., and Zanger, M., The Sadtler Guide to the NMR SPectra of Polymers, Sadtler Research Lab. Inc. Pennsylvania, (1973).
5. Bovey, F.A., High Resolution NMR of Macromolecules, Academic Press, New York, (1972).

CHAPTER FOUR

The Application of Labelled Polymers to Degradation Studies

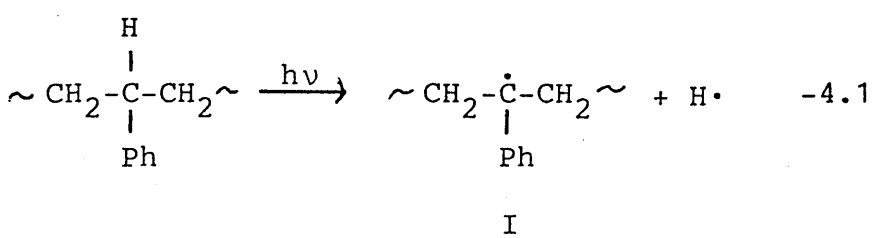
4.1 Introduction

In the development of new polymers having improved chemical and physical properties, the study of the degradation of existing materials is of vital importance. A comprehension of the mechanisms of polymer degradation is most essential if such processes are to be retarded or inhibited. Ideally, polymer degradation studies should be performed under natural conditions over real time scales; unfortunately such long periods of time, often years, precludes such studies as results are frequently required more rapidly, e.g. as part of a PhD study. To overcome this problem, it is necessary to accelerate degradation reactions to enable them to be studied within a suitable time period. The acceleration of the reactions inevitably involves the use of harsher conditions than found during the materials' normal lifetime e.g. excesses of heat, chemical attack and irradiation etc. which may well complicate the mechanisms of any degradation process. However, while such methods require artifical conditions, the results obtained may still be pertinent and provide an understanding of mechanisms that occur naturally. In certain situations extrapolation to less stringent conditions may be possible.

The following material is concerned with a review of degradation studies performed on the polymers whose

labelling with tritium and deuterium has already been discussed. The review is relatively brief and intended only to detail the accepted mechanisms of degradation of the polymers while indicating the complexity of some of the reactions.

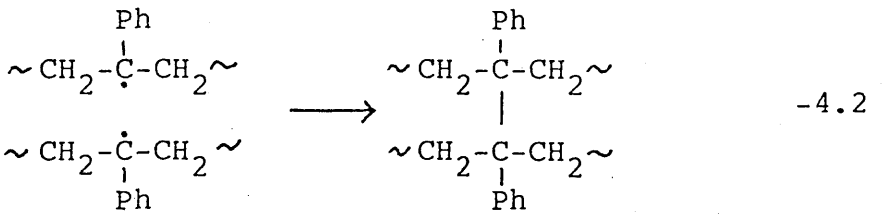
The action of ultra-violet (UV) light in the presence or absence of oxygen is one of the most commonly studied polymer degradation reactions, as resistance to photolysis is necessary for everyday use of the material. Polystyrene degrades rapidly under the influence of UV irradiation, the polymer chains crosslink, leading to rapid insolubilisation and form unsaturated groups.[1] The initiation mechanism of the reactions depends on the wavelength of the irradiated light. The phenyl ring is a chromophore which absorbs below 290nm and studies carried out at 254 nm indicate the initiation reaction to be the formation of a macroradical (I) (eqn 4.1):-



$$\sim CH_2\text{-}\underset{\underset{Ph}{|}}{\overset{\overset{H}{|}}{C}}\text{-}CH_2\sim \xrightarrow{h\nu} \sim CH_2\text{-}\underset{\underset{Ph}{|}}{\dot{C}}\text{-}CH_2\sim + H\cdot \qquad \text{-4.1}$$

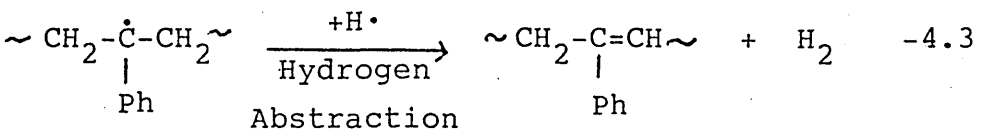
I

which can then crosslink (4.2):-



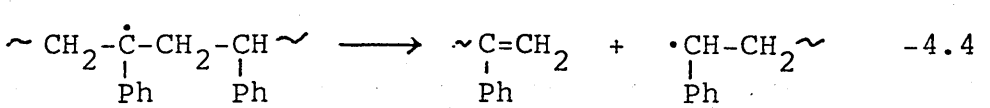
-4.2

or form various unsaturated groups by hydrogen abstraction (eqn 4.3):-



-4.3

or chain scission (eqn 4.4):-



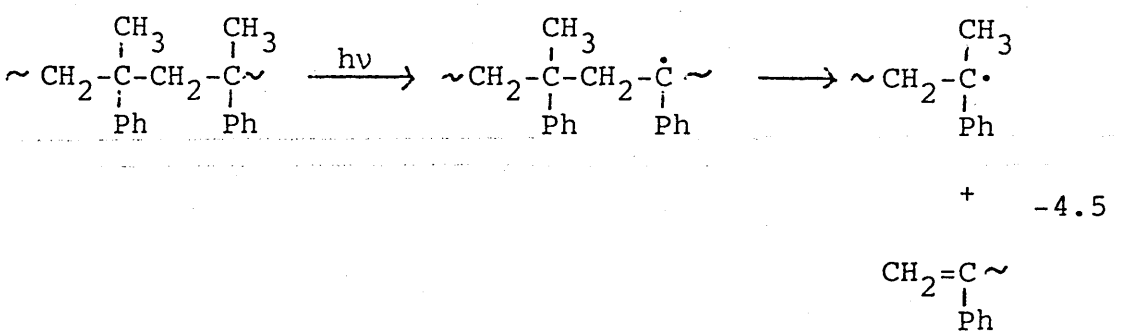
-4.4

At wavelengths of light greater than 290 nm, the phenyl ring is no longer a chromophore and initiation is believed to be via peroxide and ketone impurities from the polymer manufacture.

