An investigation into the synthesis and crosslinking of some polymers containing cyclopropyl groups

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AN INVESTIGATION INTO THE SYNTHESIS AND CROSSLINKING OF SOME POLYMERS CONTAINING CYCLOPROPYL GROUPS

By

Keith Yeats B.Sc.
Graduate Society.

A thesis submitted for the degree of Doctor of Philosophy
to the University of Durham

1990

AN INVESTIGATION INTO THE SYNTHESIS AND CROSSLINKING OF SOME POLYMERS CONTAINING CYCLOPROPYL GROUPS

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ABSTRACT

The thesis describes an investigation into the use of polymers containing cyclopropyl groups as network forming materials.

The initial route investigated involved the synthesis and homopolymerization of novel acrylate and methacrylate monomers containing cyclopropyl groups. Preliminary crosslinking experiments revealed the unsuitability of this approach.

The second route examined involved the synthesis of a series of all hydrocarbon copolymers containing pendant cyclopropyl groups. Crosslinking experiments using a variety of initiators demonstrated the feasibility, in principle, of the proposed network forming system. In order to provide a practical crosslinking system further investigation into suitable initiators would be required.

ACKNOWLEDGEMENTS

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I would also like to thank a large number of the other members of the research group for many interesting and valuable discussions,especially Dr. E. Khosravi-Babadi for demonstrating the techniques involved in the safe handling of the reagents for the Ziegler-Natta polymerizations. I am also especially grateful to Dr. A. Marrion for many valuable discussions.

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Finally, I am happy to express my deep gratitude to my family, especially my wife Sian and my son Andrew, for their continual encouragement and support.

MEMORANDUM

The work reported in this thesis was carried out in the Chemistry Department of the University of Durham between May 1987 and April 1990.

This work has not been submitted for any other degree and is the original work of the author except where acknowledged by references.

CONTENTS

CHAPTER 1

INTRODUCTION AND BACKGROUND TO THE WORK DESCRIBED IN THIS THESIS

1.1. A Brief Survey of Polymers Used in Surface Coatings

The formation of a coating from a paint applied to a surface usually involves the transformation of a liquid into a solid.

The liquid paint must have a viscosity appropriate to the method of application, typically in the range 0.05-1 $Pa.s^{-1}$. The liquid film is converted into a solid coating which must provide the required mechanical properties. The conversion is referred to as the 'drying' of the film. The film may be defined as being solid if it does not flow under the force applied under a particular test. A paint film will appear 'dry to touch' if it has a viscosity greater than 10^3 $Pa.s^{-1}$, while a viscosity of greater than 10^7 $Pa.s^{-1}$ is said to be required to resist blocking when the two coatings are put against each other for two seconds under a pressure of 20psi ($1.4x10^5Pa^{-1}$).[1]

The polymers used in surface coatings may be placed in two broad categories: thermoplastic and thermosetting polymers.

1.1.a. Thermoplastic Polymers

Thermoplastic polymers represent the simplest type of film-forming polymers, and are employed in lacquers. Lacquers contain a solution of polymer containing the required pigments and other additives formulated to provide the required viscosity for the chosen method of application. Evaporation of the solvent leads to the formation of the final dry coating, which remains soluble. Thermoplastic acrylic resins are widely used in automotive top coats, in this application the solubility of the coating is an advantage in allowing re-touching of any defects.

In order to obtain satisfactory mechanical properties a minimum M.Wt. of 75000 has been said to be required for an acrylic resin used in an automotive topcoat.[1] The relatively high molecular weight required means that in order to obtain paint viscosities suitable for application the lacquers contain typically 10-12% volume solids when applied. Where possible it is desirable to use volume solids greater than 12% in order to minimise the volatile organic content of the paint, for environmental and economic reasons.

1.1.b. Thermosetting Polymers

Thermosetting coating formulations contain low molecular weight polymers, which undergo further polymerization after application to provide a crosslinked network in the dry coating. They allow formulations containing higher volume solids than thermoplastic systems to be achieved.

A large number of chemical reactions are employed to crosslink thermosetting coatings, and for industrial coatings the choice of coating system must provide an acceptable combination of properties chosen from chemical resistance, adhesion, impact resistance, corrosion resistance and cost.

1.1.b.i. Drying Oils

The earliest thermosetting coatings were prepared from drying oils, which are triglycerides of mono, di and triunsaturated acids. The films crosslink by an auto-oxidative process occurring through a complex series of reactions, which have been shown to occur in four stages[2]. An induction stage in which antioxidants present in the film are consumed is followed by a second stage in which a measurable uptake of oxygen occurs, next the decomposition of hydroperoxides formed in the second stage occurs to produce radicals leading to the final stage in which polymerization reactions occur, giving crosslinked networks. A simplified scheme showing a series of reactions leading to crosslinking is shown in Figure 1.1

Figure 1.1

Reactions Involved in the Crosslinking of Drying Oils

Initiation $RH + O_2 \dashrightarrow R\cdot + \cdot OOH$

Propagation $R\cdot + O_2 \dashrightarrow ROO\cdot$

$ROO\cdot + RH \dashrightarrow ROOH + R\cdot$

Termination $ROO\cdot + R\cdot \dashrightarrow ROOR$

$ROO\cdot + ROO\cdot \dashrightarrow ROOR + O_2$

$R\cdot + R\cdot \dashrightarrow R\text{-}R$

The rate of crosslinking depends on the nature of the fatty acids employed, and the factors controlling the choice are given in recent reviews.[3,4] In order to achieve satisfactory rates of crosslinking it is usually necessary to add catalysts, such as fatty acid salts of cobalt, manganese, zirconium and lead. The catalytic effect cobalt and manganese salts is due to their ability to catalyse the decomposition of hydroperoxides to radicals[5], as shown in Figure 1.2:

Figure 1.2

The Decomposition of Peroxides Catalysed by Cobalt Ions

$Co^{2+} + ROOH \dashrightarrow Co^{3+} + RO\cdot + OH^-$

$Co^{3+} + ROOH \dashrightarrow Co^{2+} + ROO\cdot + H^+$

More detailed discussions of the role of catalysts and the choice of drying oils are given references 5 and 6.

Drying oils have several advantages, including cheapness, ability to produce high-solids coatings and good wetting ability. A disadvantage in the use of drying oils is that the crosslinking reaction continues after the film has formed a network, leading to embrittlement of the coating. The films are also subject to yellowing with ageing, the extent of yellowing is influenced by film thickness, and of the type of drier used.[7]

1.1.b.ii. Alkyds and Polyesters

Alkyds first found commercial use approximately 50 years ago, and still represent the largest volume of industrial coatings. Alkyds are a class of polyesters prepared from oils or fatty acids, dibasic acids and polyhydric alcohols. Conventional alkyds contain unsaturated fatty acids and therefore crosslink by auto oxidation. The variety of materials which may be prepared from the simple building blocks is vast, and can be used to prepare a huge range of alkyd resin types. Oil-free alkyds or hydroxylated polyesters do not contain oil-derived fatty acids and must therefore be crosslinked by the incorporation of suitable functional groups, which leads to reduced discolouration of the film and overcomes the problem of embrittlement. Further discussions of the classification and formulation of alkyds are given in references 3 and 8.

The largest volume crosslinking reaction used in industrial baking coatings is the reaction of melamine-formaldehyde resins with hydroxy-functional alkyds or polyesters.[1] The two main reactions occurring when a hydroxyl functional polymer is heated with an amino resin under acidic conditions are shown in Figure 1.3:

Figure 1.3

The Reaction of an Amino Resin With a Hydroxyl Functional Polymer

Co-condensation

$\mathrm{POH} + \text{-}\mathrm{NCH_2OR} \text{ ----> } \text{-}\mathrm{NCH_2OP} + \mathrm{ROH}$

Self-condensation

$\text{-}\mathrm{NCH_2OR} + \mathrm{ROCH_2N} \text{ ----> } \text{-}\mathrm{NCH_2N}\text{-} + \mathrm{CH_2O} + \mathrm{ROR}$

(Where P represents a polymer backbone)

Reaction conditions are chosen to ensure that co-condensation predominates over the self-condensation. The crosslinking reaction requires elevated temperatures and the addition of an acidic catalyst, and therefore the polymer and amino resin can be used in a one-pot system. The crosslinked coatings produced from alkyds/polyesters with amino resins generally show good resistance to chemicals. With growing emphasis on the reduction of volatile organic carbon (VOC) emissions, high solids coatings have been developed from these systems. The co-condensation reaction leads to the formation of an alcohol, while the self-condensation reaction produces formaldehyde and therefore provision must be made to contain these volatile side products. Further details on this class of network forming polymers are given in references 9 and 10.

1.1.b.iii. Polyfunctional Isocyanates

The most important crosslinking reactions of isocyanates are with compounds containing active hydrogens, to form urethane and urea linkages as shown in Figure 1.4:

Figure 1.4

Crosslinking Reaction of an Isocyanate With an Alcohol

$$\mathrm{RNCO} + \mathrm{R'OH} \text{ -----> } \mathrm{RNHCO_2R'}$$

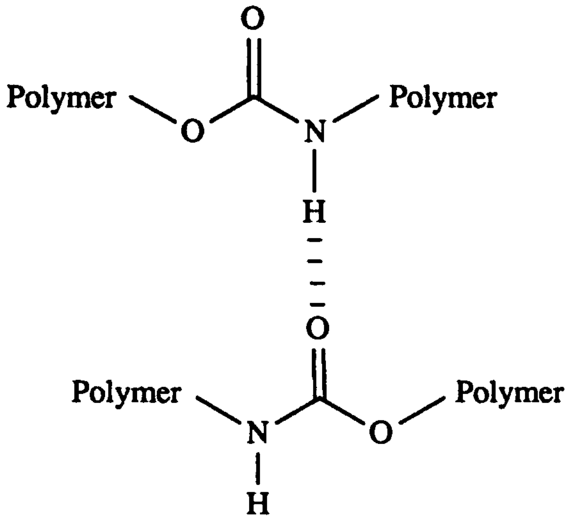
$$\mathrm{RNCO} + \mathrm{R'NH_2} \text{ -----> } \mathrm{RNHCONHR'}$$

Polyurethanes give coatings which combine a number of desirable characteristics, including high gloss, toughness, flexibility, good adhesion, resistance to chemical attack and abrasion resistance. The abrasion resistance has been ascribed to the presence of hydrogen bond 'crosslinks' between urethane groups,[11] shown in Figure 1.5.

A further advantage of two-pack polyurethanes is that the crosslinking reaction will occur even at 0°C allowing coatings to be applied at low temperatures unsuitable for other coatings such as epoxy resins. Two-pack polyurethanes are widely used in yacht, furniture and industrial coatings. The two-pack system consists of a hydroxyl functional polymer and a multifunctional isocyanate, the two components are stored separately and mixed shortly before application.

Figure 1.5

Hydrogen Bond 'Crosslinks' in Polyurethanes



The main disadvantage of polyurethane systems is the high toxicity of isocyanates, which are severe irritants to eyes and respiratory system, additionally toluene diisocyanate, which is widely used, is a sensitizer causing severe asthma attacks. The hazards may be overcome under the controlled conditions employed during paint manufacture, but are likely to present potential problems during application. The problems of toxicity by skin absorption and inhalation may be reduced by increasing the molecular weight of the isocyanate, for example by using isocyanate-terminated prepolymers rather than low molecular weight isocyanates.

Because of the outstanding properties achievable by using polyurethanes it is highly desirable to develop two-pack curing systems possessing the advantages of polyurethanes but with decreased toxicity.

One alternative approach has been to use a blocked isocyanate, which may provide reduced toxicity and allow the formulation of stable one-pot systems as shown in Figure 1.6. In such systems the isocyanate function is only released during the thermal cure stage.

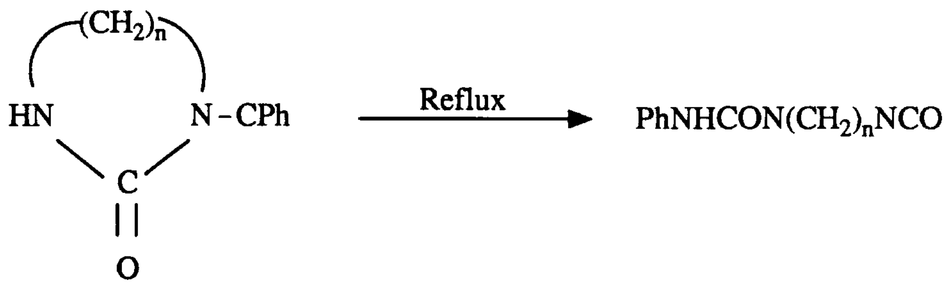
Figure 1.6

$$R\text{-}N{=}C{=}O \;+\; BH \;\rightleftharpoons\; RNHCOB$$

(B = Blocking agent)

Phenols are widely used, although these are obviously toxic and require ventilation during curing. Difunctional macrocyclic urea amides have also been used and have the advantage that no volatile components are evolved during deblocking:[12]

Figure 1.7



1.1.b.iv. Epoxy Resins

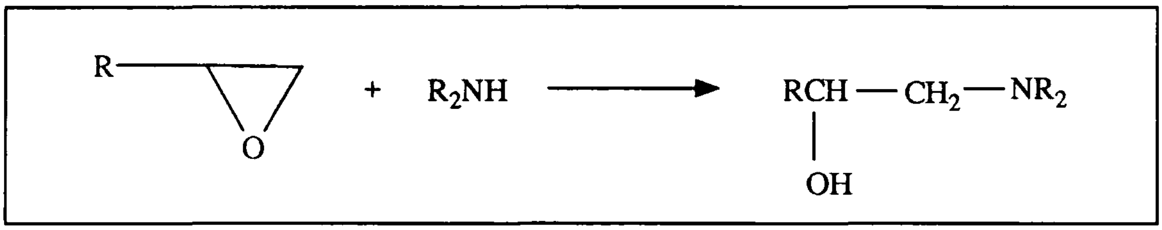
Poly-functional oxiranes, so called epoxy resins are widely used in surface coatings because they can provide a combination of toughness, adhesion, chemical resistance and good electrical properties. Comprehensive reviews of the crosslinking reactions of epoxy resins are available in references 3 and 13.

Epoxy resins are low molecular weight materials which require crosslinking to form insoluble networks. The crosslinking reactions can be divided into two types, the first type are polyaddition reactions with compounds containing labile hydrogen atoms such as polyamines, polyacids or polyphenols; the second type of reaction involves polymerization of epoxy groups via an ionic mechanism.

One of the widely used polyaddition reactions for crosslinking epoxy resins is that with an amine group:

Figure 1.8

Reaction of an Epoxy With an Amine



The crosslinked networks contain amine groups, this leads to the films being strongly adsorbed onto the hydrated iron oxide present on steel surfaces. The adsorbed amine group is not readily displaced by water and therefore the systems are excellent primers for steel substrates. Epoxy resins may be crosslinked at low temperatures by using polythiol curing agents, which has allowed curing temperatures down to -20°C to be achieved.[14] A problem associated with epoxy resin-polyamine systems is the toxicity of polyamines, while epoxy resins are also skin sensitizers. Polymerization of epoxy resins initiated by Lewis acids gives cationic polymerization leading to polyether crosslinks. The most important initiator is BF_3, which is usually used as a complex such as BF_3-amine. Epoxy resins may also be crosslinked by photoinitiators, allowing the formulation of solvent-free low-temperature curing systems, photocrosslinking and photoinitiators have been the subjects of recent reviews.[15,16] For photoinitiated coatings epoxy resins have an advantage over acrylates in showing less shrinkage during curing which results in fewer internal stresses within the crosslinked material.

1.1.b.v. Thermosetting Acrylic Resins

The use of thermoplastic acrylics in lacquers was mentioned previously, the acrylates combine a number of desirable properties, including: outstanding outdoor durability, water-white colour, excellent flexibility and toughness, good chemical resistance, high gloss and minimal pigment reactivity.[9] There are a large number of functional groups used in crosslinking reactions of acrylates, including epoxy/amide, isocyanate/amide and hydroxyl/amino resins as described in earlier sections, details of other reactions are given in reference 9.

More recent developments in crosslinking reactions for acrylic resins have included the use of methylacrylamidoglycolate methyl ether (MAGME).

$$CH_2{=}CHCONHCH(OMe)CO_2Me$$

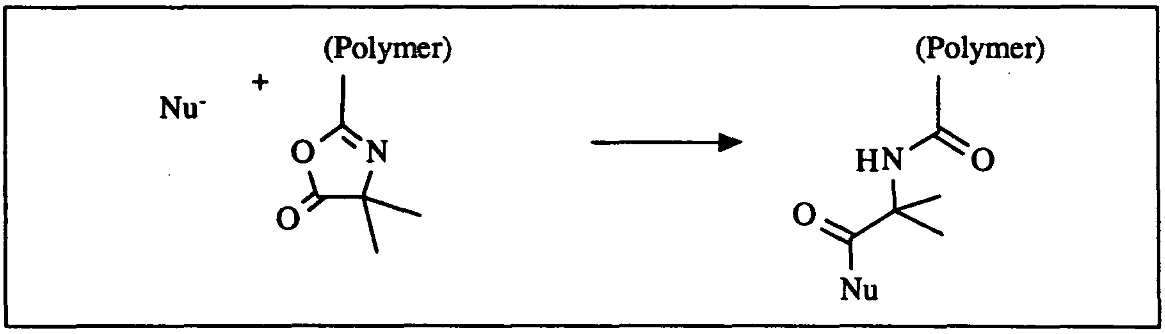
The monomer contains two functional groups in addition to the polymerizable vinyl group, an activated methyl ester and a methyl ether. The methyl ether can be crosslinked with amines at room temperature or with alcohols under acid catalysis. The use of MAGME therefore allows the preparation of isocyanate free room temperature curing coatings and acid catalysed coatings which do not evolve formaldehyde during curing.

Anhydride functional acrylates have been investigated as alternatives to two pack polyurethanes. The reaction of such polymers with hydroxyl or amine functional crosslinking agents leads to the formation of ester or amide crosslinks. The formation of adjacent carboxylic acid groups can however lead to problems with compatibility, stability and chemical resistance.[17]

Vinyloxazolones (commonly referred to as vinylazlactones) have been considered as an alternative to anhydrides, with the oxazolone ring showing a reactivity intermediate between isocyanates and epoxides.[18] Reaction of the oxazolone with a nucleophile does not lead to the formation of free carboxylic acid as shown in Figure 1.9:

Figure 1.9

Nucleophilic Ring Opening of an Azlactone



The oxazolones must be disubstituted in the 4 position to prevent rearrangements occurring during storage.[19,20]

1.2. Requirements For Alternative Crosslinking Systems

There is continual pressure on all industries to develop environmentally favourable products, this is reflected in demand for coatings with lower toxicity, reduced volatile organic content and in the case of baking systems in reduced baking schedules.

There are a number of general requirements which a potential new crosslinking system must possess, although clearly each type of coating application will have its own specific requirements.

The crosslinking reaction must occur a rate which provides both acceptable pot life and cure times. The system must posses low toxicity, and hence the components would ideally be non toxic. The chemistry must not be expensive and therefore any components must be readily synthesised by techniques capable of being scaled up to plant scale. In addition to the other factors, it is highly desirable that any potential crosslinking system should be patentable.

1.3. Consideration of the use of Cyclopropanes in Network Forming Polymers

In the previous section the types of crosslinking reactions currently employed in coating systems were discussed, and the desirability of utilising novel, low toxicity coatings was outlined. In this section the feasibility of employing ring-opening reactions of cyclopropane groups in a manner analogous to the use of epoxy groups is considered.

In order to merit investigation as potential crosslinking groups it must be demonstrated that cyclopropanes can undergo ring-opening under conditions appropriate for coatings applications. It must also be possible to incorporate cyclopropyl groups into polymers by a practical synthetic procedure. By analogy with epoxy resins there are possibly two methods to obtain networks from polymers containing cyclopropanes, by addition reactions with polyfunctional crosslinking agents or by ring opening polymerization.