In the presence of oxygen (photooxidation), the degradation of polystyrene is characterised by the formation

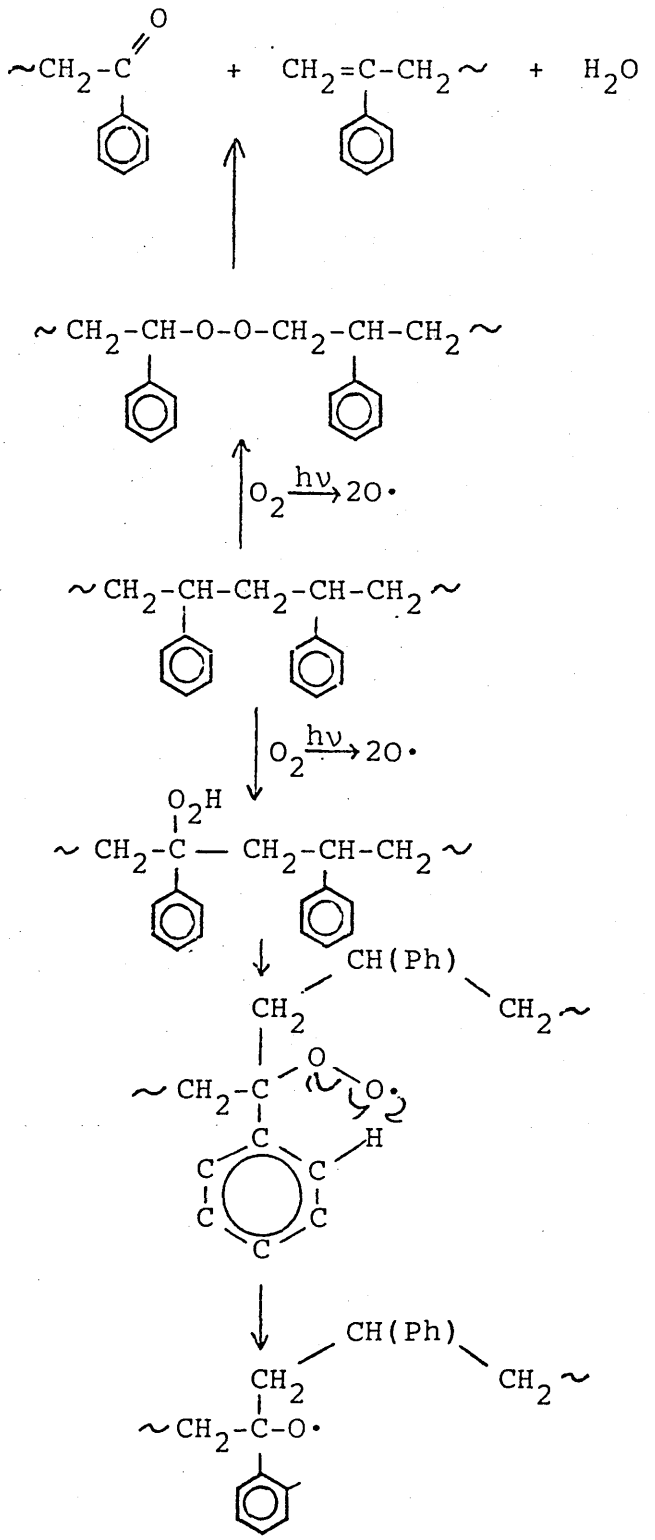
of unsaturated hydrocarbons and conjugated carbonyl groups.[2] The initiation reactions are by both carbon-carbon and carbon-hydrogen bond cleavage and decomposition of oxidation products such as peroxides, examples of which are given in scheme I.[1,3]

The photolysis of poly(α-methylstyrene) is characterised by random chain scission leading to an initial rapid decrease in the molecular weight with production of the monomer.[4] Energetically, main chain scission is unlikely for the initiation reaction, but results from electron spin resonance (ESR) studies give an indication of how this might occur (eqn 4.5):-



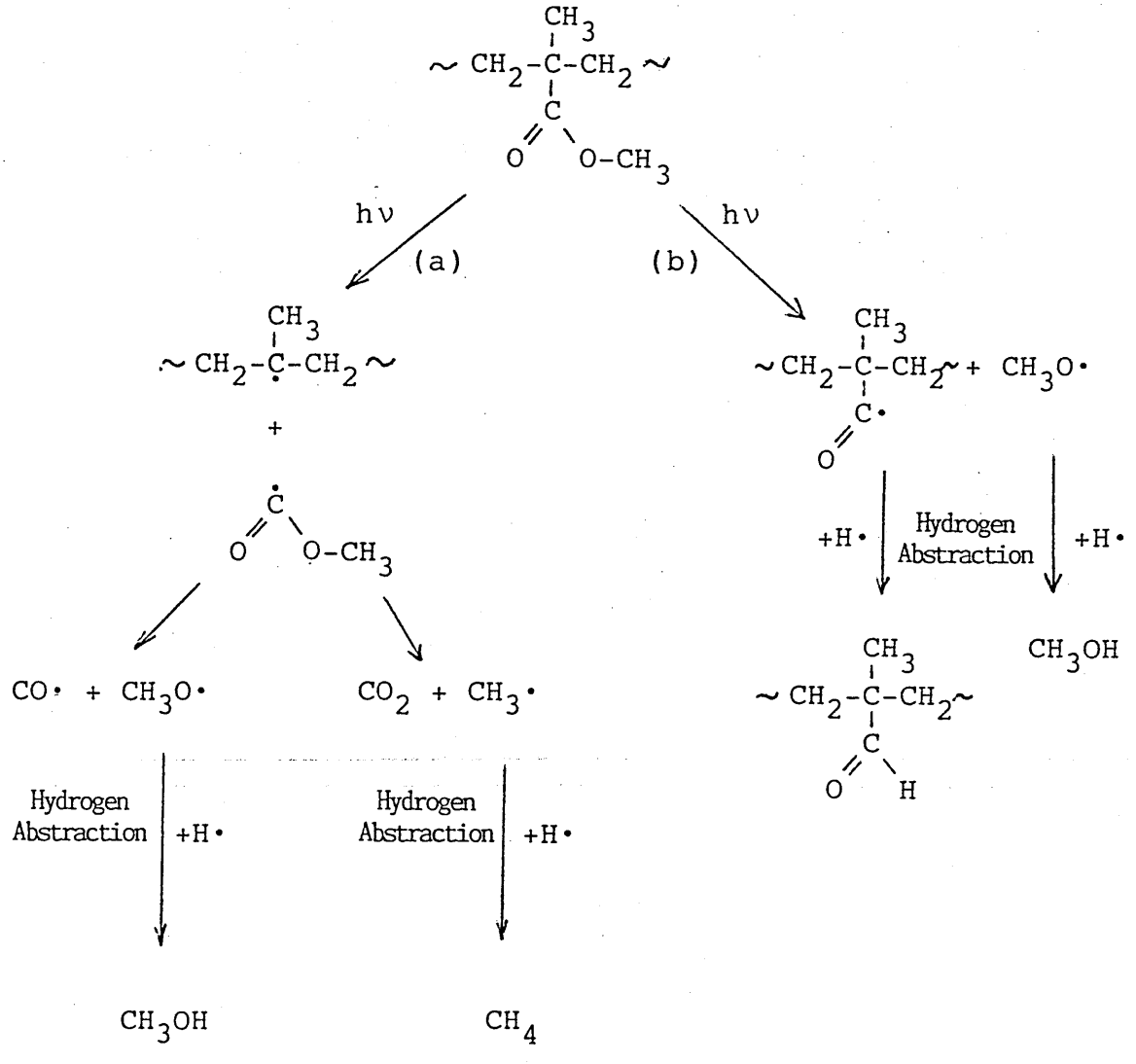
-4.5

An initial rapid decrease in molecular weight is also observed for the photolytic degradation of polymethylmethacrylate accompanied by a high quantum yield of methanol.



Scheme I

The main chromophore in the molecule is the ester carbonyl which is cleaved off initially by two possible mechanisms (scheme II)[6,7]

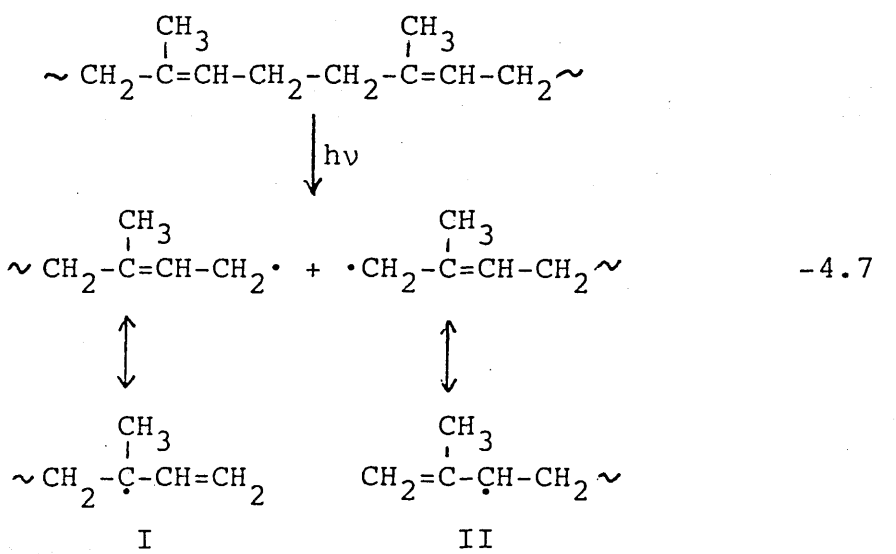


Scheme II

As the production of methane (scheme (a)) is minimal and aldehyde formation is often observed, scheme (b) is favoured.

Studies performed on the photolysis of polybutylmethacrylate over a range of temperatures[8] have revealed that depolymerisation yielding the monomer is the primary degradation process initiated by photochemically labile fragments of initiator e.g. AIBN. The production of 1-butene was also observed and believed to occur via the formation of a 6-membered intermediate involving the β-hydrogen of the ester side chain (eqn 4.6).

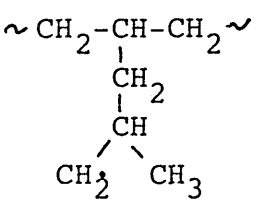
The photolysis of poly(1,4-isoprene) leads to the formation of unsaturated groups and insolubilisation of the polymer by crosslinking (eqn 4.7)[9]:-



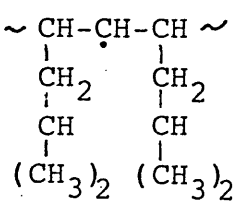
-4.7

Recombination of the allylic radicals I and II will lead to insolubilisation.

The UV irradiation of poly(4-methyl-1-pentene) leads to crosslinking of the polymer and the formation of unsaturated groups. These reactions were believed to stem from the production of radicals of the type III or IV.[10]

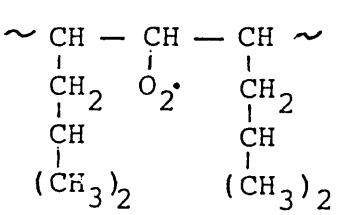


III



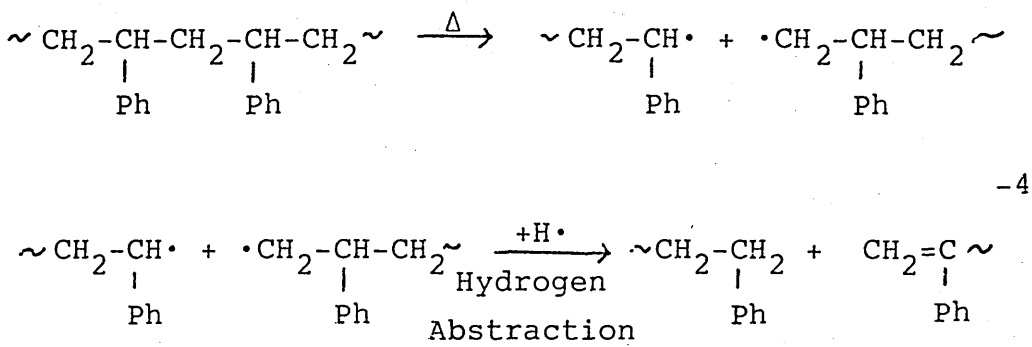
IV

Later work on degradation in the presence of oxygen indicated that free radical species, particularly type IV, were formed, which reacted with oxygen that had diffused rapidly into the polymer matrix. Peroxy radicals (V) were thus formed which lead to further degradation of the polymer.[11]



V

The thermal degradation of polystyrene occurs by a single step to yield up to 40% monomeric styrene[1], together with smaller amounts of benzene, toluene and a range of oligomers. Initiation is via the homolytic cleavage of carbon-carbon bonds followed by hydrogen abstraction (eqn 4.8):[12]



-4.8

The depolymerisation is characterised by a rapid initial decrease in molecular weight, thought to be due to the presence in the chain of weak links. Much work has been carried out to identify these weak links but without success.[13]

The thermal degradation of poly(α-methylstyrene) is brought about by random chain scission,[14,15] in much the same way as its UV degradation, and under the correct conditions can yield 100% monomer.[12]

The thermal degradation of both polymethylmethacrylate[16] and polybutylmethacrylate[17] at moderate temperatures yields