1.3.a. Addition Reactions of Cyclopropanes

Cyclopropane and its derivatives undergo addition with electrophilic, radical and nucleophilic reagents.[21]

1.3.a.i. Electrophilic Additions

The first reported example of an electrophilic addition to cyclopropane was the formation of propyl iodide from the treatment of cyclopropane with hydrogen iodide, reported in 1881.[22] Bromine reacts with cyclopropane to give a mixture of products, the presence of iron(III)chloride, aluminium chloride or aluminium bromide increases the rate of reaction.[23] Cyclopropane alkylates benzene in the presence of aluminium chloride/hydrogen chloride or with anhydrous hydrogen fluoride to give n-propyl benzene.[24] Using sulphuric acid either n-propyl benzene or isopropyl benzene is obtained, depending on the reaction temperature. Cyclopropane reacts with carboxylic acids in the presence of boron trifluoride to form the corresponding esters.[25] Alkyl substituted cyclopropanes have generally provided similar results to cyclopropane, examples are available in reviews[21,26]

1.3.a.ii. Radical Additions

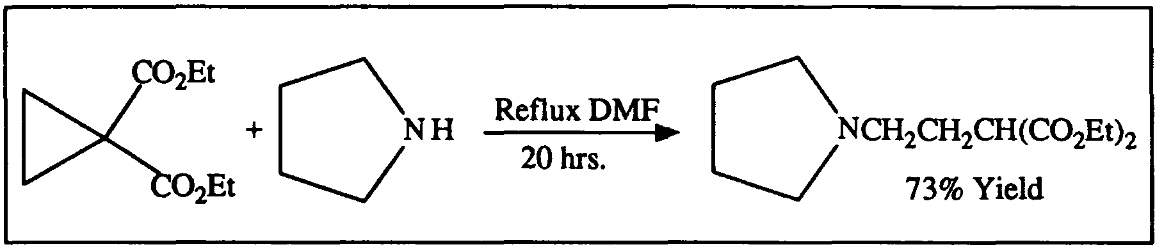
Radical additions of bromine and iodine to cyclopropane have been observed. With chlorine, substitution occurs rather than addition.

1.3.a.iii. Nucleophilic Additions

The addition of nucleophiles to a cyclopropane usually requires the presence of two geminally placed electron acceptor substituents. The majority of additions are 1,3 and can be considered analogous to the Michael addition of alkenes.[26,27] The reaction conditions are usually quite vigorous, reflecting the high energy required to break the strained carbon-carbon σ bond, as shown for example in Figure 1.10:

Figure 1.10

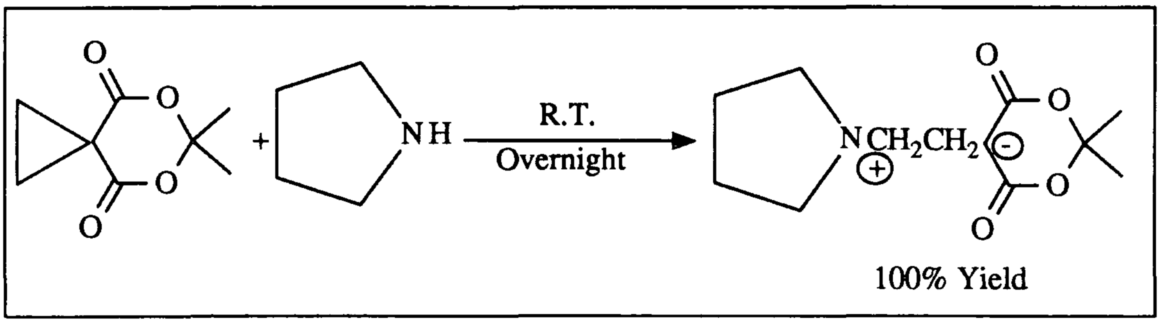
Nucleophilic Addition to a Cyclopropane in a Michael Type Addition



In order to activate the cyclopropane ring the carbonyl groups must be orthogonal to the ring, as this allows delocalization of the carbanion intermediate to occur. Danishevsky and Singh[28] found that if the carbonyls could be fixed orthogonal to the ring then the reactivity markedly increased, this is shown in Figure 1.11:

Figure 1.11

Nucleophilic Addition to a Cyclopropane With Carbonyls Fixed in an Orthogonal Position



Consideration of the addition reactions of cyclopropane derivatives suggests that, although in principle they offer a method of crosslinking, they do not appear to be very promising for initial studies into network forming systems.

The electrophilic substitution of benzene by cyclopropanes requires large amounts of acid, which makes it impractical as a crosslinking reaction. The limited scope of radical additions appear to offer no promise of obtaining useful systems.

The conditions required for nucleophilic additions are generally too severe to provide materials of practical use in coatings curing. An additional disadvantage of utilising nucleophilic addition reactions is that the nucleophilic reagents, such as amines, thiols or phenols are generally toxic, and are therefore best avoided if possible.

1.3.b. Ring Opening Polymerization of Cyclopropanes

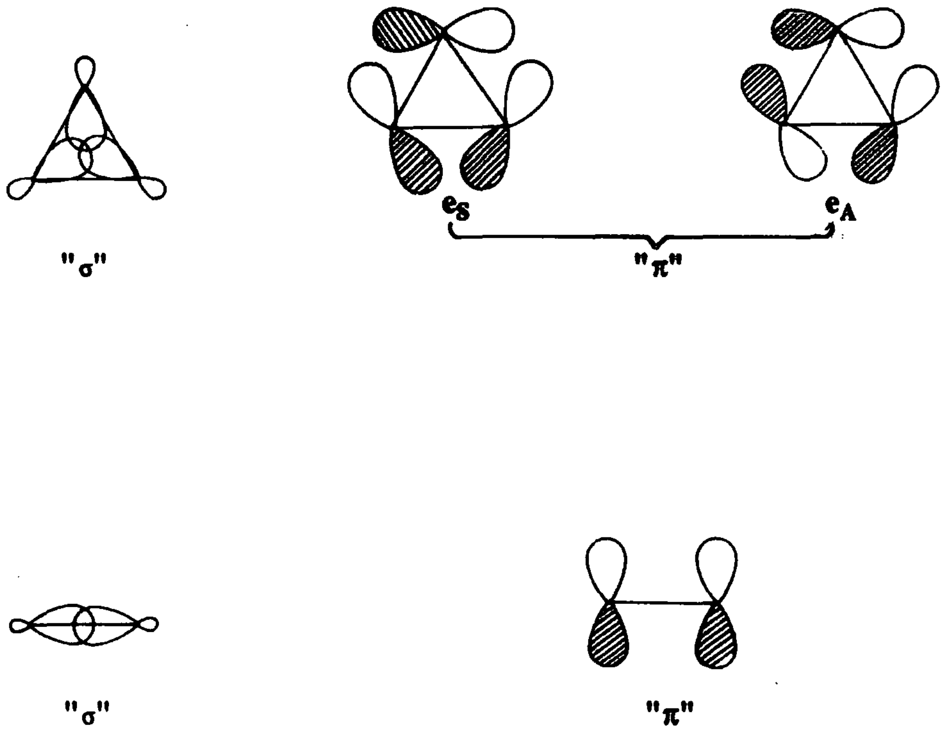
1.3.b.i Cyclopropanes as Monomers

There is a marked similarity between the bonding in alkenes and in cyclopropane, as a result the chemistry of the cyclopropyl ring closely resembles that of the carbon-carbon double bond.[21]

Using a molecular orbital (MO) model, the three occupied MO's determine the nature of the C-C bonds in the three membered ring.[29,30,31](see Figure 1.12).

Figure 1.12

Molecular Orbital Model Of Bonding in Cyclopropane and Ethene



The lowest energy orbital (σ) is a linear combination of the three sp^2 hybrid atomic orbitals (AO's), the other two orbitals (e_s and e_a) are equal energy combinations of three p AO's with different symmetry properties(these orbitals are referred to as π or "quasi" π). This MO description is very similar to the common description of a C=C double bond, containing one linear combination of two sp^2 AO's (σ MO) and two p AO's (π MO). The similarity extends to the fact that the LCAO (p AO's) are orthogonal to the sp^2 set.

In the valence bond (VB) model of cyclopropane the C-C bonds are considered to arise from the overlap of two hybrid orbitals at each carbon.

The 60° internuclear C-C-C bond angle is less than the natural bond angle of 109.5° for an sp^3 hybridised carbon, increasing the amount of p character in the orbitals reduces the natural bond angle, but even for a pure p orbital the natural bond angle is 90^0. The C-C σ bond orbitals in cyclopropane has more p character than sp^3 (between sp^4 and sp^5)[32], and the orbitals are directed out from the direction of bonding resulting in a 'bent' bond, as shown in Figure 1.13:

Figure 1.13

Valence Bond Model of Cyclopropane and Ethene

A further similarity between the bonding in cyclopropane and in alkenes is the participation of sp^2 hybrid orbitals of the carbon atoms in C-H bond formation. The C-H bond length of cyclopropane is therefore shorter than the normal aliphatic C-H bond(see ref 21 p524), the C-H bonding orbitals have been estimated to have 32% s character, based on measurements of the ^{13}C-H coupling constants.

The similarities between bonding in cyclopropanes and alkenes explains the similarity in behaviour between the two systems. Both cyclopropanes and alkenes react with electrophilic reagents, metal complexes, undergo addition reactions with strong acids, halogens, ozone: and undergo catalytic hydrogenation and cycloaddition.

The cyclopropane ring is highly strained, and it is the strain energy of the small ring which explains the reactivity of such systems. The ring strain can be determined from the difference in the heat of combustion for a cycloalkane to that for linear n-alkane of the same molecular weight.[33] There are three main components which give rise to ring strain. The main contribution (Angular strain) is due to the deformation of the C-C-C bond angles and the resulting smaller overlap of orbitals compared to n-alkanes, this is the classical description of ring strain of Von Bayer. Torsional strain arises from the CH$_2$ groups all being eclipsed, this effect is less marked than in ethane, due to the greater distance between hydrogens in cyclopropane. The third contribution is due to transannular Van der Waals repulsion between non-bonded atoms.

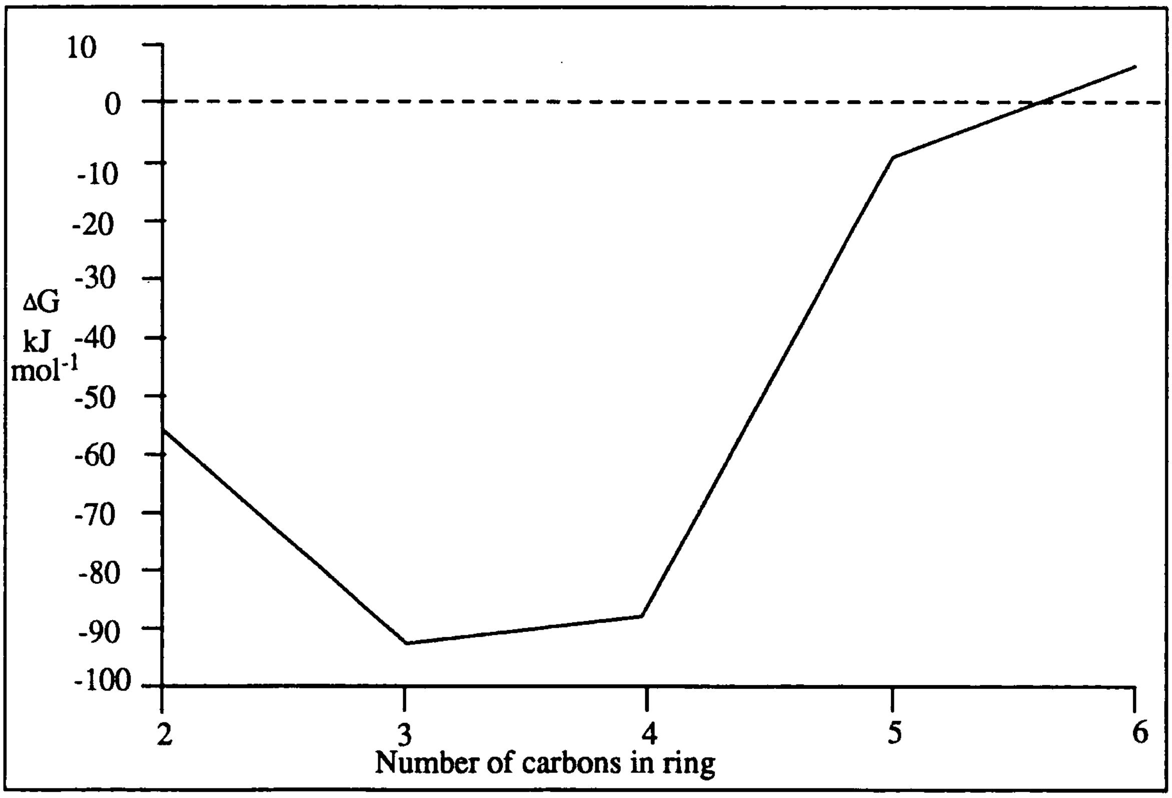
It is the relief of strain energy upon the formation of an alicyclic polymer which provides the thermodynamic driving force for the polymerization of cyclopropanes.

In order to successfully polymerize a monomer two thermodynamic criteria must be satisfied, the Gibbs free energy must be negative and the activation energy must not be too high.

The Gibbs free energy for the polymerization of cycloalkanes as a function of ring size can be calculated from literature values[34] of ΔS and ΔH, the results are shown graphically in Figure 1.14:

Figure 1.14

Plot of Gibb's Free Energy Function Against Ring Size for Cyclic Hydrocarbons



Consideration of the graph shows that polymerization of cyclopropane and cyclobutane are thermodynamically favourable provided a suitable mechanism is available. Unfortunately the cleavage of a carbon-carbon σ bond has a high activation energy, and there is not a good general pathway for the polymerization of cyclopropanes.

1.2.b.ii. Polymerization of Cyclopropane and Alkylcyclopropanes

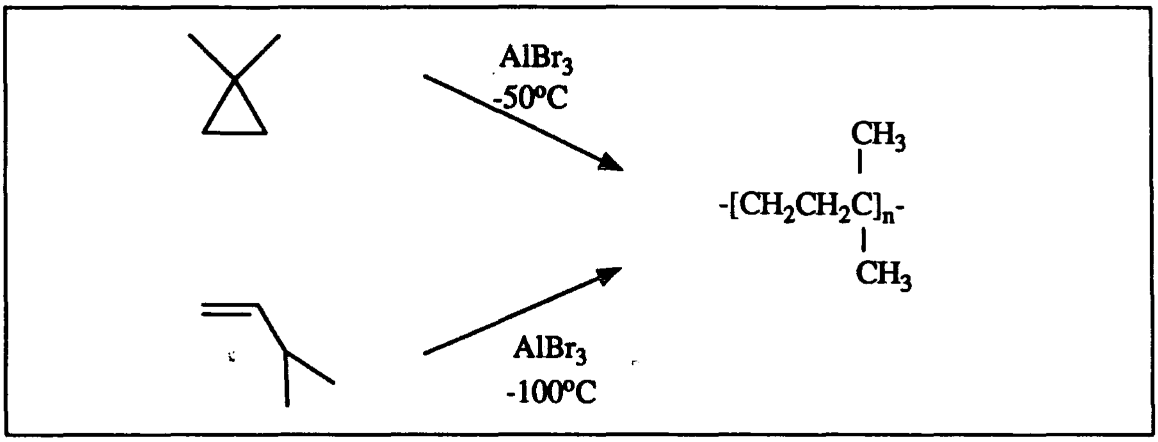
Cyclopropane was shown to alkylate benzene in a Friedel Crafts reaction in a similar way to olefins by Ipatieff and co-workers.[35,36] Cyclopropane was shown to polymerize in the gas phase in a mercury photosensitized reaction to give a low molecular weight polymer[37] and in heptane solution to give an uncharacterized polymer with a molecular weight lower than 700.[38]

Pines and co-workers investigated the isomerization accompanying the alkylation of benzene by alkylcyclopropanes,[39] then studied the isomerization of alkylcyclopropanes alone in the presence of aluminium halide catalysts[40] to determine whether isomerization to give hydrocarbons with 5- or 6-membered rings would occur. No formation of such cyclic compounds was observed, but instead polymerization occurred, 1,1-dimethylcyclopropane gave 100% yield of polymer initiated by $AlBr_3/HBr$, ethylcyclopropane gave 50% yield of polymer with no isomerization of unreacted monomer, while n-propylcyclopropane gave 90% yield of polymer with the rearrangement of unpolymerized material to form hexane and 2-methylpentane.

It was demonstrated[41] that the cationic polymerization of 1,1-dimethylcyclopropane gave a polymer with the same structure as that obtained from the low temperature polymerization of 3-methyl-1-butene, as shown in Figure 1.15:

Figure 1.15

Comparison Between the Polymerization of 1,1-Dimethylcyclopropane and 3-Methyl-1-butene



A similar result was obtained by Aoki,[42] who obtained oligomers from the aluminium bromide initiated polymerization of 1,1-dimethylcyclopropane. In copolymerizations with styrene the rate of polymerization of 1,1-dimethylcyclopropane was found to be markedly lower than the rate of polymerization of styrene. Both 1,1-dimethylcyclopropane and phenylcyclopropane underwent polymerization with a co-ordination catalyst (ethylaluminiumdichloride / titanium(III)chloride) to give resinous polymers with molecular weights of less than 1500, although other co-ordination catalysts failed to provide polymer.

The literature reports therefore suggest that the ring opening polymerization of cyclopropanes may merit investigation to provide a crosslinking system, if suitable methods for the incorporation of cyclopropyl groups into polymers are available.

1.3.c. Polymerization of Vinylcyclopropanes

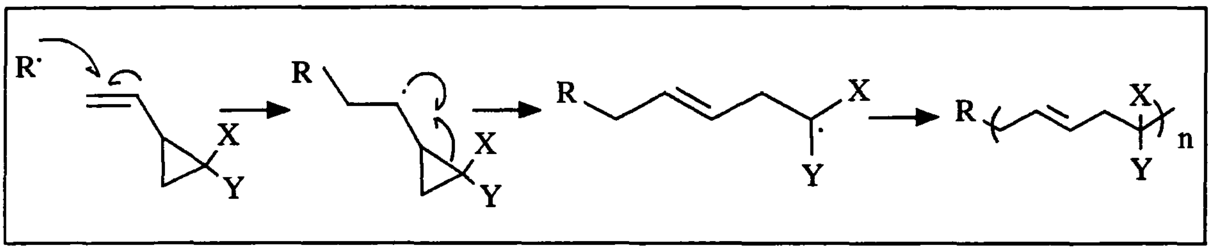
The polymerization of alkylcyclopropanes has been the subject of relatively little study, perhaps because only low molecular weight oils were obtained, by contrast the polymerization of vinylcyclopropanes has been widely investigated. Hall and Snow[43] have reviewed the polymerization of vinylcyclopropanes, which may be achieved by free radical, anionic, or cationic mechanisms.

1.3.c.i. Radical Polymerizations

The mechanism for the free radical initiated polymerization of vinylcyclopropanes is believed involve the addition of the radical to the double bond, giving a cyclopropyl substituted radical which isomerizes to give opening of the cyclopropyl ring.[43] The mechanism is shown in Figure 16:

Figure 1.16

Free Radical Polymerization of Vinylcyclopropanes

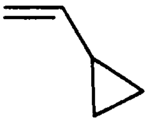
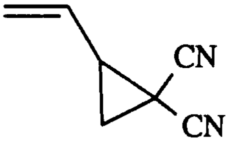
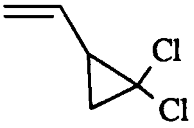


Support for this mechanism came from Takahashi and co-workers,[44] who found that the polymer obtained from the free radical polymerization of 1,1-dichloro-2-vinylcyclopropane contained nearly 100% 1,5 repeat units. The observation that 1,1-dichloro-2-ethylcyclopropane and 1-cyclopropyl-1-methylcyclopropane did not polymerize when heated with AIBN was taken as evidence that the cyclopropane skeleton itself was not opened by direct radical attack. Further evidence for the lack of a direct attack of radicals on the cyclopropyl skeleton was given by Hammond and Todd[45], who showed that cyclopropylnitrile and cyclopropyl methyl ketone both failed to polymerize in the presence of radical initiators.

The yield of polymers obtained by radical polymerization of vinylcyclopropanes is increased by the presence of electron withdrawing groups at the developing radical centre which can help to stabilise the radical intermediate,[46] this is demonstrated by the results shown in Figure 1.17:

Figure 1.17

Results for the Radical Polymerization of Some Vinylcyclopropanes

	CONDITIONS	% YIELD	REFERENCE
	0.53% BPO Neat 70°C 4 days	14	47
	5% BPO Neat 40 hrs	36	46
	0.48% AIBN 55°C 16 hrs	86.6	48

(BPO = Benzoyl peroxide)
(AIBN=2,2'Azobisisobutyronitrile)

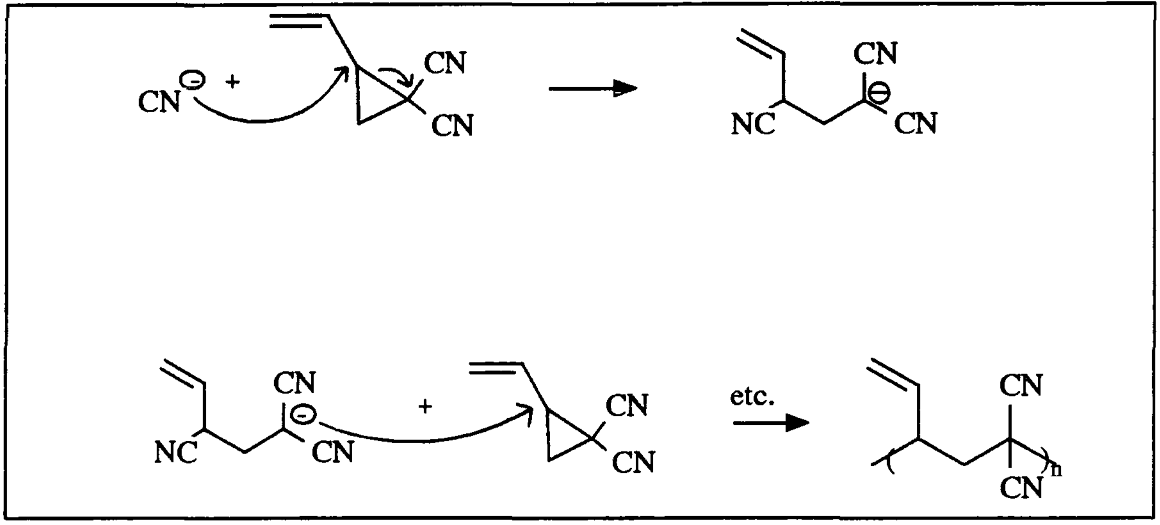
The diphenyl substituted monomer failed to polymerize, this was attributed to the excessive stability of the radical intermediate.[48] The polymers obtained from radical polymerization contain unsaturated polymer main chains, which is undesirable from the view of stability, as it provides sites for oxidative degradation.

1.3.c.ii. Anionic Polymerization

The anionic polymerization of vinylcyclopropanes containing at least one strongly electron withdrawing substituent can lead to high yields of polymer,the conversion is increased by increasing the electron withdrawing effect of the substituents. A mechanism has been proposed[46] involving direct attack at the cyclopropyl group which results in 3,5 addition, leading to the formation of polymers containing pendant vinyl groups, such polymers would be undesirable for the preparation of stable surface coatings. The mechanism is shown below in Figure 1.18:

Figure 1.18

Mechanism for the Anionic Polymerization of Vinylcyclopropanes

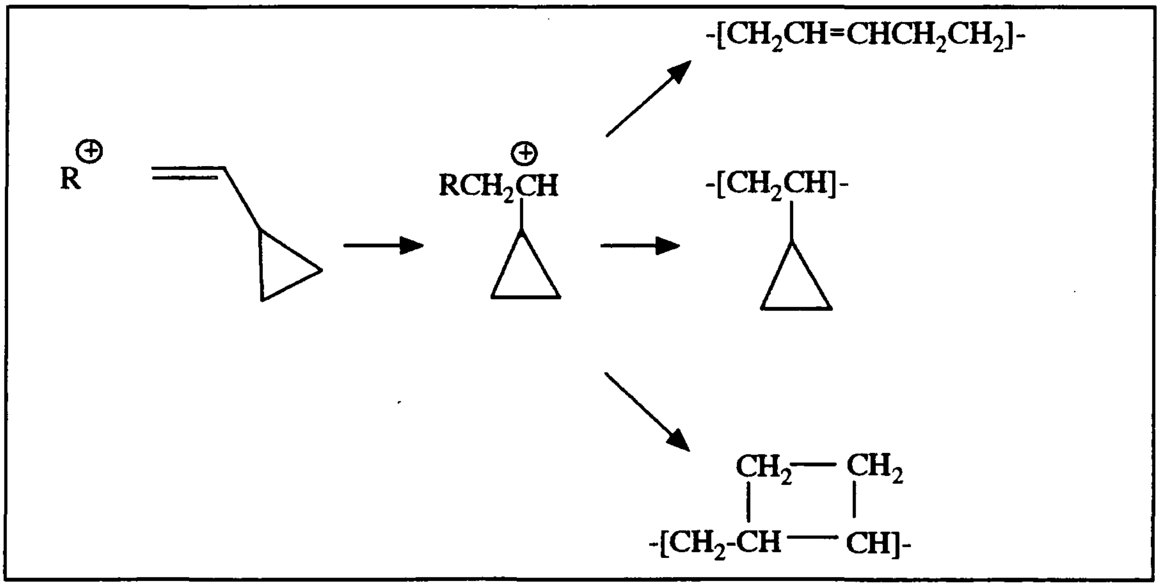


1.3.c.iii. Cationic Polymerization

Cationic polymerization of vinylcyclopropanes leads to polymers containing pendant cyclopropyl groups (1,2-polymerization), along with smaller amounts of 1,2-cyclobutane units and 1,5 units, as shown in Figure 1.19:

Figure 1.19

Cationic Polymerization of Vinylcyclopropanes



1.4. The Use of Cyclopropane in Anaesthesiology

The anaesthetic properties of cyclopropane were first discovered during a search for impurities in propene. Three other methyl substituted derivatives were tested as anaesthetics, methyl, dimethyl and trimethylcyclopropanes, which also proved to be powerful anaesthetics, however the numerous side effects in test animals (cats) precluded further investigation for use in anaesthesiology.[49]

The advantages of cyclopropane as an anaesthetic are the freedom from a drop in arterial blood pressure under anaesthesia and a rapid return to normal heart rate after recovery from anaesthesia.[50]

The flammability of cyclopropane compared to the more recently introduced halothane anaesthetics has been the main reason for the decline in its general use.

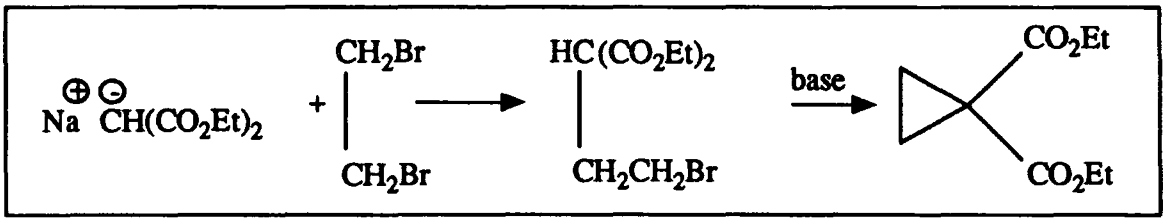
1.5. Synthesis of Cyclopropane Rings

A wide variety of functionalized cyclopropanes have been synthesised, and have found use in the synthesis of complex organic compounds[51,52,53]

The first systematic synthesis of cyclopropyl derivatives was reported by Perkin[54] in 1885 using the addition of malonic acid ester or acetoacetic ester with vicinal dihalides, as shown in Figure 1.20 below.

Figure 1.20

Perkin's Synthesis of Cyclopropane



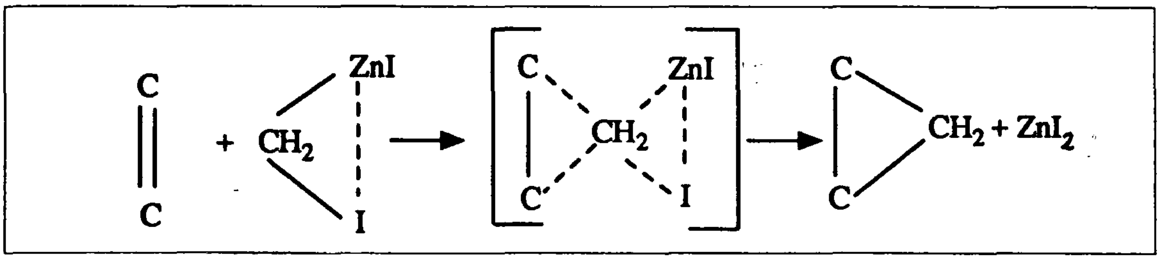
Other routes to cyclopropanes are provided in reviews[51,55] but many of the early methods suffered from the lack of general application to provide a wide range of products.

The most versatile procedures for the synthesis of cyclopropane derivatives involve the addition of carbenes or carbenoids to alkenes. The addition of diazomethane to simple alkenes leads to the formation of large amounts of side products which are difficult to separate from the required product.[56]

The insertion of a methylene group into the double bond of an alkene in a controlled, stereospecific manner was described by Simmons and Smith[57,58] using the reaction of diiodomethane and a zinc-copper couple in ether with a variety of olefins. The Simmons-Smith reaction has proved to be a versatile and convenient method for the synthesis of cyclopropanes. The exact nature of the intermediate has not been established, however it has been suggested[58,59] that the reaction is a one-step methylene transfer in which a quasi-trigonal methylene group of iodomethyl zinc adds to the alkene π bond, so that the new carbon-carbon bonds are formed essentially simultaneously, as shown in Figure 1.21.

Figure 1.21

Formation of the Cyclopropyl Ring in the Simmons-Smith Reaction

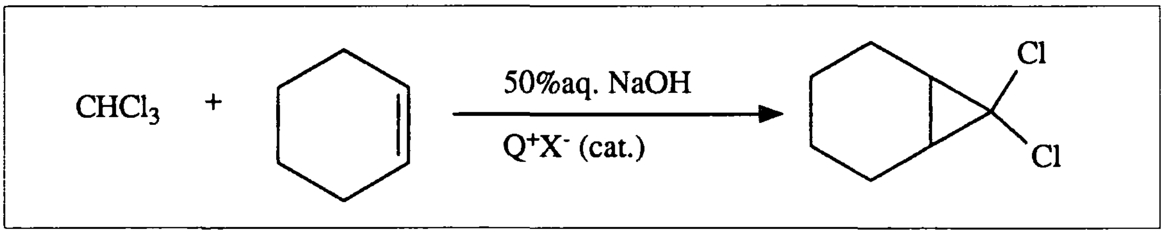


The scope of the usefulness of the reaction, and details of a number of modifications to the basic procedure are given in a review article.[59] Insertion of the methylene group in olefins occurs without attack at saturated carbons, unlike the case for the addition of free carbenes. The zinc reagent behaves as a weak electrophile towards the double bond, and hence the reactivity of the olefin increases with increased alkyl substitution on the double bond, unless this has an adverse steric effect.

The formation of dichlorocarbene generated from chloroform with aqueous base under phase transfer conditions was first reported in the late 1960's[60] and has provided a simple, high yield route to cyclopropanes. The reaction is shown in Figure 1.22

Figure 1.22

Formation of a Cyclopropane Ring by the Addition of Dichlorocarbene to an Alkene

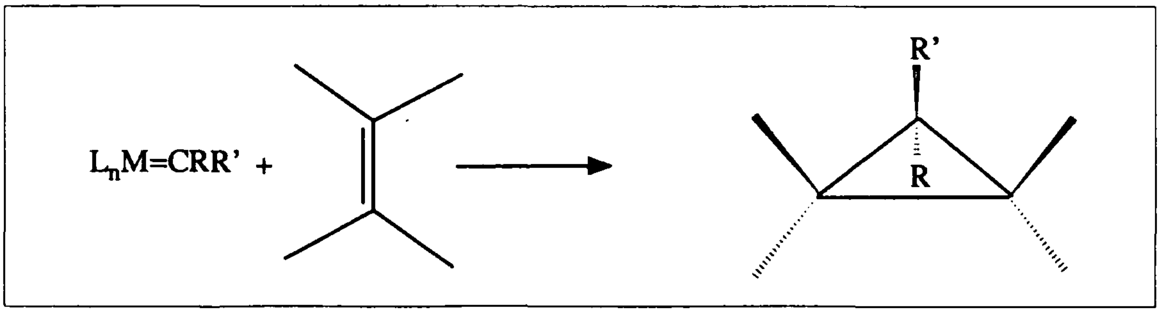


The 1,1-dichlorocyclopropanes obtained may be reduced with sodium in ethanol[61] or sodium in liquid ammonia[62] providing an alternative to the Simmons-Smith reaction. A wide range of cyclopropane derivatives have been synthesised utilizing this phase transfer catalysis procedure.[63,]

The reaction of transition metal carbene complexes with alkenes is another versatile synthetic route to a wide range of cyclopropane derivatives,[64] these reagents often provide reactivities which are complimentary to the techniques described previously. A generalised reaction scheme is shown in Figure 1.23

Figure 1.23

Formation of Cyclopropanes From the Reaction of a Metal Carbene With an Alkene



An advantage of the use of these reagents is their high selectivity and ability to prepare almost exclusively the sterically more crowded, thermodynamically less stable cyclopropane isomer. A further advantage in the use of the carbene complexes is their ability to be used where other carbenoid reagents are too unstable to give efficient transfers.

1.6. Previous Uses of Cyclopropanes in Polymer Crosslinking and Surface Coatings Applications.

Jones[65] noted the similarity between the chemistry of the cyclopropane ring and the ethylene bond, which led him to suggest that vinylcyclopropane and it's homologues and derivatives should be capable of polymerizing in a manner similar to that of isoprene. He proposed the use of vinylcyclopropane as a potential monomer for synthetic rubber and suggested that, "This unique hydrocarbon class will produce interesting results". Jones was subsequently granted two patents relating to the use of vinylcyclopropane in synthetic rubbers, one covering materials produced by free radical polymerization,[66] the secondrelating to materials produced by a cationic mechanism.[67] The patents describe the preparation of copolymers of vinylcyclopropane, and it's analogues, with styrene, although no structural details were reported. Based on literature reports for the polymerization of other vinylcyclopropanes it seems likely that two types of structural units would be derived from the two types of polymerization. Free radical initiated polymerization would be expected to lead to 1,5-polymerization, giving rise to unsaturated polymer backbones (see Section 1.3.c.i.), while cationically initiated polymerization would retain at least some cyclopropyl groups (see Section 1.3.c.ii.). It was claimed that polymers prepared by either method could be vulcanised with sulphur to provide materials which were elastic and resistant to solvents such as aromatic hydrocarbons and acetone.

Ketley[68] was granted a patent for the polymerization of 1,1-dichloro-2-vinylcyclopropane using an initiator prepared from titanium(III)chloride and a trialkylaluminium. The process was claimed to provide a stable film-forming polymer. Sartori and co-workers[69] described the copolymerization of olefins containing at least one cyclopropyl group with ethylene and propylene. The copolymers were completely saturated, and evidence for the presence of intact cyclopropane rings was provided from their IR spectra. The copolymers were vulcanized with mixtures based on peroxides and sulphur, to give products which were insoluble in hydrocarbons, and showed good mechanical properties. No evidence for the nature of the crosslinking process was provided.

Two patents utilising the ability of vinylcyclopropanes to undergo radical polymerization, to produce crosslinked polymers have been granted. Oligomeric polyesters prepared by the reaction of 2-vinyl-cyclopropane-1,1-dicarboxylic acid and 1,6 hexanediol were reacted with vinyl acetate and butyl acrylate in an emulsion polymerization to give a latex claimed to have "improved wet adhesion".[70] In a second patent oligomers prepared by the transesterification of vinylcyclopropane carboxylic acid ethyl ester and 1,6-hexane diol were irradiated in the presence of a radical initiator with low intensity light to give a tack free coating after 3 seconds irradiation.[71]

1.7. Conclusions

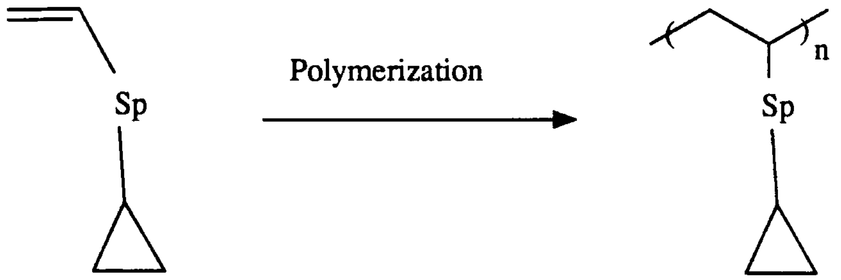
The combination of the low toxicity of cyclopropane with the ability of cyclopropyl groups to undergo ring opening polymerization suggested that it may, in principle, be possible to utilize polymers containing cyclopropyl groups in a crosslinking surface coating.

The general concept for such a system is shown schematically below in Figure 1.24.

Figure 1.24

Stage 1

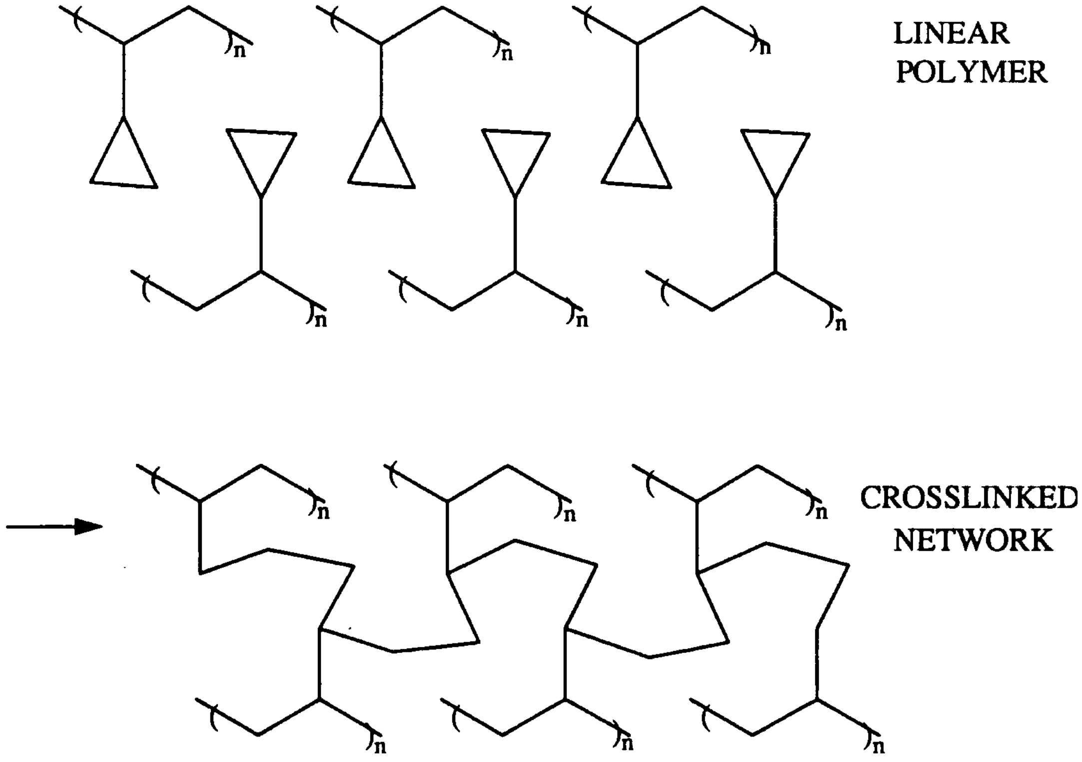
Formation of Linear Polymers With Pendant Cyclopropyl Groups



Sp = Spacer Group

Stage2

Ring Opening Polymerization of Cyclopropyl Groups to Form a Network



There are several requirements that such a system must fulfil in order to provide a viable crosslinkable coating.

A suitable polymerization initiator must be available, which will polymerize the monomer through the vinyl group while leaving the cyclopropyl group intact.

The spacer group should provide a simple synthetic procedure for combining the cyclopropyl and vinyl groups, while allowing scope for the variation in the length and bulk of the spacer group. Additionally the spacer group must not interfere with either the polymerization or the subsequent crosslinking reaction.

Consideration of the literature reports for the synthesis and polymerization of cyclopropanes led to the conclusion that the concept was worthy of further investigation, although clearly there were likely to be problems encountered in obtaining suitable conditions for the polymerization and crosslinking reactions.

CHAPTER 2

THE SYNTHESIS AND POLYMERIZATION OF VINYL MONOMERS CONTAINING CYCLOPROPYL GROUPS

Introduction

In Chapter One the need for vinyl monomers containing at least one cyclopropyl group, to allow the synthesis of linear polymers containing pendant cyclopropyl units was outlined.

In this chapter a brief history of the development of the project is given.

The initial route chosen involved the use of cyclopropyl acrylates, this proved to be unsatisfactory and it was decided that an all hydrocarbon system was required. Polymerization of alkenyl cyclopropanes has been reported using cationic initiators and Ziegler-Natta catalysts. The application of various types of Ziegler-Natta catalysts to provide linear polymers with pendant cyclopropyl groups were considered. The main features of the catalyst types available is discussed, then a brief summary of the work carried out in our study is given. The possibility of using cationic initiated polymerization was also considered but appeared less satisfactory.