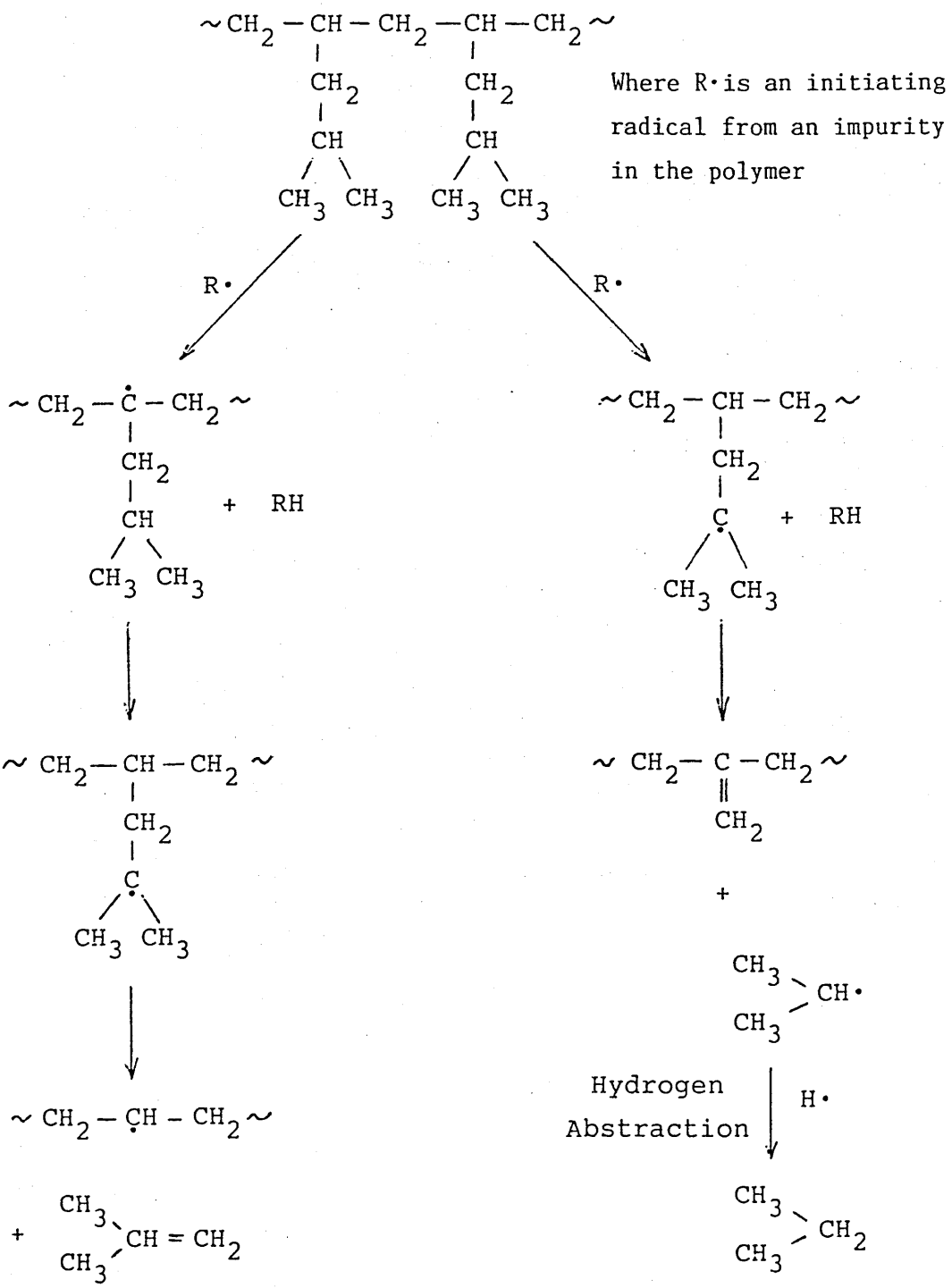
the monomers. However, at temperatures greater than 250 °C, the butyl ester side chain of polybutylmethacrylate decomposes producing butene, methacrylic acid and anhydride.

Poly(4-methyl-1-pentene) degrades thermally to form a range of volatile compounds including primarily isobutene and propane. The initiation reaction is the formation of a tertiary carbon radical at which occurs a range of inter- and intra-molecular radical transfers (scheme III).[18]

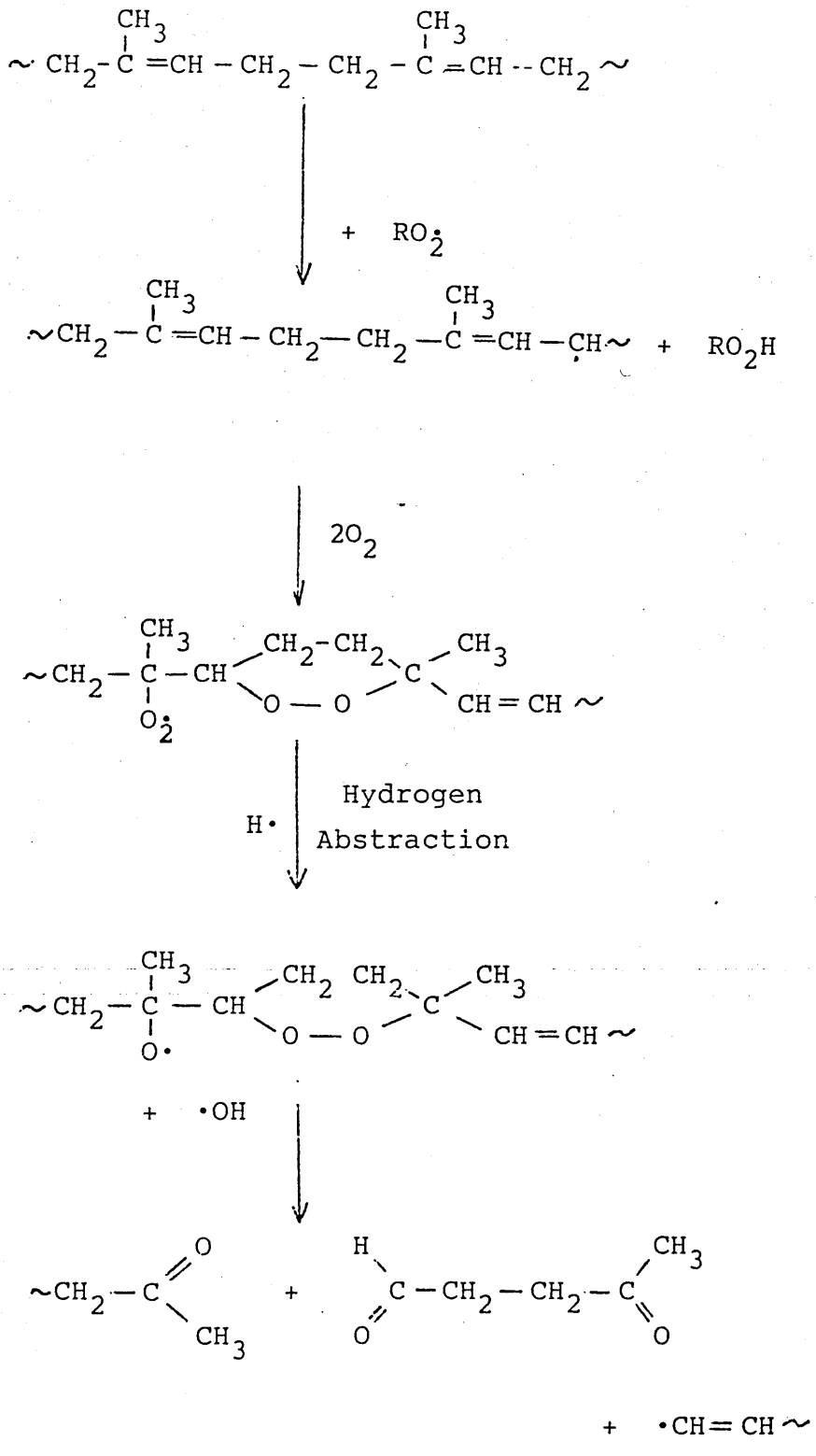
Isoprene, dipentene and 1,5 dimethyl-5-vinylcyclohexene are the primary products of the thermal degradation of polyisoprene (in the absence of oxygen) produced by a complex series of cage recombination reactions of the various allylic radicals formed during the initial decomposition reaction.[19]