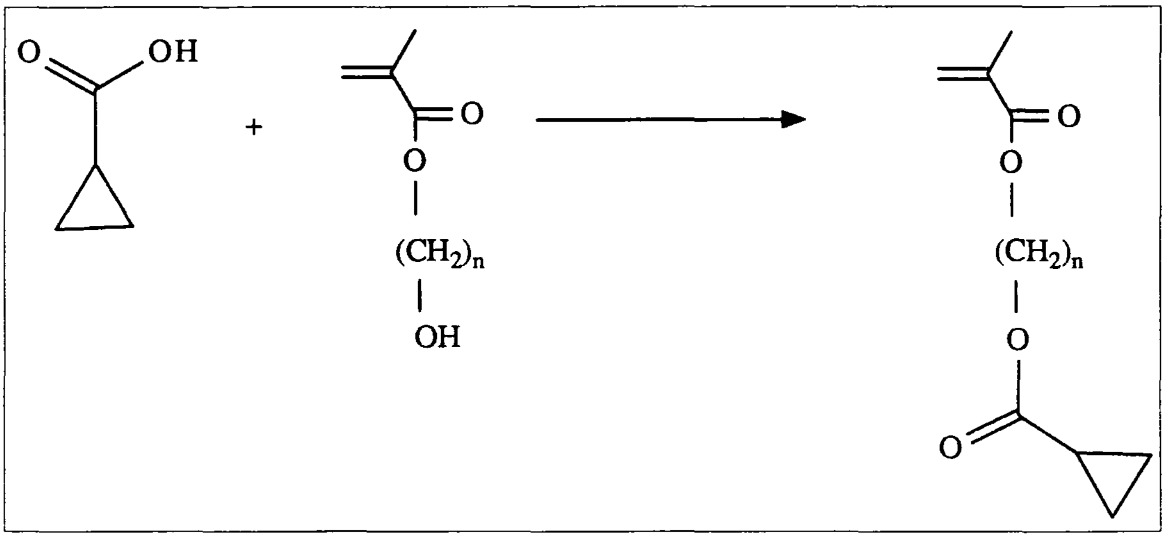
2.1. Cyclopropyl Acrylates

Our initial synthetic approach towards the required monomers was to produce esters of acrylic and methacrylic acid containing cyclopropyl groups. Acrylic resins are widely employed in the surface coatings industry, and therefore the chemical plant and experience require for the polymerization of acrylic monomers is readily available. Acrylate polymers can be obtained by the use of free radical initiated polymerizations, which are experimentally simple to manipulate, and provide the potential for simple control of both polymer molecular weight distribution and of copolymer compositions. By far the cheapest cyclopropane derivative available is cyclopropane carboxylic acid, and therefore this appeared to be the most suitable material with which to begin our investigation.

The simplest synthetic approach is via esterification of hydroxyl functional acrylates or methacrylates with cyclopropane carboxylic acid, as shown in Figure 2.1.

Figure 2.1

Formation of Acrylates Containing Cyclopropyl Groups



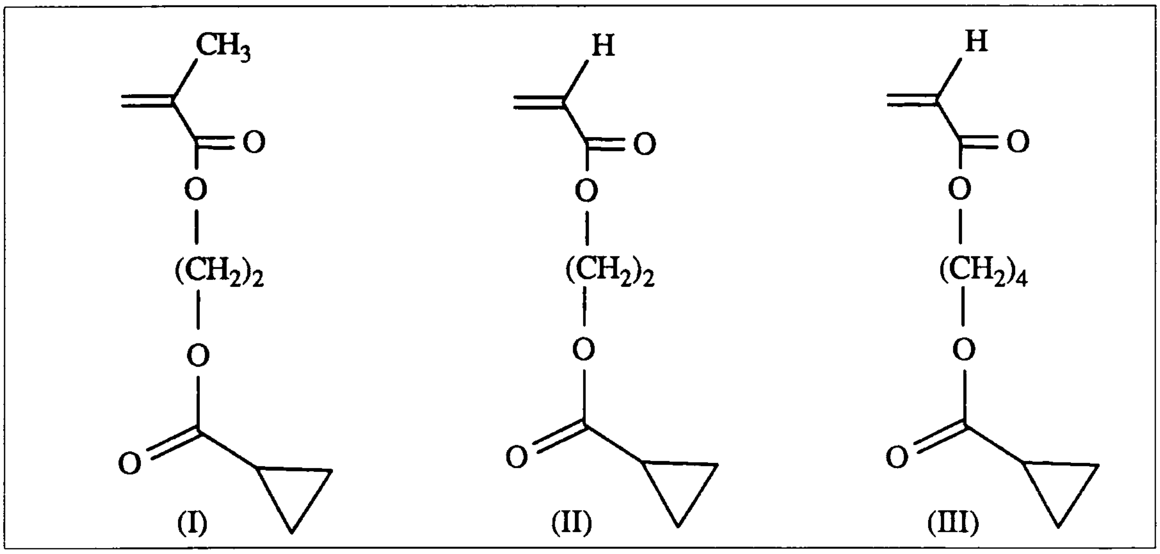
Hydroxyl functional acrylates and methacrylates are available as bulk industrial products and therefore this route provided the potential advantage of allowing a simple scale-up procedure. A further advantage was that the size of the spacer group could easily be altered by varying the value of n.

Alternative routes for the synthesis of acrylic resins containing cyclopropyl groups were also feasible, using commercially available cyclopropane derivatives. Cyclopropylamine and cyclopropyl methanol are both commercially available, and would be expected to react with acrylic acid in high yield, however both are markedly more expensive than cyclopropane carboxylic acid.

As part of our investigation acrylate and methacrylate monomers were prepared from cyclopropane carboxylic acid. The monomer structures are shown in Figure 2.2.

Figure 2.2

Structures of Acrylate and Methacrylate Monomers



The synthesis and characterization of the homopolymers of these monomers was undertaken.

Investigation of the cationically initiated ring opening polymerization of the polymers revealed the basic flaw in this approach. The ester groups prevented cationic polymerization, presumably due to complexation with the cationic initiating species. Model studies showed that ether or ketone groups also prevented the cationic ring opening polymerization of the cyclopropane rings.

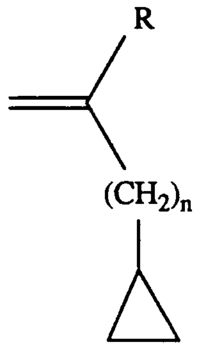
With the benefit of hindsight, the naivety of this approach is well summarized by the comments of Kennedy and Marechal[72] regarding the choice of suitable alkene monomers for cationic polymerizations. "***It is a truism, nonetheless often overlooked, that the double bond system must be the most nucleophilic site in the monomer***"

The details of the investigation into the use of acrylates are given in Appendix 1.

2.2. Hydrocarbon Polymers

The results from our work on acrylate monomers led to the conclusion that an all hydrocarbon polymer was required in order to allow crosslinking via ring opening polymerization of the cyclopropane ring. Monomers of the type shown in Figure 2.3 were required.

Figure 2.3



(R = H or Alkyl)

Networks produced from this type of monomer would be essentially saturated hydrocarbons. The coatings obtained from such materials might show interesting properties, and additionally they might be suitable for applications in which poly(ethene) and poly(propene) are currently used.

In addition to its widespread use in packaging films, poly(ethene) finds application in sheathing electrical cables, where its ability to provide insulation without causing losses at high frequency is extremely valuable in T.V., radar and multicircuit long distance telephone lines. The high resistance to attack by a wide range of chemicals makes poly(ethene) valuable for use in pipeworks. Crosslinking poly(ethene) to provide a thermosetting material combines low cost, easy processing and chemical resistance with improved tensile strength and resistance to stress cracking. Crosslinking can be achieved by chemical methods, in which the polymer is heated with dicumyl peroxide or di-t-butyl peroxide to initiate radical reactions, or by radiation using an electron beam. The chemical crosslinking process is used in the wire and cable industry and is of interest for the manufacture of moulded articles. Poly(propene) also has excellent chemical and moisture resistance, although it is more sensitive to heat, light and oxidative attack due the presence of tertiary hydrogens on the backbone. Copolymers of ethene and propene are used as elastomers, often with the incorporation of diene comonomers to provide sites for crosslinking.

As described in Chapter One, a method of polymerizing the monomer through the vinyl group while leaving the cyclopropyl group intact was required. There appeared to be two main potential methods available, cationically initiated polymerization, or Ziegler-Natta polymerization. The literature methods for the monomer synthesis and polymerization are considered in the next sections.

2.3. Synthesis of Cyclopropanes Using the Simmons-Smith Reaction

Methods for the synthesis of cyclopropane rings were discussed briefly in Chapter One. The Simmons-Smith reaction appears to have been the most widely employed procedure for the formation of cyclopropanes, as it gives high yields from a one step reaction. The effect of variations in the experimental conditions are now considered in more detail.

2.3.a. Experimental Considerations

In the original procedure[67,58] for the Simmons-Smith reaction a zinc-copper couple was prepared by the reaction of zinc dust, copper(I)oxide and hydrogen at 500°C, the couple was subsequently activated by the addition of a trace of iodine. Shank and Schechter[73] used a simpler procedure, by washing zinc powder successively with hydrochloric acid, aqueous copper(II)sulphate, water, ethanol and finally diethyl ether. The advantages of this method are the ease of preparation combined with reproducible high yields of cyclopropanes. LeGoff[74] described a method for the preparation of a highly active couple by refluxing zinc dust with copper(II)acetate in acetic acid, followed by washing with diethylether. A particularly convenient method for the formation of the zinc-copper couple was introduced by Rawson and Harrison[75], in which the couple is prepared in situ by refluxing a mixture of zinc dust with copper(I)chloride in diethyl ether. Alternative zinc reagents have also been employed instead of the zinc-copper couples.

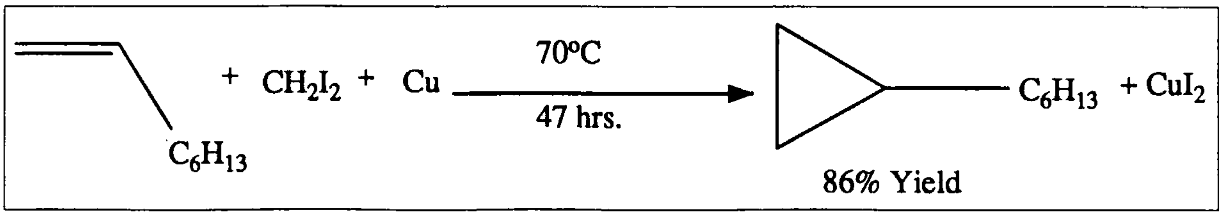
Conia, Denis and Girard[76] prepared a zinc-silver couple by heating granular zinc and silver acetate in acetic acid. This couple is more active than the zinc-copper couples, and therefore requires a smaller excess of couple.

Diethylzinc can be used as a replacement for zinc-copper couples to provide the corresponding cyclopropane in high yield.[77,78] The reaction between diethylzinc and diiodomethane is homogeneous, and therefore the formation of the active species is rapid by comparison with the use of zinc powder. Diethylzinc has been described as being especially useful for the conversion of cationically polymerizable alkenes to cyclopropanes,[79] where a conventional zinc-copper couple causes some polymerization. Diethylzinc allows other gem dihalides to be used, for example 1,1-dibromoethane[77] to provide methyl substituted cyclopropanes.

It has been reported that ultrasound can be used to activate the surface of the zinc-copper couple,[80,81] and it allows the use of dibromomethane, rather than the more expensive diiodomethane.[82] The addition of a small amount of titanium tetrachloride[83] or acetyl chloride[84] has also been found to improve the yields of cyclopropanes, possibly by the removal of traces of water form the reaction mixture. The use of copper powder as a replacement for the zinc-copper couple has been reported,[85,86] with several advantages being claimed regarding the greater simplicity of this procedure. Commercial grade copper powder was used without further purification, the reaction was not very sensitive to moisture, and the inorganic residues could be removed by simple filtration. An example of the use of copper is given in Figure 2.4:

Figure 2.4

The Use of Copper in the Simmons-Smith Reaction

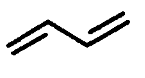
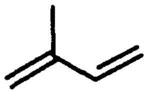
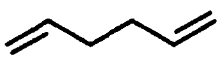
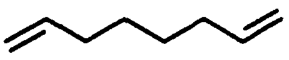


The choice of solvent can have an important effect on the yields obtained in the Simmons-Smith reaction.[59] The solvent must support the heterogeneous reaction between diiodomethane and zinc, stabilize the zinc intermediate involved in methylene transfer, and not solvate the zinc intermediate so strongly that it interferes with the methylene transfer process. Ethers promote the reaction of diiodomethane with zinc-copper couple, the order of reactivity is dimethoxyethane > tetrahydrofuran > diethyl ether. The ethers also react with the zinc intermediate, and the order of reactivity for this undesirable side reaction is the same as for the promotion of the reaction of the diiodomethane with zinc. The choice of suitable solvent therefore requires a compromise, and diethyl ether generally provides the best results.

2.3.b. Synthesis of Alkenylcyclopropanes

The reaction of dienes (shown in Figure 2.5) in the Simmons-Smith reaction has been employed to prepare several alkenylcyclopropanes.

Figure 2.5

Diene	Ref.
	87,88
	44,89,90
	57,88
	91

The ratio of mono to bis products can be altered by varying the ratio of reagents.

A general feature of the Simmons-Smith reaction involving dienes with different degrees of substitution is that the most substituted double bond generally shows the greatest reactivity. This is illustrated by the reaction of an excess of 2-methyl-1,3-butadiene with zinc-copper couple, in which the product contained an approximate ratio of 3:1 of 1,2 addition product: 3,4-addition and about 5% bis product.[90]

2.4. Earlier Polymerizations of Alkenylcyclopropanes to Provide Polymers With Pendant Cyclopropyl Groups.

In order to produce well characterized polymers for subsequent crosslinking studies it is important that polymerization occurs only through the double bond, leaving the cyclopropane groups intact.

2.4.a Cationic Polymerization

As discussed in Chapter One, the cationic polymerization of vinylcyclopropanes generally leads to a mixture of 1,2 and 1,5 addition, along with the formation of some cyclobutane units in the backbone, arising from re-arrangement of the growing cation. Takahashi[44,47] studied the polymerization of several vinylcyclopropanes, using radical, cationic and co-ordination catalysts. Polymerization of vinylcyclopropane initiated by aluminium bromide provided a 38% yield of a polymer which was insoluble in a wide range of organic solvents and hence was probably crosslinked due to ring opening of some of the cyclopropane units in addition to polymerization through the vinyl group. Initiation by tin(IV)chloride gave a completely soluble polymer. The IR spectra of both polymers were identical, and showed maxima at 965cm^{-1} due to trans double bonds arising from 1,5-polymerization. The polymerization of 2-cyclopropyl propene initiated by tin(IV)chloride gave a 72% yield of low molecular weight polymer which contained 100% 1,2 repeat units. The occurrence of only 1,2- addition was explained as being due to the stability of the tertiary carbocation intermediate. These results suggested that it may be possible to obtain some suitable hydrocarbon polymers from cationic polymerizations, but that this procedure was unlikely to be completely satisfactory.

2.4.b. Ziegler-Natta Polymerization

The polymerization of alkenyl cyclopropenes initiated by Ziegler-Natta catalysts has been the subject of only a few studies. Natta used α-titanium(III)chloride / triisobutylaluminium to polymerize vinyl cyclopropane, giving 76% yield[92] of isotactic polymer which was insoluble in n-heptane, hydrogenation of this material gave a soluble product.

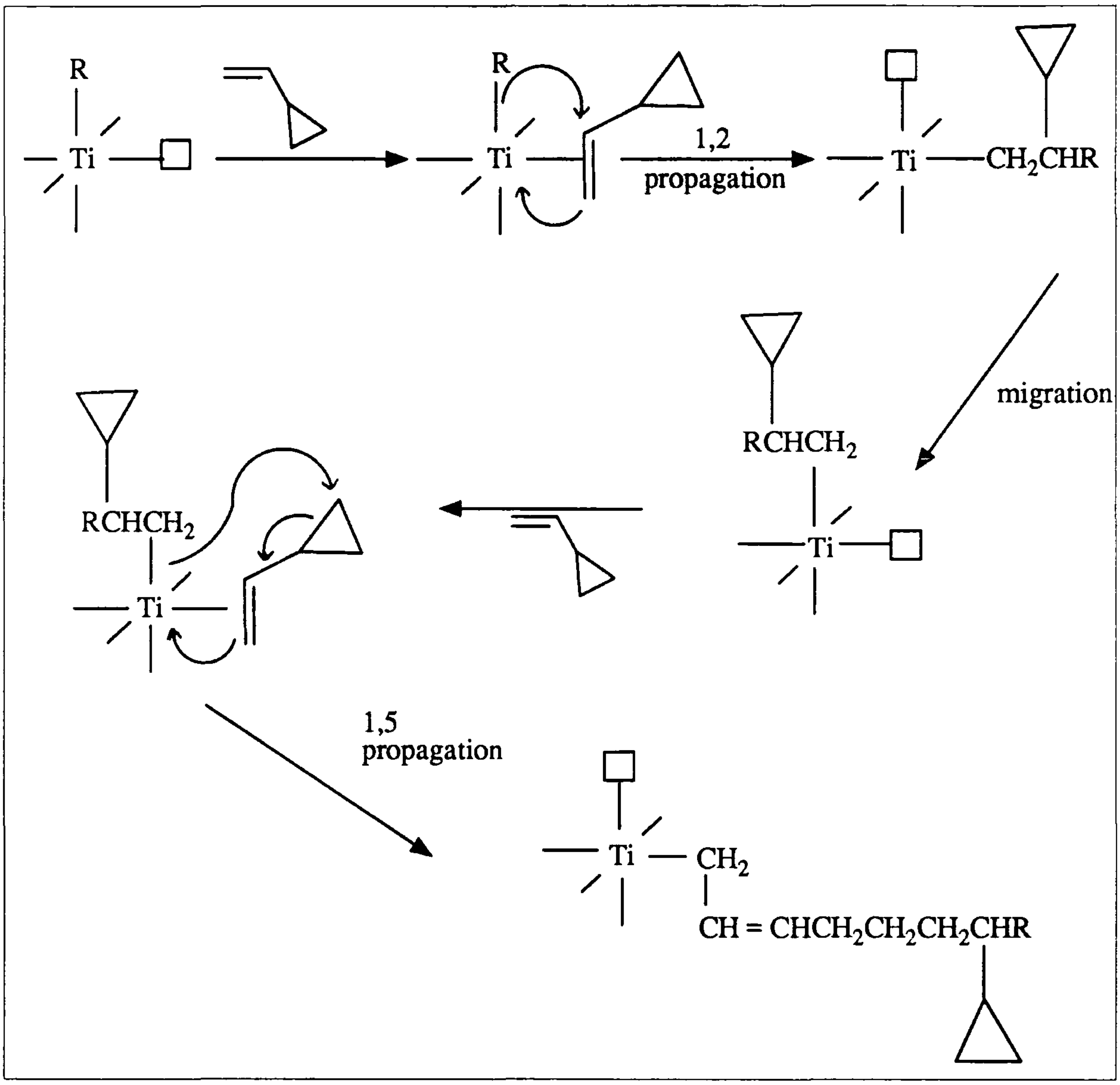
Takahashi[44] polymerized 2-cyclopropyl propene using titanium(IV)chloride/triethylaluminium catalyst to provide 7% yield of 1,2-addition polymer.

Overberger[87] used titanium(III)chloride/diethylaluminiumchloride catalyst to polymerize vinylcyclopropane in 26% yield. The polymer was mainly (79%) isotactic, some amorphous polymer was obtained which was found to contain mainly 1,2-repeat units with a smaller number of 1,5 units. By analogy with the Cossee-Arlman model[93-95] a mechanism was proposed which explained the incorporation of 1,5 units, see Figure 2.6

In the Cossee-Arlman model the active site of the catalyst is an octahedrally co-ordinated titanium at the surface of the catalyst. The titanium has an alkyl group attached, which arises from the alkylaluminium co-catalyst, and has a vacant octahedral position. The first step in the polymerization of an alkene is the co-ordination, through the π system of the double bond, to the vacant position. The next step is a concerted process in which the alkyl group migrates onto carbon-2 of the alkene while the alkene forms a σ bond with the metal through carbon-1. The growing polymer chain then has to migrate to the original site of the vacancy, before the addition of the next monomer unit takes place. In the polymerization of vinylcyclopropane 'abnormal' alkylation was postulated to occur by the attack of the growing polymer chain onto the cyclopropane group at carbon-5 instead of at carbon-2 in the usual process.

Figure 2.6

Polymerization of Vinylcyclopropane Using a Ziegler-Natta Catalyst



The addition reactions of the poly(vinyl cyclopropane) with hydrogen bromide, acetic acid, sulphur dioxide and hydrogen were also studied by Overberger. Addition of hydrogen bromide gave mainly poly(3-bromo-1-pentene), with the formation of some cyclohexane rings due to the reaction of adjacent cyclopropyl units.

The synthesis and polymerization of 6-cyclopropyl-1-hexene has been reported in a patent relating to the production of cross-linkable materials.[91] Terpolymers of ethene, propene and 6-cyclopropyl-1-hexene were heated with carbon black, sulphur and dicumyl peroxide to give vulcanized materials showing good mechanical properties.

2.4.c. Conclusions From Previous Work

The results obtained by previous workers show that alkenyl cyclopropanes can be conveniently synthesised, and are capable of undergoing polymerization with either cationic initiators or with co-ordination catalysts. Because of the tendency for cationic polymerization to cause ring opening of cyclopropanes, it appeared that the use of Ziegler-Natta catalysts was the most desirable approach.