The oxidation of polyisoprene is initiated by free radical attack of peroxyradicals and yields a range of volatile products including isoprene, levulinaldehyde and methanal. The following reaction scheme has been suggested to account for the formation of these compounds (scheme IV).[20]

To perform a degradation study on a labelled polymer within the time available, it was necessary to choose a simple reaction with a well understood mechanism that could be carried out reasonably quickly. The acid catalysed


Where R· is an initiating radical from an impurity in the polymer
R·
R·
+ RH
+ RH
Hydrogen Abstraction
H·

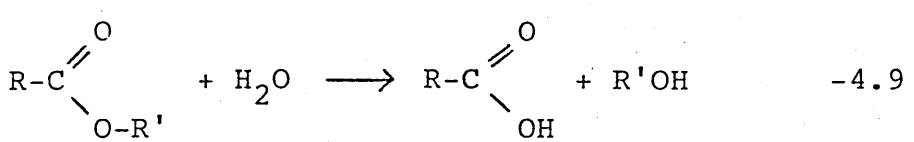
Scheme III



Scheme IV

hydrolysis of an ester is a common reaction and well studied; hence, it was felt that this would be a suitable medium through which the merit of a specifically labelled polymer in a degradation study could be demonstrated. Polybutylmethacrylate has an alkyl ester side chain that is susceptible to hydrolytic attack and has been labelled with tritium and analysed. Using some of the techniques available to radio-labelled compounds a study was performed on the acid catalysed hydrolysis of poly([G-^{3}H]butylmethacrylate).

Esters undergo acid catalysed hydrolysis to form the constituent carboxylic acid and alcohol (eqn 4.9):-



-4.9

Common techniques for studying the kinetics of this reaction using unlabelled materials would be by titration to detect the formation of the carboxylic acid, or by spectroscopic methods. If however the ester is specifically labelled with a radioisotope, the reaction can be monitored by an appropriate extraction procedure. As mentioned previously (p.82), poly([G-^{3}H]butylmethacrylate) is labelled specifically in the alcohol side chain, which

has enabled the hydrolysis of the polymer to be followed by the extraction of the alcohol as it is formed and then counted.

4.2 Experimental

Poly([G-^{3}H butylmethacrylate) (0·3 g) prepared as described in section 2.4.2 was dissolved in tetrahydrofuran (5 ml); this polymer solution was used for all the kinetic runs. A portion of the polymer solution (usually 100 µl) was hydrolysed by addition to concentrated sulphuric acid (10 ml). Aliquot portions of the reaction mixture were removed at various time intervals and added to a test tube containing chloroform (10 ml), water (5 ml) and methanol (5 ml). The mixture was shaken vigorously and allowed to settle for approximately 30 minutes. The aqueous layer was removed, a known amount dissolved in a liquid scintillant and the radioactivity of the sample determined by liquid scintillation counting. The rate of the reaction was determined over a range of temperatures and acid concentrations. For the purposes of comparison, the rate of hydrolysis of [G-^{3}H]-butylmethacrylate was also determined.

4.3 Results

The results of a typical kinetic run from which the rate constant under these conditions may be determined, are given in Table 4.1.

Table 4.1 Kinetic Data from the Hydrolysis of Poly([G-^{3}H]butyl-methacrylate) in Concentrated Sulphuric Acid (98%) at 45 °C

Time mins.	Scintillation Count C_t (cts/m)	$\ln(C_\infty - C_t)$*
0	18500	11·55
5	29700	11·44
10	36100	11·37
15	51600	11·17
20	64800	10·96
25	70500	10·86
30	79600	10·67
35	84900	10·53
40	95900	10·19
45	95000	10·22

* Scintillation count at end of reaction C_∞ = 122500 (Reading taken after 24 hours)

A graphical analysis of these data is given in fig. 4.1 from which the rate constant may be obtained.

The effect of temperature on the rate of hydrolysis of the polymer is given in Table 4.2. An Arrhenius plot (fig. 4.2) of this data gives a value for the activation energy of $1{\cdot}23 \pm 0{\cdot}10 \times 10^{5}$ J mol^{-1} and an A value of $4{\cdot}28 \pm 0{\cdot}38 \times 10^{18}$ min^{-1}.

Table 4.2 The Effect of Temperature on the Rate of Hydrolysis of Poly([G-^{3}H]butylmethacrylate)

Temperature °C	Rate Constant $k/min^{-1} X10^{-2}$
35·0	0·53
40·0	2·01
45·0	3·10
50·0	7·28
60·0	22·7

The results in table 4.3 detail the effect of the strength of the sulphuric acid on the rate of hydrolysis. A plot of $\log_{10} k$ vs -Ho (fig 4.3) has a gradient of 0·89.