In order to obtain materials of potential use for surface coatings the polymerization method must provide polymers with a known structure, allow the control of molecular weight and molecular weight distribution.

Before considering the application of co-ordination catalysts for our specific use it is useful to consider the relevant features of the main types of Ziegler-Natta catalysts.

2.5. Ziegler-Natta Polymerization

The original method for the production of poly(ethene) employed free radical polymerization at high temperatures (up to 250°C) and pressures (typically between 1000-3000 atmospheres).

The free radical polymerization is often carried out using continuous flow processes in stainless steel tubular reactors (which are similar in appearance to the barrel of a long range artillery weapon capable of firing a 1m diameter shell several hundred miles, or part of a satellite launching system). The poly(ethene) produced by the free radical process is highly branched, and typically has a density of between 0.91-0.94 $g.cm^{-3}$; it is referred to as low density poly(ethene).

Ziegler and co-workers[96] discovered that ethene could be polymerized at moderate temperatures and pressures, using catalysts prepared from alkyl aluminium compounds and transition metal halides. The poly(ethene) obtained using the new class of catalysts was highly linear. Linear poly(ethene) provides improved stiffness, tensile strength, hardness, resistance to vapour permeability and slightly improved resistance to chemical attack compared to low density poly(ethene).[97] Natta and co-workers[98] extended the scope of the catalysts to the homopolymerization of propene and higher α-alkenes to produce high molecular weight linear polymers.

The commercial exploitation of Ziegler-Natta polymerization has led to the formation of huge production facilities for materials which have become essential commodities in modern society. In view of the tremendous commercial importance of these polymerization processes a great deal of research has been undertaken into the development of Ziegler-Natta catalysts. For the present discussion it is only necessary to consider the main features of the various types of Ziegler-Natta catalysts, there are many review articles available which cover the subject in greater detail, recent reviews are available in reference 99.

In this discussion the catalysts will be considered in two broad categories, heterogeneous and homogeneous systems.

2.5.a. Heterogeneous Catalysts

Ziegler used a catalyst prepared by the reaction of a soluble transition metal halide, for example titanium(IV)chloride, with a soluble metal alkyl to give a precipitate of catalyst. Natta employed solid metal halides, such as titanium(III)chloride, which were reacted with trialkyl aluminium to provide catalysts which gave higher yields in the polymerization of propene, and increased the amount of isotactic polymer. Titanium(III)chloride can exist in four different crystalline forms,[100] which display different catalytic activities and stereospecificities. The δ form is more active than either the α or γ modifications for the preparation of isotactic poly(propene), while the β form gives mainly atactic polymer.

The method of preparation of the titanium(III)chloride determines the crystalline form produced. There have been a large number of different procedures developed commercially with the aim of obtaining catalysts giving high activity and stereospecificity. One of the most widely used type of titanium(III)chloride is a solid solution of δ $TiCl_3/0.33AlCl_3$, prepared by reacting aluminium metal or alkyl aluminium with titanium(III)chloride followed by ball milling the product.[101] The choice of alkyl aluminium also has an effect on both the activity and stereoselectivity of the catalyst, for example triethylaluminium provides greater activity for the polymerization of propene, but decreases the proportion of isotactic polymer.

Because the polymerization takes place at the surface of crystallites, the rate of polymerization is dependant on the particle size of the catalyst and on the particle morphology. In the case of δ titanium(III)chloride the solid consists of primary crystallites of approximately 0.03-0.7μm in diameter[95,102] which form loose agglomerates of approximately 20-40μm diameter. During the initial stages of polymerization polymer grows within the interstices of the solid, the growing polymer chains cause the disintegration of the agglomerates which leads to an increase in the surface area, and hence to an increase in the rate.

A feature of the heterogeneous catalysts is that polymers with broad molecular weight distributions are obtained. The catalysts provide mainly isotactic poly(propene) with smaller amounts of atactic polymer. These observations led Natta to propose that the catalyst contained two major kinds of active site. The active sites which lead to the formation of isotactic polymer must exert stereocontrol on the approach of the monomer towards the catalyst and therefore such sites are sterically hindered. The sites leading to atactic polymer are more readily accessible to the monomer. Increased stereoregularity can be achieved by the addition of carefully controlled amounts of Lewis bases such as ethers, amines, ketones or esters. The addition of these materials was generally found to lead to a reduction in the catalyst activity, but increases the stereospecificity. Several modes of action have been described for effect of the Lewis bases.[99] The non-specific catalyst sites are more exposed and therefore the Lewis base will tend to react with these first, leaving the more hindered stereospecific sites intact. The formation of the active sites leads to the formation of alkyl aluminium dihalides, which act as poisons, the Lewis base can complex these species, preventing deactivation of the catalyst.

In the first generation of titanium(III)chloride catalysts fewer than 1% of titanium atoms are involved in active centres.[103] Because polymerization only occurs at the catalyst surface, considerable research has been undertaken into supporting the active transition metal species on inert matrices. Magnesium chloride has proved to be an exceptionally valuable support, this is believed to be largely due to the similarity in the ionic radii of Mg^{2+} (0.65 Å) and Ti^{4+} (0.68 Å) which allows titanium to replace magnesium in the crystal lattice. The production of magnesium chloride supported catalysts is a complex process and requires several components, an 'internal' Lewis base, an 'external' Lewis base and an activator. In a typical catalyst preparation the first stage is to ball mill the magnesium chloride and internal Lewis base such as ethylbenzoate. The milling leads to an increase in surface area, and reduction in crystallite dimensions[104] and forms lattice defects which produce similar structures to the structure of δ titanium(III)chloride.[105] It has been found that nearly all of the surface sites of the magnesium chloride are covered by ethyl benzoate[106] which helps to prevent re-agglomeration of the particles. The ball-milled material is then treated with hot titanium(IV)chloride, displacing some of the ethylbenzoate, before activation by the addition of trialkyl aluminium. In order to achieve high stereoselectivity for propene polymerization it is necessary to add a further Lewis base (the 'external donor'). The exact nature of the active sites in these catalysts remains unresolved, as does the exact mode of action of the external donor, although part of the role is to remove non-selective sites.

A further development of these catalyst systems has resulted in the introduction of super high activity (SHAC) catalysts[107] which are believed to contain only one type of active site.

2.5.b. Homogeneous Catalysts

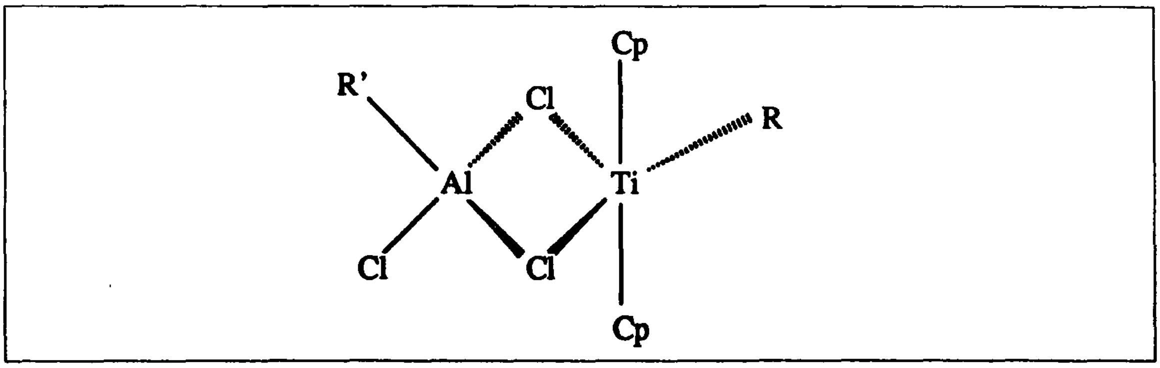
2.5.b.i. Vanadium Catalysts

Syndiotactic poly(propene) can be obtained by the use of homogeneous vanadium catalysts at low temperatures.[108] At temperatures above -50°C atactic polymer is produced and the catalyst rapidly loses its activity. Polymerization at -78°C allows very narrow molecular weight distributions to be achieved,[109] with M_w/M_n in the range 1.05-1.2. The activity of these catalysts is generally low compared to the supported titanium(III)chloride systems and the activity rapidly declines due to reduction of the vanadium. The life can prolonged by the addition of a Lewis base such as anisole.

2.5.b.ii. Metallocene Catalysts

The earliest homogeneous Ziegler-Natta catalyst system to be studied was bis(cyclopentadienyl)titanium dichloride.[110-112] The catalytic activity rapidly decayed with time due to the reduction of the titanium so that the overall activity was poor. The catalyst system was also unable to polymerize propene or higher α-alkenes. The homogeneous catalyst was therefore of limited usefulness in obtaining polymer, but proved valuable as a model to help understand the mechanism for polymerization in heterogeneous systems. The catalyst system was studied in detail by Henrici-Olivé and Olivé,[113] who showed that the active catalyst contains a Ti^{4+}species. The catalytic activity declines as the Ti^{4+} is reduced to Ti^{3+}. A model structure for the active species is shown in Figure 2.7.

Figure 2.7



Analogous zirconium systems showed no catalytic activity.[114] Reichert and Meyer[115] found that a dramatic increase in the activity of the $Cp_2TiEtCl/AlEtCl_2$ was obtained by the addition of controlled amounts of water. A similar result was observed by Breslow and Long,[116] who found that increases in both catalyst activity and polymer molecular weight were obtained by the addition of water to the $CpTiCl_2/AlMeCl_2$ system, with an optimum ratio of Al/H_2O of 2.5:1.

Halogen free systems based on bis(cyclopentadienyl)titanium(IV) compounds and trialkyl aluminium had been found to be catalytically inactive, possibly because a halogen bridge was involved in the active species. In one of the most exciting developments in Ziegler-Natta polymerization in recent years, Sinn, Kaminsky and co-workers[117] discovered that the addition of water to trimethylaluminium before the addition of $Cp_2(Ti)Me_2$ produced a homogeneous catalyst which possessed remarkable activity for the polymerization of ethene, providing 7000g PE/g Ti hr^{-1}.The catalyst also showed a very long lifetime, with catalytic activity being maintained for longer than five days, in marked contrast to the rapid deactivation observed in earlier titanocene systems. The catalyst was not active for the polymerization of propene, however it was found that by carefully preparing the methylaluminoxane (MAO) it was possible to produce poly(propene). The catalytic activity of zirconium complexes was found to be even greater,[118] with Cp_2ZrMe_2 an activity of $7.45x10^6$g PE/g Zr hr^{-1} was obtained. If Cp_2ZrCl_2 is used with the MAO even higher activities are achieved ($25x10^6$g PE/g Zr hr^{-1}).[119] Measurements on the active site concentration suggested that 100% of the zirconium atoms are catalytically active at 70°C.[120]

These catalysts are also able to polymerize propene, although with a lower activity than for ethene, and to produce propene/ethene copolymers as well as ethene/hexene copolymers. The use of non-chiral metallocene complexes provided only atactic poly(propene) and therefore the polymer remains in solution during polymerization.

A further development in the metallocene/MAO systems was the discovery by Ewen[121] that isotactic poly(propene) could be obtained from homogeneous catalysts formed from racemic ethylene bis(tetrahydroindenyl)titanium dichloride with MAO. The corresponding zirconium catalyst shows greater activity than the titanium catalyst.[119]

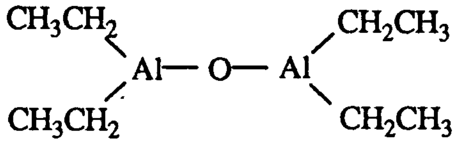
The effect of varying the alkyl substituents on the metallocene ligand has been investigated in recent studies,[122,123] showing that they alter the activity of the catalyst by steric and electronic effects.

Another notable feature of this class of catalysts is that polymers with molecular weight distributions M_w/M_n as low as 2 have been obtained, which is much lower than the distributions obtained using heterogeneous catalysts. The molecular weight of poly(ethene) can be varied between a few million and a few hundred by varying the polymerization temperature. At 10°C poly(ethene) with a M_w of 1.5×10^6 was obtained, at 90°C M_w was 90000, while at above 100°C only 1-alkenes were produced.[118] Similar temperature effects were reported for propene polymerizations,[122] where increasing the polymerization temperature from -10°C to +32°C caused a decrease in M_w from 305000 to 57000.

The activities of the catalyst systems are dependant on several experimental factors. The activity of the system is increased by using low concentrations of zirconium, typically concentrations in the range 10^{-8}-10^{-6} mol/l are employed. The activity is dependant on the ratio of aluminium to zirconium over a remarkably large range, and typically Al/Zr ratios of greater than 1000 are employed.

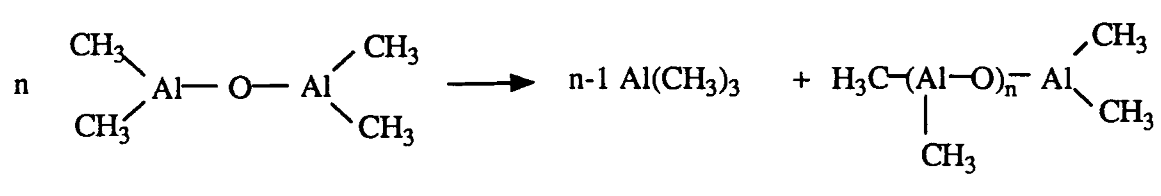
Higher trialkylaluminiums such as triethylaluminium form simple aluminoxanes as shown in Figure 2.8

Figure 2.8



Trimethylaluminium behaves differently, with further condensation taking place to give oligomeric products as shown in Figure 2.9

Figure 2.9



Evidence showing that some cyclic aluminoxanes are produced was provided by mass spectrometry,[124] although it seems likely that a mixture of linear and cyclic materials are usually obtained. The activity of the catalysts is dependant on the degree of oligomerization of the MAO,[124] as can be seen. for polyethene (PE) prepared with Cp_2TiMe_2.(Table 2.1)

Table 2.1

Degree of oligomerization of MAO	Yield PE g/hr
2	0.1
5	25.5
>10	36.05

The degree of oligomerization of the MAO is dependant on the experimental conditions used in its preparation, and this can lead to difficulties in reproducibility. Several procedures have been reported for the preparation of MAO including direct reaction between trimethylaluminium and water, either by the addition of liquid water to a solution of trimethylaluminium in toluene,[117a] or by the addition of water vapour to a solution of trimethylaluminium in benzene.[125]

A more controlled procedure is to add trimethylaluminium to a stirred slurry of a hydrated salt, such as copper sulphate pentahydrate,[121] or aluminium sulphate hexadecahydrate.[126] In a comparison between the various methods Giannetti[126] and co-workers found that the MAO providing the greatest activity was obtained using hydrated aluminium sulphate, with the removal of volatile components to leave a glassy MAO. The solution obtained from the reaction between the hydrated salt and the trimethylaluminium can be used directly as an activator in which case the degree of oligomerization is dependant on the concentration. The method of Porri[127] provides a simple *in situ* preparation of MAO, trimethyl tin oxide is added to a solution of trimethylaluminium in an inert solvent, the mixture is stirred for approximately 10-20 minutes then the MAO solution is ready for use. The tetramethyltin side product can then be removed from the product under reduced pressure.

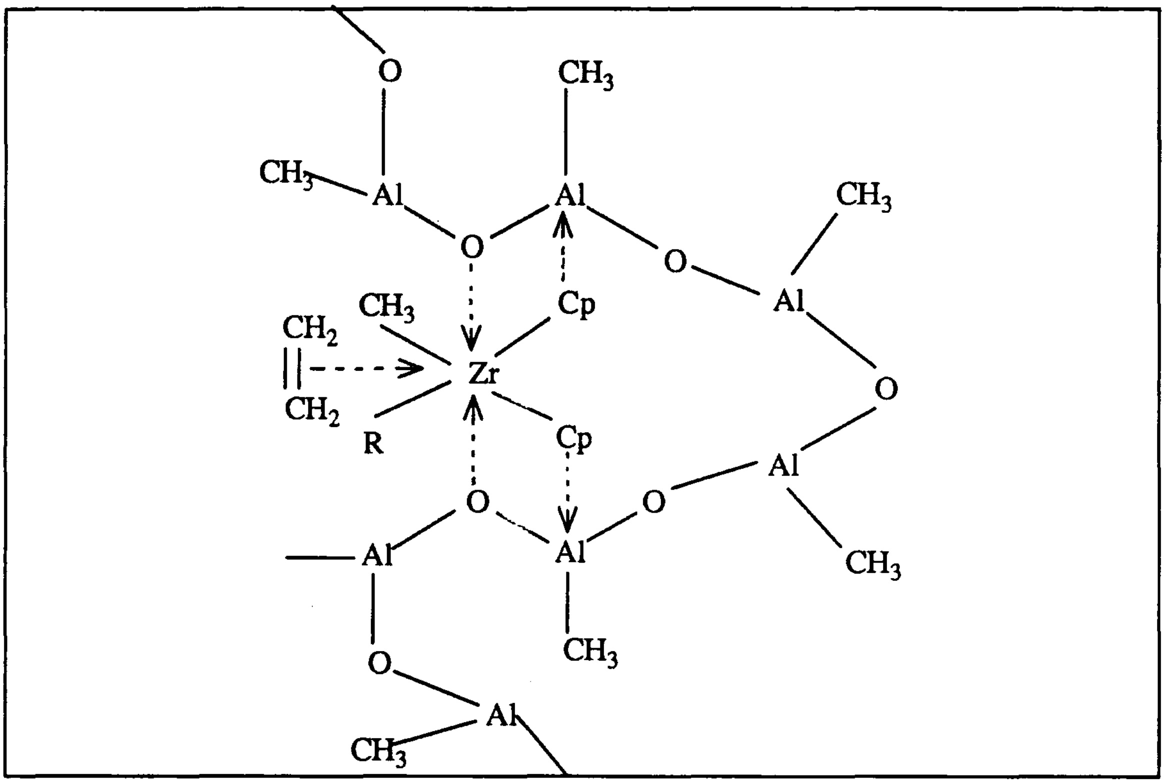
An even simpler method of obtaining MAO is now available, as Stauffer have begun to supply it commercially.

The exact role of the MAO in the formation of the active centre, and reason why such a huge excess of MAO is required has not been fully explained. The presence of large amounts of MAO makes the study of the active species involved in polymerization extremely difficult. The original model for the active site was proposed by Kaminsky[118] for CP_2ZrMe_2, this is shown in Figure 2.11

He suggested that aluminoxane surrounds the transition metal and interacts with both the metal and the cyclopentadienyl groups. The cyclopentadienyl rings donate electron density to the aluminium of the MAO. This results in a lowering of electron density on the transition metal which makes the insertion of a monomer into the metal-CH_3 bond easier.

Figure 2.11

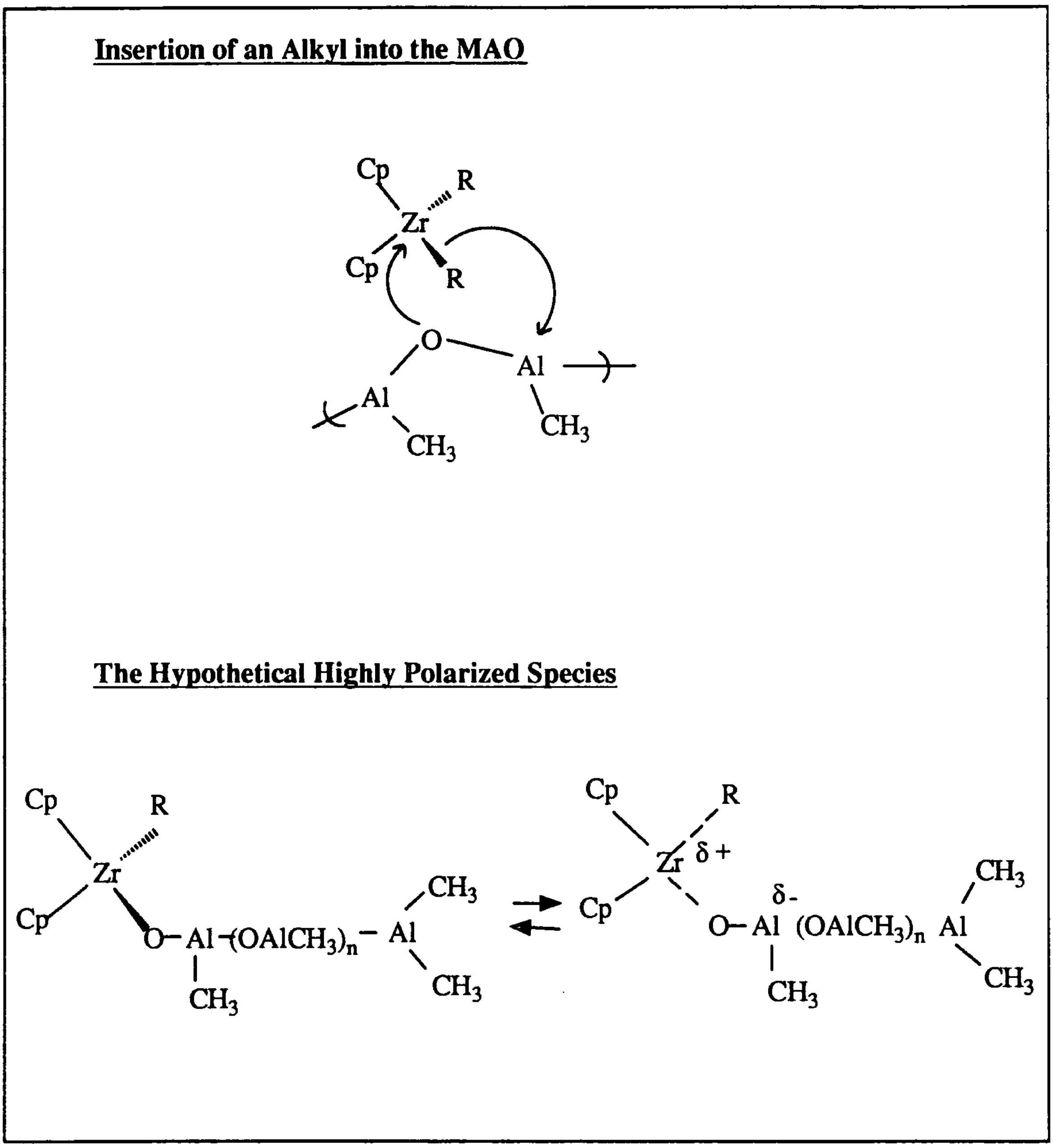
Kaminsky's Model of the Active Site in the Cp_2ZrMe_2.MAO Catalyst



The model fails to explain the need for a large excess of aluminium, or the increase in activity observed as the degree of oligomerization of the MAO increases. In this model a rise in activity would be observed upon increasing the Lewis acidity of the aluminium component, however previous workers failed to find such a correlation for Cp_2TiRCl/MAO systems. Gianetti and co-workers[126] suggested that MAO acts as an electron donor through one oxygen atom. This leads to an insertion reaction into the MAO to give a hypothetical active species having a highly polarized structure, as shown in Figure 2.12.