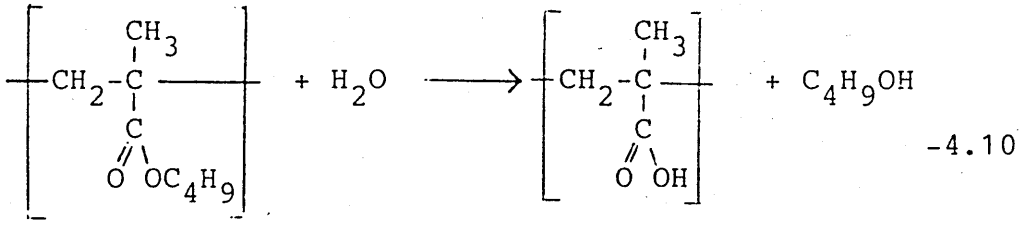
Table 4.3 The Effect of Acid Strength on the Rate of Hydrolysis of Poly([G-^{3}H]butylmethacrylate) at 40 C

Acid Strength $-H_o$	Rate Constant $k/min^{-1} x10^{-2}$
9·36	2·01
8·57	0·485
7·80	0·0812

The first order rate constant for the hydrolysis of [G-^{3}H]butylmethacrylate at 40 °C by concentrated sulphuric acid ($-H_o$=9·36) is $5·4x10^{-3}$ min^{-1}.

4.4 Discussion

The aim of these experiments was to demonstrate the ease with which a labelled polymer could be used to follow a degradation reaction. The hydrolysis of poly([G-^{3}H]-butylmethacrylate) yields polymethacrylic acid and butanol (eqn 4.10):-

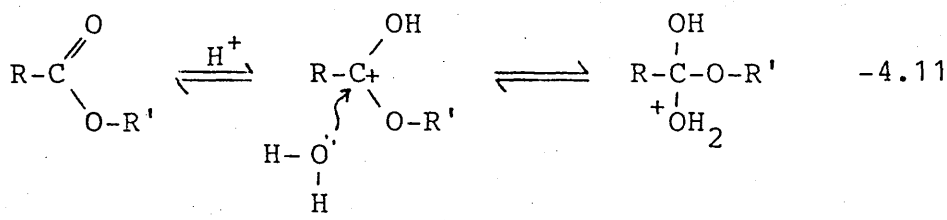


-4.10

Previous studies on this reaction[21,22] have mainly concerned themselves with the preparation of stereoregular polymethacrylic acid. One kinetic study on the acid catalysed hydrolysis of polybutylmethacrylate by concentrated sulphuric acid has been reported by Shtil'man et al[23] who obtained a value for the activation energy of 17·8 kcal mol^{-1} (74·8 kJ mol^{-1}). The agreement between the results obtained by Shtil'man and those from these experiments is not good; the discrepancies are probably due to the differences in the polymers, e.g. the molecular weight etc., which may have a large effect on the rate of reaction.

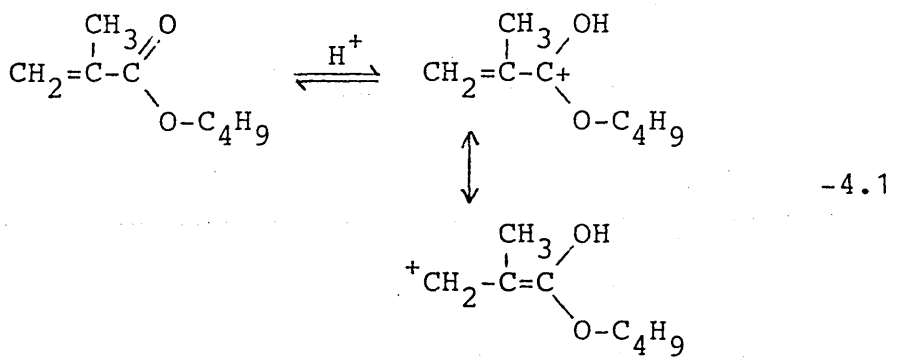
The hydrolysis of [G-^{3}H]-butylmethacrylate at 40 °C is slower than the polymer by almost a factor of four. This result was unexpected as the hydrophobic nature of the polymer molecule would be expected to inhibit the diffusion of the aqueous acid into the polymer bulk and slow the reaction.[12] An explanation for the results obtained may lie in the ability of the methacrylic ester to form a resonance hybrid. Acid hydrolysis of an ester is initiated

by the protonation of the ester followed by nucleophilic attack by a water molecule (eqn 4.11)[24]:-



-4.11

In the case of α,β-unsaturated acid esters such as methacrylic acid however, the formation of a resonance stabilized hybrid can occur (eqn 4.12), inhibiting the second step of the reaction.



-4.12

For the acid catalysed hydrolysis of esters, the dependence of the Ho acidity function on the rate of reaction can give a good indication of the molecularity of the rate determining step.[25] If a plot of $\log_{10}k$ vs -Ho is linear and the slope >0·8, it suggests the rate determining step is unimolecular, for bimolecular reactions, the relationship is non-linear or has a

slope <0·8. A plot of $\log_{10}k$ vs -Ho for the acid catalysed hydrolysis of polybutylmethacrylate is linear and has a gradient of 0·89, indicating the rate determining step is unimolecular. The acid catalysed hydrolysis of esters is generally bimolecular but in this case the steric hindrance of the polymer chain may tend to retard this mechanism and the reaction proceeds via a unimolecular rate determining step. The acidity function dependence is merely an indication of the molecularity and further confirmatory evidence is required.

4.5 Conclusions

The effect of temperature and acid strength on the acid catalysed hydrolysis of polybutylmethacrylate has been studied using a polymer labelled with tritium. The study, while in no way extensive, has served to demonstrate the usefulness labelled polymers can have in mechanistic studies of polymer degradation reactions and points the way to further investigations in this area.

Figure 4.1 Rate of Hydrolysis of Poly([G-^{3}H]butyl-methacrylate) at 45 °C by Concentrated Sulphuric Acid

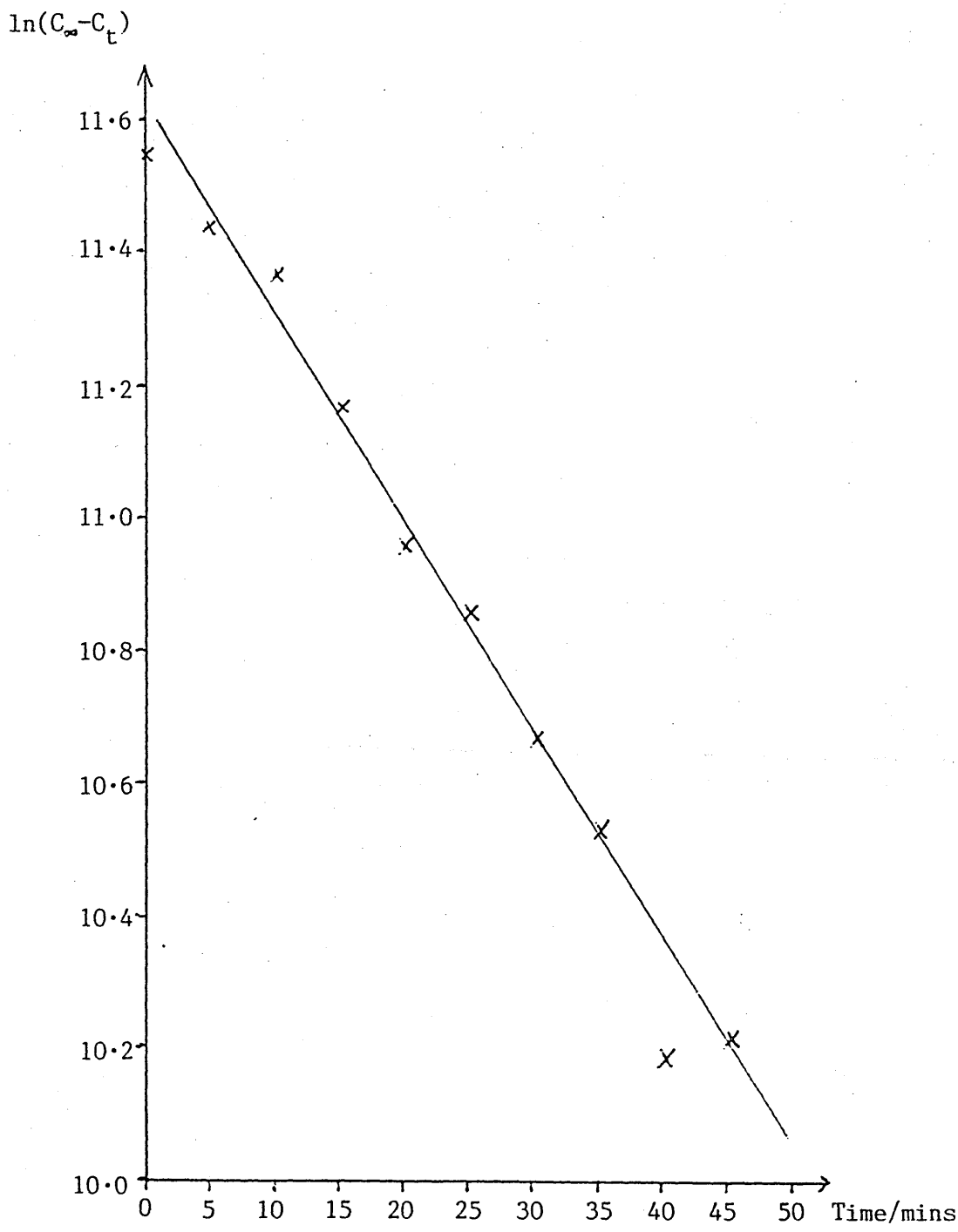


Figure 4.2 Arrhenius Plot of the Hydrolysis of Poly([G-^{3}H]-butylmethacrylate) by Concentrated Sulphuric Acid

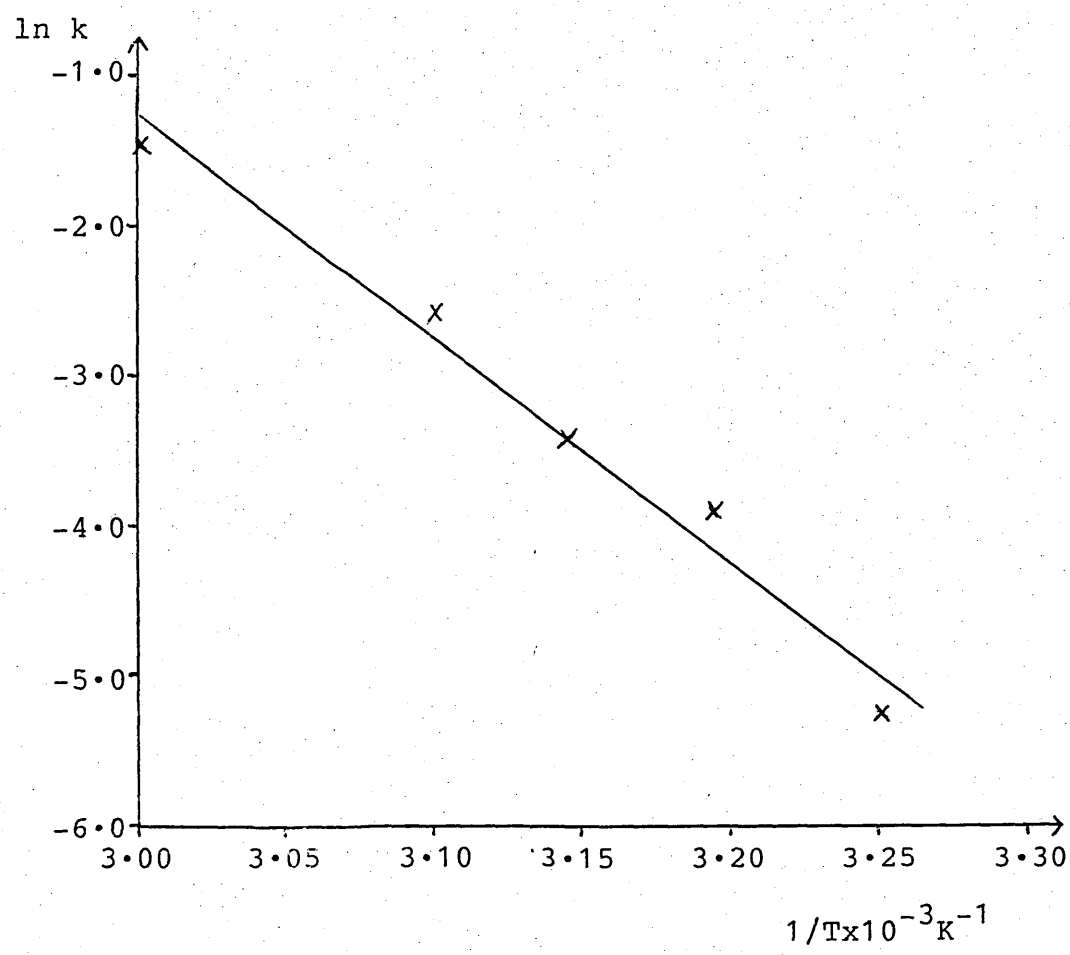
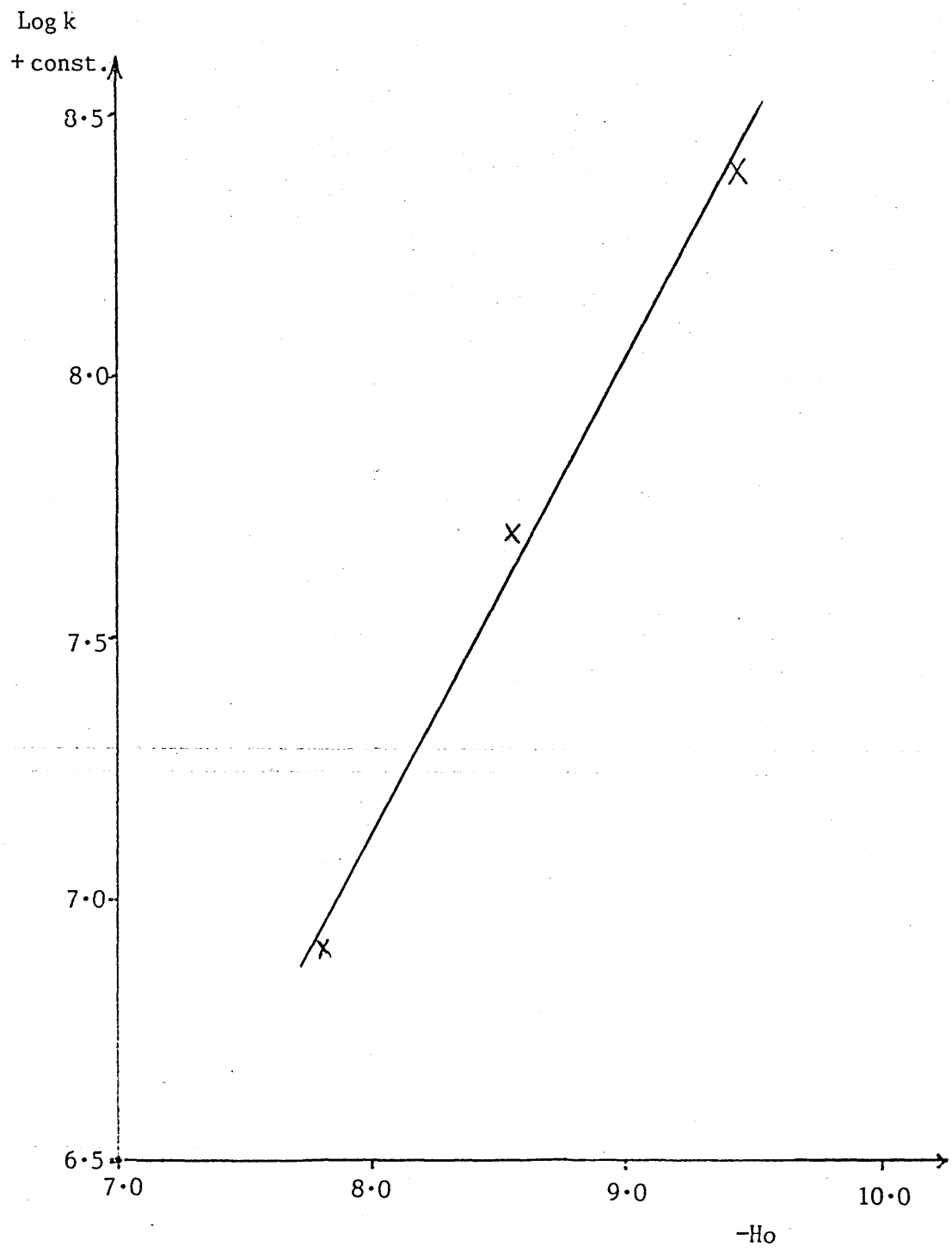