Figure 2.12

Gianetti's Model for the Formation of the Active Site in The Cp_2ZrMe_2.MAO Catalyst

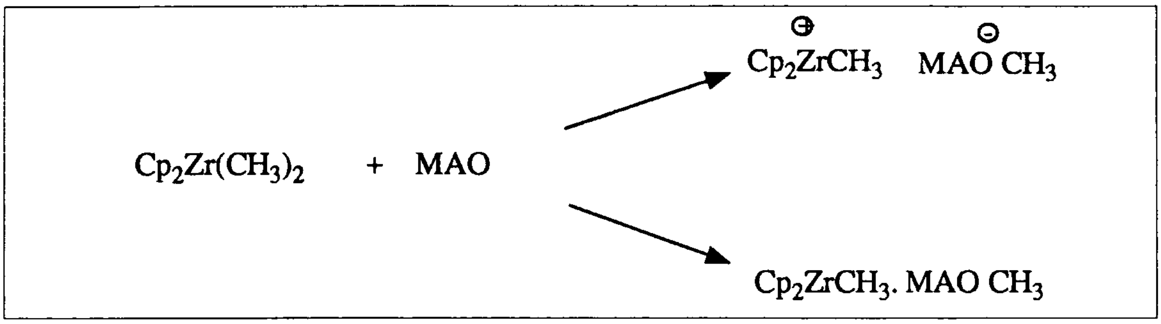

Insertion of an Alkyl into the MAO

The Hypothetical Highly Polarized Species

Atwood[128] found that organoaluminium compounds with a high oxygen content formed an unusual cyclic anionic species $[Al_7O_6(CH_3)_{16}]^-$ which had a structure similar to that of zeolites. This led to the suggestion that MAO may act as a low molecular weight analogue of the support in highly active supported catalysts. The strict structural requirements for an active site may explain why only a small fraction of the MAO is involved in the active site and why the activity is dependant on the degree of oligomerization of the MAO.

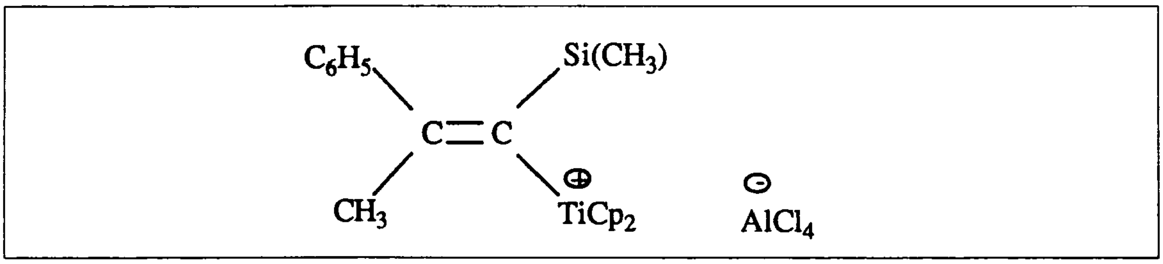
One role for the MAO in Cp_2ZrCl_2 system is to alkylate the zirconium complex, forming the active species. In the case of$Cp_2Zr(CH_3)_2$ there is no need to alkylate the transition metal. By analogy with the Cp_2TiCl_2/CH_3AlCl_2 system, the active species may be neutral or ionic, as shown in Figure 2.13.

Figure 2.13



Eisch[129] was the first to determine the structure of the initial insertion into a Ziegler catalyst, by using a highly crowded ethene model (trimethyl(phenylethynyl)silane) with the Cp_2TiCl_2/CH_3AlCl_2 catalyst. The structure of the product is shown in Figure 2.14

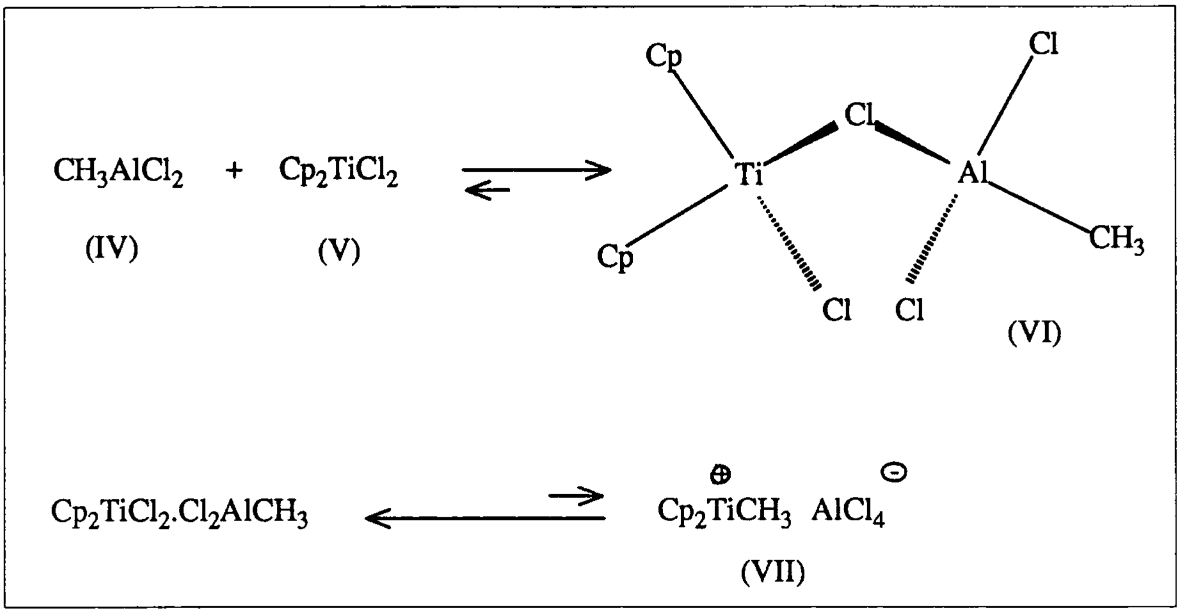
Figure 2.14



This led to the conclusion that the active species was formed from a series of equilibria as shown in figure 2.15. The concentration of species (VII) is too low to be spectroscopically detectable.

Figure 2.15

Proposed Equilibria Involved in the Cp_2ZrCl_2/CH_3AlCl_2 Catalyst



Further evidence for the involvement of a cationic species came from the observation that $(C_5Me_5)_2ScR$ (which is isoelectronic with Cp_2Ti^+R) is able to polymerize ethene.[130]

Jordan[131] demonstrated that the cationic zirconium species $Cp_2ZrCH_3.THF^+$ polymerized ethene in the absence of an aluminium co-catalyst. Evidence that a cationic species is involved in the active site of zirconocene/MAO systems came from Gassman and Callstrom.[132] Using x-ray photoelectron studies (XPS) on Cp_2ZrCl_2, $Cp_2(CH_3)ZrCl$ and $Cp_2Zr(CH_3)_2$ treated with MAO, they found that new derivatives with increased Zr(IV) binding energy were formed. The value was the same for each of the systems, suggesting that the catalytic species was $Cp_2Zr^+CH_3$ in each case.

Chien and co-workers[133] have carried out kinetic studies on polymerizations using metallocene/MAO systems. They have proposed that a series of equilibria between the metallocene and MAO are involved, as in Figure 2.16.

Figure 2.16

Proposed Equilibria Involved in the Zirconocene/MAO Catalyst

$$\mathrm{Cp_2ZrCl_2} + \mathrm{MAO} \rightleftharpoons \underset{\text{(VIII)}}{\mathrm{Cp_2ZrCl_2.MAO}}$$

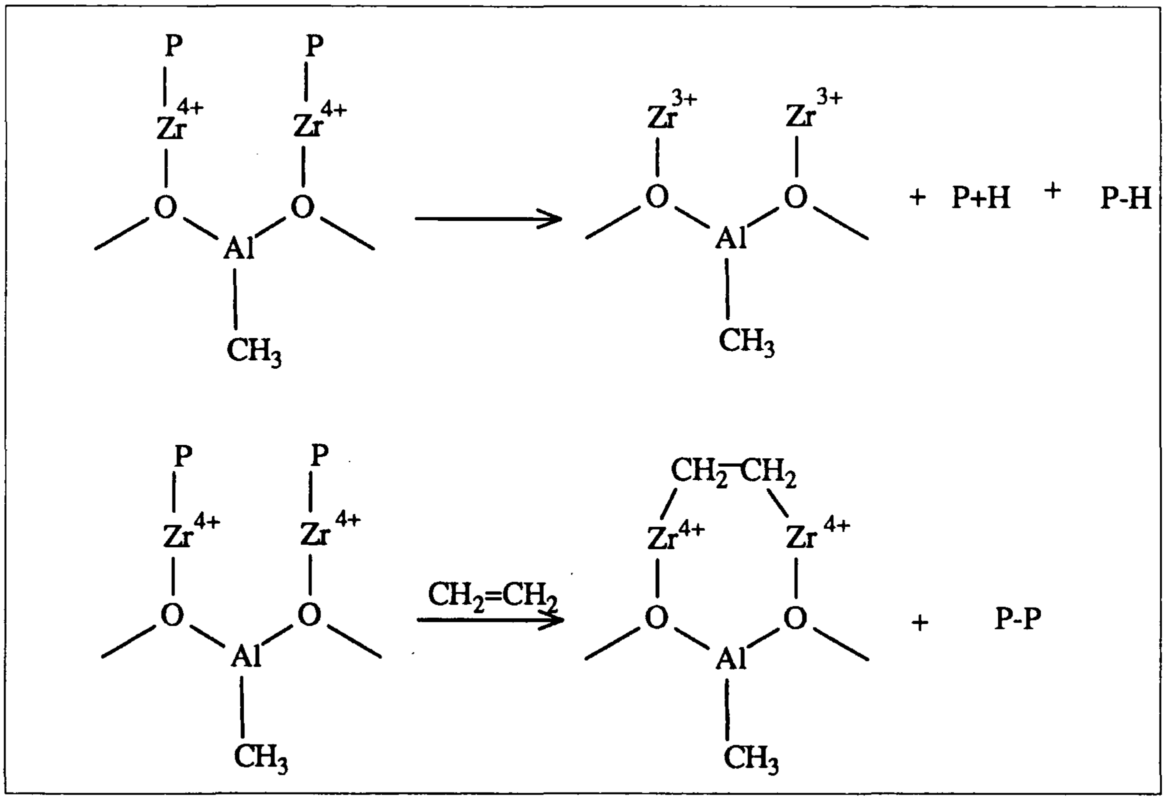
$$\mathrm{Cp_2ZrCl_2.MAO} + \mathrm{Cp_2ZrCl_2.MAO} \rightleftharpoons \underset{\text{(IX)}}{\mathrm{(Cp_2ZrCl_2\,MAO)_2}}$$

$$\mathrm{Cp_2ZrCl_2.MAO} + \mathrm{MAO} \rightleftharpoons \underset{\text{(X)}}{\mathrm{Cp_2ZrCl_2.MAO_2}}$$

The presence of a large excess of MAO favours the formation of (X). If two or more zirconium ions are complexed to the same MAO deactivation could occur by reduction or by alkyl exchange, as shown in Figure 2.17.

Figure 2.17

Deactivation of the Active Catalyst Species in the Zirconocene/MAO Catalyst



In summary, the metallocene/MAO catalysts provide a combination of very desirable properties, and although the exact nature of the active species is not fully understood they appeared very useful for our investigation.

2.6. A Brief Summary of the use of Ziegler-Natta Catalysts in the Current Study

There was no experience of Ziegler-Natta polymerization within the research group and therefore it required considerable effort to acquire the necessary experimental techniques.

In view of this lack of experience the simplest type of catalyst with which to begin the investigation was the original titanium(III)chloride/alkylaluminium system. The activity of these catalysts is much lower than that of the supported heterogeneous systems, however they are less complex to prepare and were useful to establish the principle of the proposed procedure.

Using 1-octene as a model monomer the effect of variations in the ratio of alkylaluminium to titanium(III)chloride on the yield of polymer was studied. The homopolymerization of 6-cyclopropyl-1-hexene was then undertaken, to provide an isotactic polymer with a broad molecular weight distribution, insoluble in hydrocarbons but soluble in dichloromethane. The principle of crosslinking polymers containing cyclopropane groups was established by treating the polymer with aluminium bromide to produce an insoluble network. The insolubility of the isotactic homopolymer in hydrocarbons, coupled with the broad molecular weight distribution of the polymer made it clear that an alternative catalyst was required.

The homogeneous Ziegler-Natta catalysts discovered by Sinn and Kaminsky appeared to provide several potential advantages. Using achiral metallocene catalysts such as bis(cyclopentadienyl)zirconium dichloride would provide atactic polymers, which would be more soluble in hydrocarbons than isotactic polymers. The option to produce isotactic polymers would be available if chiral catalysts were employed, and it might be valuable to compare the effect of polymer tacticity on the properties of the networks. The remarkably high activity of the metallocene/MAO catalyst systems was potentially extremely valuable in obtaining acceptable yields of polymers. The activity of 1-alkenes in Ziegler-Natta polymerization is much lower than that of ethene,[134] as shown in Table 2.2.

Table 2.2

The Relative Rates of Polymerization of 1-Alkenes in Ziegler-Natta Polymerization

Monomer	Reactivity Relative to Propene
Ethene	8-20
Propene	1
Butene	0.22-0.62
Hexene	0.16-0.36
Dodecene	0.12-0.28
3-Methyl-1-butene	0.024-0.06
5-Methyl-1-hexene	0.34-0.50

In trying to obtain acceptable yields of polymer from the cyclopropyl monomers containing relatively long alkyl groups the advantage of the high activity of the metallocene / MAO catalysts is obvious.

Preliminary investigations into the use of the homogeneous catalyst system were carried out using 1-octene as a model monomer. The effect of variations in the ratio of aluminium to zirconium, and the polymerization conditions on the yield and molecular weight of the polymer were studied.

Difficulties were encountered in obtaining reproducible results, this was probably partially due to the method of preparation of the MAO (at that stage in the work it was prepared by the addition of water to a solution of trimethyl aluminium in toluene) and partially due to the small amount of zirconocene catalyst involved, which is likely to lead to great sensitivity to the presence of any trace impurities.

Attempts to homopolymerize 6-cyclopropyl-1-hexene failed to provide any polymer, although it would copolymerize with 1-octene.

The search for suitable conditions to allow the homopolymerization of propene met with initial difficulties due to the lack of suitable equipment for the polymerization of known amounts of a gaseous monomer. The experimental problems arose because of the novelty of Ziegler-Natta polymerization within the research group, and were eventually overcome following discussion with workers from other groups.

Employing an improved procedure for the preparation of MAO, and a suitable polymerization vessel, high yields of poly(propene) were obtained. Series of copolymers containing 6-cyclopropyl-1-hexene and propene were prepared at 0°C and at -25°C to provide a variation in molecular weight. The use of the improved MAO preparation method still failed to allow the homopolymerization of 6-cyclopropyl-1-hexene. This was an unexpected result, which is discussed in Chapter 3.

The copolymers were characterized, then investigations into forming networks through ring opening of the cyclopropane group were undertaken. The use of cationic initiators, either simple Lewis acids or 'masked' agents such as photocationic initiators or thermal cationic initiators were tested. None of these initiators produced highly crosslinked networks when used at levels similar to those employed for the crosslinking of epoxy resins. The use of high levels of aluminium bromide produced networks which demonstrated that, in principle, alkenylcyclopropanes could be polymerized to provide polymers capable of network formation by ring opening of the cyclopropane group.

A limited investigation into the cationically-initiated polymerization of alkenylcyclopropanes to provide linear polymers with pendant cyclopropane rings was undertaken. This demonstrated the unsuitability of such an approach.

CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF POLYMERS CONTAINING PENDANT CYCYLOPROPYL GROUPS

3.1. Monomer Synthesis and Characterization

3.1.i. Synthesis of Ethylcyclopropane

The method was essentially that of Huang and Minlon.[135] Diethyleneglycol (300ml), cyclopropyl methyl ketone (42.0g, 0.50mol), potassium hydroxide (40.0g, 0.71mol) and 90% hydrazine hydrate (50ml) were placed in a 500ml round-bottom flask equipped with a thermometer, magnetic stirrer and an equalised-pressure dropping funnel topped by a water-cooled reflux condenser which was in turn topped by an acetone/carbon dioxide-cooled condenser. The mixture was warmed to 90°C by immersion in a waterbath until the potassium hydroxide had fully dissolved, then maintained between 98-110°C for 1 hour under reflux. The tap of the funnel was then closed to prevent distillate returning to the flask, the temperature was raised to 190°C and maintained at this temperature for 3 hours. The aqueous phase of the distillate was run off, the organic phase dried over magnesium sulphate to afford 23.7g (0.339mol, 67.6%) of crude ethylcyclopropane. Distillation provided 17.22g,(49.1%) of pure product b.pt 35.8-36.8°C (lit 35.5-35.6°C).[39]

The IR (Appendix 4.1),^{1}H and ^{13}C NMR and mass spectra of the product were consistent with the assigned structure; ^{1}H NMR ($CDCl_3$,250MHz) 1.2ppm(m)2H, 0.9ppm(m)3H, 0.64ppm(m)1H, 0.36ppm(m)2H, 0.0ppm(m)2H; ^{13}C NMR ($CDCl_3$,62.9MHz) 4.17ppm, 12.78ppm, 13.67ppm 27.83ppm; MS M^+ m/e 70, fragments at m/e 55,42,41,39,29,27

3.1.ii. Synthesis of Hexylcyclopropane

The method of Harrison and Rawson[75] was used. Zinc powder (32.6g, 0.49mol), copper(I)chloride (4.9g, 0.049mol) and diethylether were heated under reflux in a nitrogen atmosphere for 30 minutes in a 250 ml round bottom flask equipped with magnetic stirrer, reflux condenser and equalised pressure dropping funnel, then the heat source was removed. Diiodomethane (66.4g, 0.249mol) was added from the dropping funnel over 10 minutes, followed by 1-octene (21.4g, 0.191mol) over 10 minutes. An exotherm occurred during the addition of the alkene, bringing the mixture to reflux. The flask was immersed in a waterbath maintained at 60°C for 18 hours, then allowed to cool, the supernatant liquid was removed by decantation and the solid washed with diethylether (2x25ml). The combined organic phase was washed in succession with 5% hydrochloric acid (2x100ml), saturated sodium bicarbonate solution (100ml) and water (3x100ml), then dried over magnesium sulphate. Ether was removed using a rotary evaporator at room temperature then the residue was distilled. The yield of impure hexylcyclopropane was 12.1g (50.2%). Redistillation using a Fischer Spaltrohr distillation column at approximately 50 plates provided pure hexylcyclopropane b.pt 153.4-153.6°C (lit. 148-150°C)[73]

IR (capillary film between NaCl plates) v3080cm^{-1}(cyclopropyl C-H str.),υ1010cm^{-1}(cyclopropyl skeletal mode) (Appendix 4.2); ^{1}H NMR ($CDCl_3$, 250MHz) 1.2ppm(overlapping multiplets)10H, 0.88ppm(m)3H, 0.62ppm(m)1H, 0.37ppm(m)2H, 0.0ppm(m)2H; ^{13}C NMR ($CDCl_3$,62.9MHz) 34.85ppm, 32.0ppm, 29.7ppm, 29.2ppm, 22.7ppm, 14.1ppm, 10.9ppm, 4.4ppm; and MS (EI) M^+ m/e 126, 98, 97, 84, 83, 70, 69, 56, 55, 43, 41, 39 confirm the assigned structure.

3.1.iii. Synthesis of 1,1-Diethylcyclopropane

The procedure was essentially the same as for the preparation of hexylcyclopropane above. Reaction of 2-ethyl-1-butene (18.0g, 0.164mol) with diiodomethane (74.6g, 0.280mol) and a zinc-copper couple prepared by refluxing zinc powder (36.4g, 0.556mol) with copper(I)chloride (5.57g, 0.0557mol) in diethylether (86ml). Distillation afforded a crude distillate containing 15.57g (96.9%) of 1,1-diethylcyclopropane. Redistillation using a Fischer Spaltrohr distillation column at approximately 50 theoretical plates gave 6.22g (38.7%) of pure product b.pt. 88.8-88.9°C (lit. 88.67°C)[136].

IR (capillary film between NaCl plates) υ3010cm^{-1}(cyclopropyl C-H str.) υ1010cm^{-1}(cyclopropyl skeletal mode), (Appendix 4.3); ^{1}H NMR ($CDCl_3$, 250MHz) 0.93ppm(q)6H, 0.67ppm(t)4H, 0.0ppm(s)4H; ^{13}C NMR ($CDCl_3$, 62.9MHz) 29.2ppm, 21.4ppm, 11.5pm, 10.6ppm; MS (EI) m/e 98(M^+), 69, 55, 41, 39 confirm the assigned structure.

3.1.iv. Synthesis of 1,4-Bis(2,2-Dichlorocyclopropyl) Butane

The method of Starks[60] was employed. A solution of 1,7-octadiene (33.0g,0.30mol) and benzyl triethyl ammonium chloride (2.34g, $1.26x10^{-2}$mol) in chloroform (216g, 1.80mol) was placed in a 500ml three-neck round-bottom flask equipped with a double surface reflux condenser, mechanical stirrer and thermometer. A solution of sodium hydroxide (96.0g, 1.66mol) in water 96ml) was added over 20 minutes, with vigorous stirring. An exothermic reaction raised the temperature to 54°C, after this had subsided the temperature was maintained at 50°C for 3 hours by immersion in a waterbath. The mixture was cooled in an icebath before adding crushed ice (150g), the organic phase was separated and dried over magnesium sulphate before removing solvent using a rotary evaporator. The crude product was distilled under reduced pressure to give 1,4-bis(2,2-dichlorocyclopropyl) butane 48.7g (59%). Analysis by gas chromatography (Hewlett-Packard 5890A chromatogram with crosslinked methyl silicone coated capillary column, nitrogen carrier gas, FID detector, temperature programme 40°C to 270°C at 10°C min^{-1}) showed the product to be 98.4% pure, with 1.6% 1,1-dichloro-2-(1-hexenyl)cyclopropane as the sole impurity. The product was used without further purification.

IR (capillary film between NaCl plates) (Appendix 4.4); ^1H NMR ($CDCl_3$, 250MHz) 1.6ppm(s)10H, 1.1ppm(s)4H and ^{13}C NMR ($CDCl_3$, 62.9MHz) 61.5ppm, 30.7ppm, 30.2ppm, 28.2ppm, 28.7ppm spectra were in agreement with the assigned structure.

3.1.v. Synthesis of 1,1-Dichloro-2-Hexylcyclopropane

The procedure was essentially the same as that above. Reaction of 1-octene (37.3g, 0.33mol) with chloroform (120g, 1.00mol) and a solution of sodium hydroxide (53.3g, 1.33mol) in water (53ml) in the presence of benzyl triethyl ammonium chloride (1.30g, $5.71x10^{-3}$mol) gave 60.2g (93%) of the required product. Distillation gave 58.7g (90.4%) of product b.pt. 89.5-91.5°C at 10mmHg (lit. 85°C at 11mmHg).[137] Gas chromatography (Hewlett-Packard 5890A chromatogram with crosslinked methyl silicone coated capillary column, nitrogen carrier gas, FID detector, oven temperature 200°C) showed the product was 98.7% pure, with a single unidentified impurity.

^{13}C NMR ($CDCl_3$, 62.9MHz) 61.7ppm, 31.7ppm, 30.9ppm, 30.4ppm, 29.0ppm, 28.6ppm, 26.8ppm, 22.6ppm, 14.1ppm; MS m/e 123, 102, 81, 70, 69, 56, 55, 43, 42, 41; and IR (capillary film between NaCl plates) spectra (Appendix 4.5) were in agreement with the assigned structure.

3.1.vi. Attempted Reduction of 1,4-Bis(2,2-Dichlorocyclopropyl) Butane With Lithium Aluminium Hydride

1,4-bis(2,2-dicyclopropyl)butane (10g, 0.0362mol) and lithium aluminium hydride (5.49g, 0.145mol) were stirred together in refluxing tetrahydrofuran (200ml) for 11 days. The mixture was then treated successively with the dropwise addition of water (5.5ml), 15%w/w aqueous sodium hydroxide (5.5ml) and finally with water (16.5ml). After drying over magnesium sulphate and removal of solvent in vacuo the product was analysed by gas chromatography coupled mass spectrometry. This showed that a number of partially reduced products had been obtained, but none of the required fully reduced product.

3.1.vii. Synthesis of 1,2-Bis-(1-Methylcyclopropyl) Ethane

Zinc powder (61.2g, 0.944mol) and copper(I)chloride (9.44g, 0.094mol) were stirred together in refluxing diethylether (125ml) under a nitrogen atmosphere for 45 minutes. Diiodomethane (126.0g, 0.472mol) was added over 25 minutes, followed by the addition of 2,5-dimethyl-1,5-hexadiene over 12 minutes. The mixture was maintained at 60°C for 14 hours then allowed to cool before filtering. The filtercake was washed with diethylether (2x50ml) then the combined filtrate was washed successively with water

(2x100ml), 5% hydrochloric acid (50ml), saturated sodium bicarbonate solution (50ml) and finally water (50ml). The combined aqueous phase was extracted with diethylether (2x50ml) before drying the ether extracts over magnesium sulphate. Diethyl ether was removed using a rotary evaporator at room temperature before the crude product was separated from involatile residues by vacuum transfer. Analysis by gas chromatography (Hewlett-Packard 5890A chromatogram with crosslinked methyl silicone coated capillary column, nitrogen carrier gas, FID detector, oven temperature 150°C) showed the crude mixture contained 11.55g (71%) of the required product, this was combined with a previous batch then distilled using a Fischer Spaltrohr distillation column at 50 theoretical plates efficiency to provide pure product.

IR (capillary film between NaCl plates) υ 3062cm^{-1} (cyclopropyl C-H str.), υ 1010cm^{-1} (cyclopropyl skeletal mode)(Appendix 4.6); and ^{13}C NMR spectra ($CDCl_3$,62.9MHz) 36.5ppm, 22.8ppm, 15.0ppm, 13.1ppm were consistent with the assigned structure.

3.1.viii. Synthesis of 2-Cyclopropyl-2-Propanol

The method described by Takahashi[44] was employed. To a mixture of magnesium turnings (14.6g, 0.595mol) and diethylether(200ml) in a 500ml round bottom flask equipped with nitrogen inlet, mechanical stirrer, dropping funnel and reflux condenser protected by a calcium chloride guard tube, was added iodomethane (84.5g, 0.595mol) over 80 minutes. The exothermic reaction maintained the mixture refluxing during the addition, the flask was then heated on a waterbath for a further 30 minutes. The mixture was cooled in ice then cyclopropyl methyl ketone (50g, 0.595mol) was added,with rapid stirring , over 30 minutes. After refluxing the mixture for 1 hour and allowing to cool the crude product was poured onto crushed ice (700ml) and 2M sulphuric acid, the aqueous phase was extracted with diethylether (4x75ml). The combined ether phase was washed with saturated sodium bicarbonate solution (100ml), then water (2x100ml) before drying over magnesium sulphate. The crude product was distilled using a Fisher Spaltrohr distillation column at approximately 50 theoretical plates efficiency. The purity of the distillate was determined by gas chromatography (Hewlett-Packard 5890A chromatogram with crosslinked methyl silicone coated capillary column, FID detector, nitrogen carrier gas, oven temperature 110°C.) and found to contain three main components, 2-cyclopropylpropene (4.1%), cyclopropylmethyl ketone (2.1%) and 2-cyclopropyl-2-propanol (93.8%) the distillate was used without further purification.

3.1.ix. Synthesis of 2-Cyclopropylpropene

A mixture of 2-cyclopropyl-2-propanol (18.93g of 93.8% pure material, 0.178mol) and concentrated sulphuric acid (2 drops) was heated gently for 48 hours in a 25ml Claisen flask equipped with a short fractionating column and side arm condenser, the rate of heating was controlled to give a steady distillation of crude 2-cyclopropylpropene. The distillate was diluted with diethylether, then dried over magnesium sulphate prior to distillation using a Fischer Spaltrohr distillation column at approximately 50 theoretical plate efficiency to provide pure 2-cyclopropylpropene b.pt. 69.9-70.2°C (lit.71°C).[44]

IR (capillary film between NaCl plates) v3080cm^{-1}(cyclopropyl C-H str), v1645cm^{-1}(C=C str), v1010cm^{-1}(cyclopropyl skeletal mode) (Appendix 4.7); and ^{1}H NMR spectra ($CDCl_3$, 250MHz) 4.5ppm(d)2H, 1.6ppm(s)3H, 1.4ppm(m)1H, 0.6ppm(m)2H, 0.4ppm(m)2H confirm the assigned structure.

3.1.x. Synthesis of 6-Cyclopropyl-1-Hexene

The procedure was essentially that described by Harrison and Rawson.[75] Powdered zinc (149.1g, 2.28mol), copper(I)chloride (14.9g, 0.151mol) and diethylether (250ml) were placed in a 1 litre three neck round bottom flask equipped with a mechanical stirrer, thermometer and a reflux condenser with an equalised pressure dropping funnel fitted above it, protected with a nitrogen inlet. The mixture was refluxed for 45 minutes then the heat source was removed before adding diiodomethane (309.8g, 1.16mol) over 35 minutes. 1,7-octadiene (100.3g, 0.911mol) was added over 12 minutes, the addition was accompanied by an exothermic reaction which raised the temperature to 60°C. The temperature was maintained at 60°C for a further 17 hours, then allowed to cool before filtering the mixture through a number three porosity sinter. The filtercake was washed with diethylether (2x100ml), the combined filtrate was washed successively with water (2x100ml), 5% hydrochloric acid (3x100ml), saturated sodium bicarbonate solution (2x100ml) and finally with water (100ml). The combined aqueous phase was then saturated with sodium chloride prior to extraction with diethylether (2x50ml). Removal of diethylether followed by vacuum transfer gave 95.8g of crude product. Analysis by gas chromatography (Hewlett-Packard 5890A chromatogram, crosslinked methyl silicone coated capillary column, FID detector, N_2 carrier gas, oven temperature 120°C) showed the mixture to contain 6-cyclopropane-1-hexene (42.7g, 37.8% yield), 1,4-dicyclopropylbutane (15.6g, 12.4%) and unreacted 1,7-octadiene (36.3g, 36.2%). The crude mixture was combined with another batch then distilled using a Fischer Spaltrohr distillation column at approximately 50 theoretical plates efficiency to provide pure 6-cyclopropyl-1-hexene b.pt. 150.1-150.3°C (no literature b.pt. available)

IR (capillary film between NaCl plates) v 3065cm^{-1} (cyclopropyl C-H str.), v 1645cm^{-1} (C=C str.) v 1010cm^{-1} (cyclopropyl skeletal mode) (Appendix 2.8); ^{1}H NMR ($CDCl_3$, 250MHz) 5.9-4.9ppm(ABX system)3H, 2.1ppm(m)2H, 1.4ppm(m)4H, 1.3ppm(m)2H, 0.6ppm(m)1H, 0.4ppm(m)2H, 0.0pm(m)2H; ^{13}C NMR ($CDCl_3$, 62.9MHz) 139.2ppm, 114.1ppm, 34.7ppm, 38.9ppm, 29.2ppm, 28.6ppm, 10.9pm, 4.4ppm; and MS (EI) M$^+$ not observed m/e 96, 95, 81, 68, 67, 55, 54, 41, 39; confirm the assigned structure.

3.2. Polymer Synthesis and Characterization

3.2.1. Ziegler-Natta Polymerization

1-Octene was chosen as a model monomer to obtain experience in Ziegler-Natta polymerization and to establish conditions which would give satisfactory yields. The size of the alkyl groups of octene and 6-cyclopropyl-1-hexene are similar and therefore the polymerization behaviour of the two monomers was expected to be comparable.

3.2.1.a. Heterogeneous Ziegler-Natta Catalysts

A series of polymerizations were carried out using triethylaluminium and diethylaluminiumchloride, the details of a polymerization using the optimum ratios of triethylaluminium/titanium(III)chloride are given.

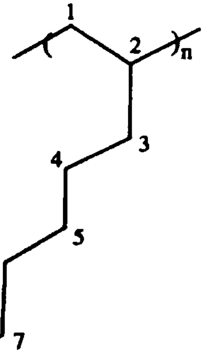
3.2.1.a.i. Polymerization of 1-Octene Initiated by Titanium(III)chloride / Triethylaluminium

Triethylaluminium (0.282g, 2.47×10^{-3}mol) was added to a stirred slurry of titanium(III)chloride (0.1271g, 8.24×10^{-4}mol) in hexane (1.66ml) in a Schlenk type reaction vessel (Appendix 5) under a nitrogen atmosphere. After the addition of 1-octene (1.39g, 12.4×10^{-3}mol) the vessel was sealed,the mixture maintained at 50°C for 48 hours before terminating the reaction by pouring the mixture into methanol (200ml). The polymer which precipitated was refluxed for 16 hours with a 1:1:0.5 (parts by volume) mixture of methanol,isopropanol and 10N aqueous hydrochloric acid (400ml), washed with a mixture of 1:1 water and methanol (2x200ml) and finally dried to constant weight *in vacuo* at room temperature to give 1.16g (88%) of poly(octene).

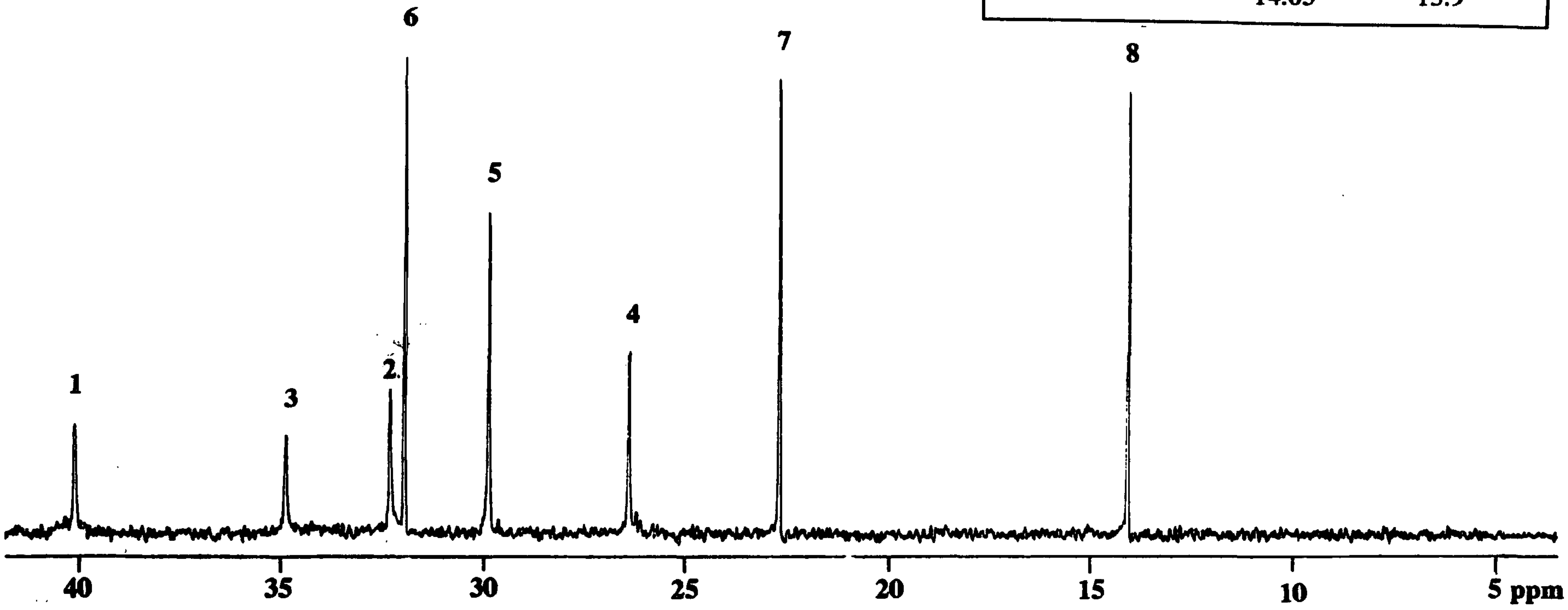
The IR spectrum (thin film supported on NaCl plate) (Appendix 4.9) was in agreement with the assigned structure.

Figure 3.1

^{13}C NMR Spectrum of Isotactic Polyoctene



Carbon	Shift /ppm Observed	Shift /ppm Calculated
1	40.13	40.6
2	32.31	32.5
3	34.89	35.8
4	26.39	28.3
5	19.87	30.5
6	31.95	31.1
7	22.68	23.0
8	14.05	13.9



GPC (1% solution, tetrahydrofuran eluent, 10^5Å, 10^3Å and 100Å crosslinked polystyrene columns, RI detector) M_n 55000 M_w/M_n 3.0; The ^{13}C NMR spectrum ($CDCl_3$, 62.9MHz) is shown in Figure 3.1, the assignments were made by comparison with the expected chemical shifts calculated from the Grant and Paul parameters,[138] the results given by Randall[139] for 1-octene/ethene copolymers, and from the DEPT spectra.

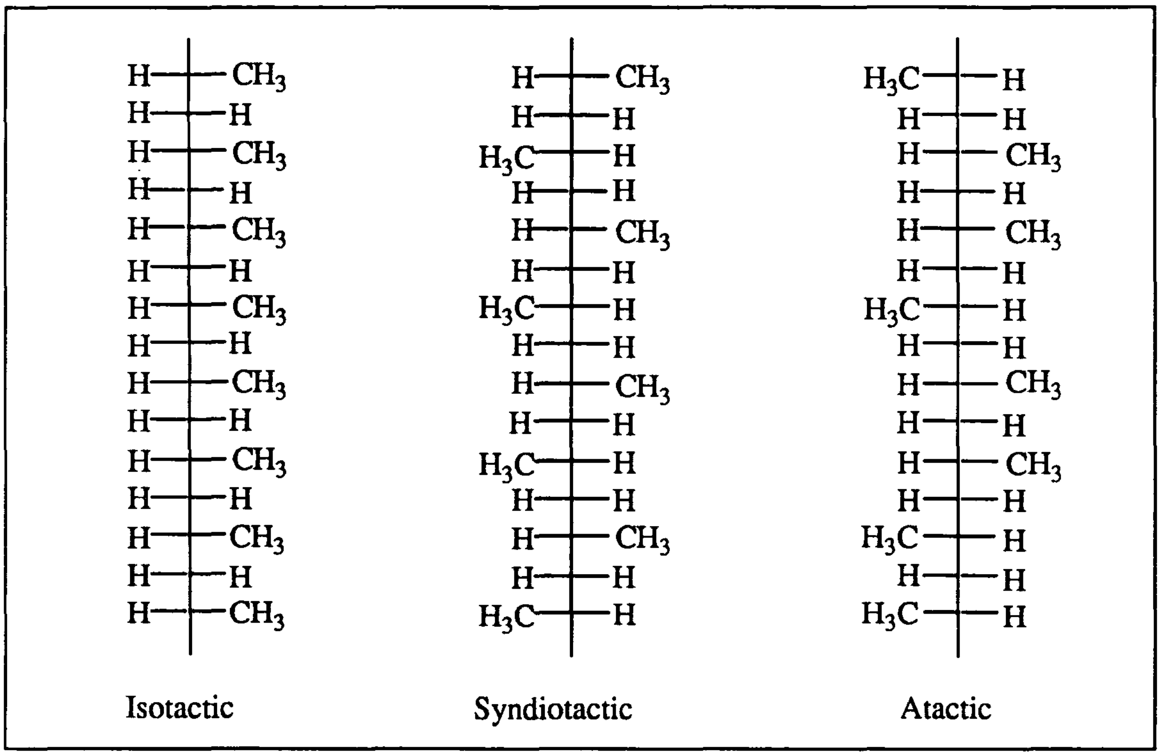
The most notable feature of the spectrum is that the methylene of the main chain and the first methylene of the side chain appear as singlets. This shows that the polymer is essentially tactic, as would be expected for this catalyst system, which is known to produce isotactic polymers from alk-1-enes.[140,141,142]

At this stage it is useful to consider the expected effect of polymer tacticities on the ^{13}C NMR spectra.