Figure 4.3 Plot of Log k vs -Ho for the Hydrolysis of Poly([G-^{3}H] butylmethacrylate) by Concentrated Sulphuric Acid



4.6 References

1. Weir, N.A., Developments in Polymer Degradation Vol.4, Ed. Grassie, N., Elseveir, London, (1982).
2. Grassie, N., and Weir, N.A., J. Appl. Polymer Sci. 9, 987, (1965).
3. Allen, N.S., Photochem. 11, 555, (1981).
4. Stokes, S., and Fox, R.B., J. Polymer Sci. 56, 507, (1962).
5. Cozzens, R.F., Monig, W.B., and Fox, R.B., J. Chem. Phys. 48, 581, (1968).
6. Fox, R.B., Issacs, L.G., and Stokes, S., J. Polymer Sci. A1, 1079, (1963).
7. Allison, J.P., J. Polymer Sci. A1, 4, 1029, (1966).
8. Grassie, N., and MacCullum, J.R., J. Polymer Sci. A2, 983, (1964).
9. Comprehensive Chemical Kinetics, Vol.14, Ed. Bamford, C.H., and Tipper, C.F.H., Elseveir, Amsterdam, (1975).
10. Browning, H.L., Ackerman, H.D., and Patton, H.W., J. Polymer Sci. A1, 4, 1433, (1966).
11. Goodhead, D.T., J. Polymer Sci. A2, 9, 999, (1971).
12. Grassie, N., and Scott, G., Polymer Degradation and Stabilisation, Cambridge Univ. Press, London, (1981).

13. Cameron, G.G., Meyer, J.M., and McWalter, I.T., Macromolecules, 11, 696, (1978).

14. Brown, D.W., and Wall, L.A., J. Chem. Phys. 62, 848, (1958).

15. Jellinek, H.H.G., and Kachi, H., J. Polymer Sci. C23, 97, (1966).

16. Grassie, N., Scotney, A., and Mackinnon, L., J. Polymer Sci. Polymer Chem. Ed. 15, 251, (1977).

17. Thermal Stability of Polymers, Vol.1, Ed. Conley, R.T., Dekker, New York, (1970).

18. Reginato, L., Makromol. Chem. 132, 125, (1970).

19. Golub, M.A., Developments in Polymer Degradation, Vol.4, Ed. Grassie, N., Applied Science, London, (1982).

20. Schnabel, W.S., Polymer Degradation, Hanser, New York, (1981).

21. Katchalsky, A., amd Eisenberg, H., J. Polymer Sci. 6, 145, (1951).

22. Chlanda, F.P., and Donamura, K.G., J. Appl. Polymer Sci. 15, 1195, (1971).

23. Shtil'man, M.I., Korshak, V.V., Lyalyushkan, S., and Sudakova, N.Yu., Deposited Doc. VINTI, 2790, (1974).

24. Sykes, P., A Guidebook to Mechanism in Organic Chemistry, Longman, London, (1970).

UNIVERSITY OF SURREY LIBRA

25. Rochester, C.H., Acidity Functions, Academic Press, London, (1970).

MATERIAL REDACTED AT REQUEST OF UNIVERSITY