Each methine carbon of a poly(1-alkene) is a chiral centre and can have either an R or S configuration. Natta[14] originally introduced the term isotactic to describe adjacent repeat units with the same configuration, and syndiotactic to describe adjacent units with opposite configurations. The terms isotactic and syndiotactic are now generally applied to describe a polymer sequence of any length, rather than just a dyad, with atactic sequences consisting of a random arrangement of diads as shown for poly(propene)in Figure 3.2:

Figure 3.2

Fischer Projections for Polypropenes



Dyads are referred to as meso(*m*) if the configurations of the repeat units are the same (R,R) or (S,S), and racemic(*r*) if they are different (R,S).

For isotactic poly(propene) the polymer contains a series of *m* diads, and three singlets are observed in the ^{13}C NMR spectrum due to methylene, methine and methyl carbons showing that each type of carbon experiences a single microenvironment. The observed chemical shifts show good agreement with the values calculated using the Grant and Paul parameters.[144] The chemical shifts are calculated by treating the carbon of interest as an alkyl-substituted methane. Chemical shift contributions are added for each carbon up to five carbons adjacent. This approach works well for isotactic poly(propene) and for short chain branching in poly(ethene). For atactic poly(propene) and higher poly(alkenes) the spectra show a greater complexity due to conformational differences between different stereosequences.

Considering the methyl group of poly(propene), the simplest situation would be if the chemical shift was only sensitive to the configuration of the adjacent repeat units. There are three possible triad combinations, *mm, mr* and *rr.*

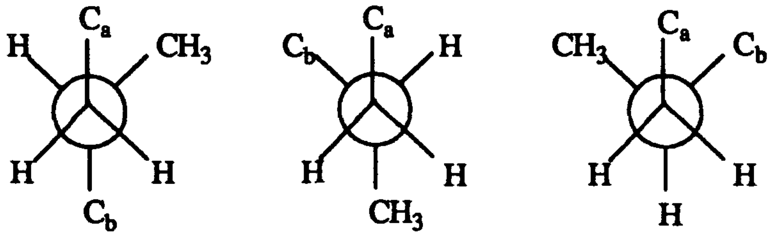
If the shift was sensitive to the next nearest unit as well then there are 10 possible pentad combinations, *mmmm, mmmr, rmmr, mmrm, mmrr, rmrm, rmrr, mrrm, mrrr* and *rrrr* which can give rise to separate chemical shifts. The pentad sequences can be split into three main groups *mm, mr and rr* centred diads, which can be seen in the spectrum given in reference 121.

If the chemical shift is sensitive to the configuration of units further away then an even greater multiplicity of chemical shifts will be observed, if the chemical shift is sensitive to the configuration of three units on either side there are 36 unique combinations of heptads.

Assignments of the methyl signal at the heptad level have been made, by comparing the shifts of model compounds with calculated values and taking into account the conformational effects of nearby units.[145] The effect of a gauche arrangement of carbon atoms separated by three bonds(γ substituents) causes an upfield shift (the γ effect) relative to the trans planar conformation. For poly(propene) the methyl group is gauche to the methine carbon of the adjacent unit when the chain is trans or gauche- but not when it is gauche+, as shown in Figure 3.3 [146]

Figure 3.3

Chain Conformations of Poly(propene)



trans
C_a-C_b :t
C_a-CH_3:g
γ effect

gauche +
C_a:C_b :g
C_a-CH_3:t
no γ effect

gauche -
C_a:C_b :g
C_a-CH_3:g
γ effect

The size of the γ effect experienced by a carbon in a polymer chain will depend on the probability of it adopting a gauche arrangement with respect to carbon atoms attached in the γ position.

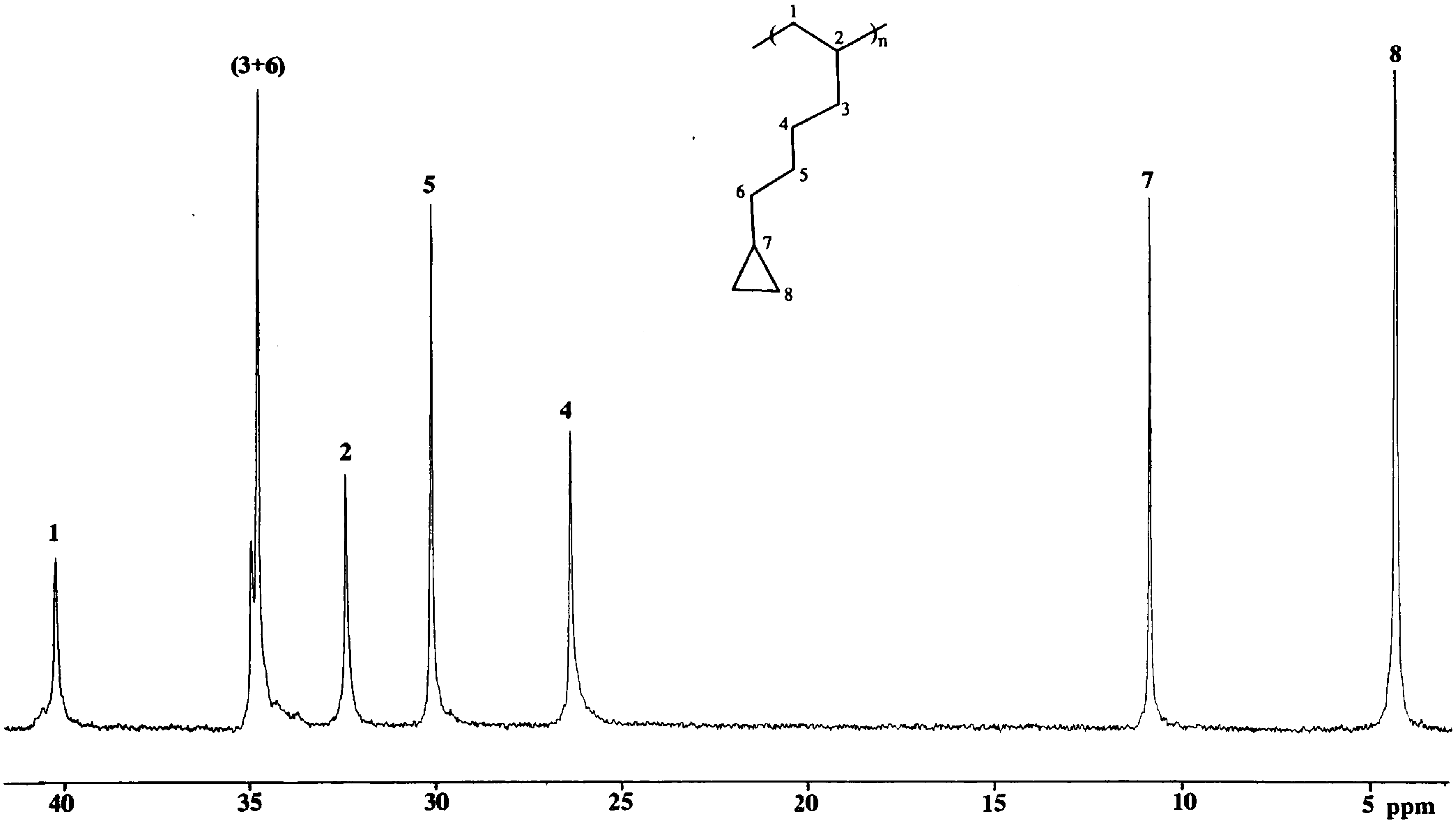
3.2.1.a.ii. Polymerization of 6-Cyclopropyl-1-hexene Initiated by Titanium(III)chloride / Triethylaluminium

Following the procedure described above, polymerization of 6-cyclopropyl-1-hexene (3.11g, 2.5×10^{-3}mol) initiated by titanium(III)chloride (0.2467g, 1.60×10^{-3}mol) and triethylaluminium (0.547g, 4.79×10^{-3}mol) in hexanes (6.4ml), at 50°C for 48 hours, provided 1.88g (60.5%) of poly(6-cyclopropyl-1-hexene). The presence of cyclopropyl groups in the polymer was confirmed by IR and NMR spectroscopy.

The IR spectrum(thin film supported on NaCl plate) showed two bands characteristic of cyclopropyl groups at: v $3075 cm^{-1}$(cyclopropyl C-H str.) v $1015 cm^{-1}$(cyclopropyl skeletal mode), the spectrum is recorded in Appendix 2.10.

Figure 3.4

^{13}C NMR Spectrum of Isotactic Poly(6-Cyclopropyl-1-Hexene)



^{1}H NMR ($CDCl_3$, 250MHz) 1.3-1.0ppm(overlapping multiplets)(11H), 0.6ppm(m)1H, 0.4ppm(m)2H, 0.0ppm(m)2H. The ratio of the peak areas showed that there had been no loss of cyclopropyl groups during polymerization. GPC (1% solution, tetrahydrofuran eluent, 10^5Å, 10^3Å and 100Å crosslinked polystyrene columns, RI detector) M_n 9100, M_w/M_n 12 relative to polystyrene standards. The ^{13}C NMR spectrum ($CDCl_3$, 62.9MHz) is shown in Figure 3.4. The assignments were made by comparison with the spectrum for poly(octene) and from the DEPT spectrum.

The spectrum indicates that mainly isotactic polymer was obtained. the presence of small peak at 40.4ppm adjacent to the main chain methylene, and at 33-34ppm adjacent to the first side chain methylene may be due to some atactic product.

3.2.1.b. Polymerization Initiated by Bis(cyclopentadienyl)zirconium dichloride / Methylaluminoxane Homogeneous Ziegler-Natta Catalyst

3.2.1.b.i. Homopolymerization of 1-Octene

Toluene (62.5 ml) and trimethylaluminium (1.22ml, 12.8mmol) were charged to a Schlenk type reaction vessel under a nitrogen atmosphere. The solution was cooled in ice, then water (0.224ml, 12.4mmol) was added by syringe with rapid stirring. The mixture was stirred for 15 minutes while the apparatus was cooled in ice, then for a further 45 minutes while it was allowed to warm to room temperature. A solution of bis(cyclopentadienyl)zirconium dichloride in toluene (0.44ml, 1.05×10^{-5}mol Zr) was injected, and the mixture stirred at room temperature for a further 60 minutes then cooled in ice for 15 minutes before adding 1-octene (5ml, 32mmol). The vessel was securely stoppered then placed in an ice bath and stirred for 117 hours. Polymerization was terminated by the addition of methanol (50ml), causing the vigorous evolution of methane and the formation of a gel in the reaction vessel.

Volatile components were removed using a rotary evaporator, then the waxy residue was extracted with petrol (b.pt.40-60^{0}C)(3x50ml). The bulk of the solvent was removed using a rotary evaporator (waterbath temperature 50°C), and the last traces removed by evacuating the flask to 1 torr at 95°C for 4 hours to give 15.96g (52.7%) of poly(octene). The polymer was soluble in toluene and petrol.

IR (thin film supported on a NaCl plate) peaks were observed at 3080cm^{-1} (C(sp^2)-H str.) and 1645cm^{-1}(C=C str.) due to vinylidene end groups in addition to the peaks expected for a saturated hydrocarbon. The spectrum is shown in Appendix 4.11. ^{1}H NMR ($CDCl_3$ 250MHz) 1.3ppm (series of overlapping signals), 1.0ppm(s), 0.86ppm(t). In addition to these main signals weak resonances were observed at 4.74ppm(d) and 2.0ppm(m), arising from vinylidene end groups. The ^{13}C NMR ($CDCl_3$ 90.5MHz) spectrum is shown in Figure 3.5

The main difference between this spectrum and that of the isotactic polymer is the multiplicity of the C1(~40ppm)and C3(~34ppm) resonances, clearly showing that the polymer produced from the metallocene catalyst is atactic. An additional feature of the spectrum is the presence of peaks at 110.2ppm and 150.0ppm due to vinylidene end groups. There were also a series of small signals at 42ppm, 35.8ppm, 29.4ppm, 29.1ppm, and 27.6ppm,assignments have not been made for each of these minor peaks. The intensity of the minor resonances was greater for lower molecular weight polymers, and therefore they must be due to terminal units.

Polymers produced from MAO/metallocene catalysts generally contain one vinylidene and one n-alkyl chain end. This was demonstrated by Tsutsui and co-workers[147] in ^{13}C NMR studies on poly(propene). The reactions involved in the formation of chain ends are shown in Figure 3.6 for the generalised case of polymerization of an alkene.

Figure 3.5

^{13}C NMR Spectrum of Atactic Poly(Octene)

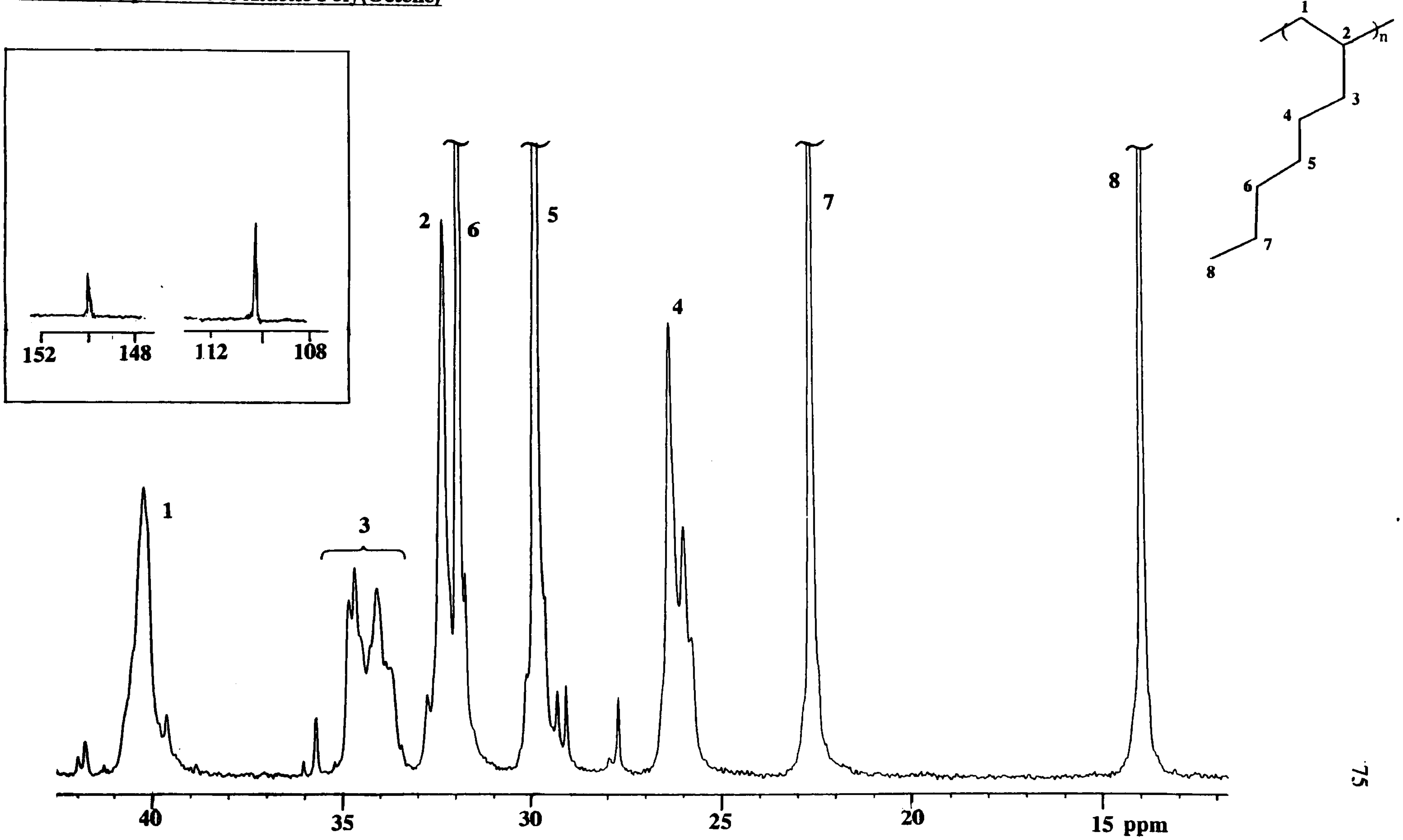
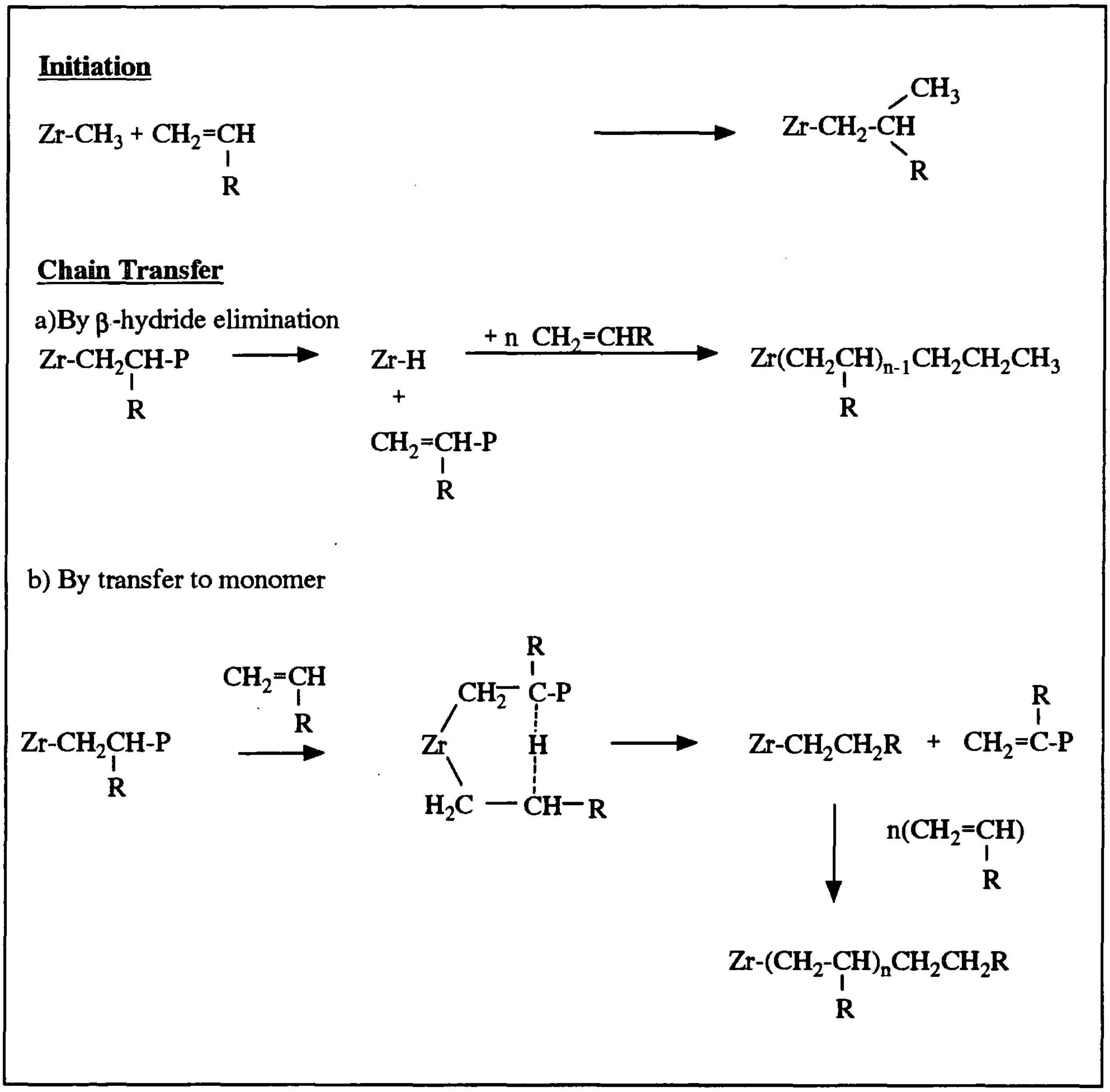


Figure 3.6

Formation of Chain Ends in Alkene Polymerization With the Kaminsky Catalyst System

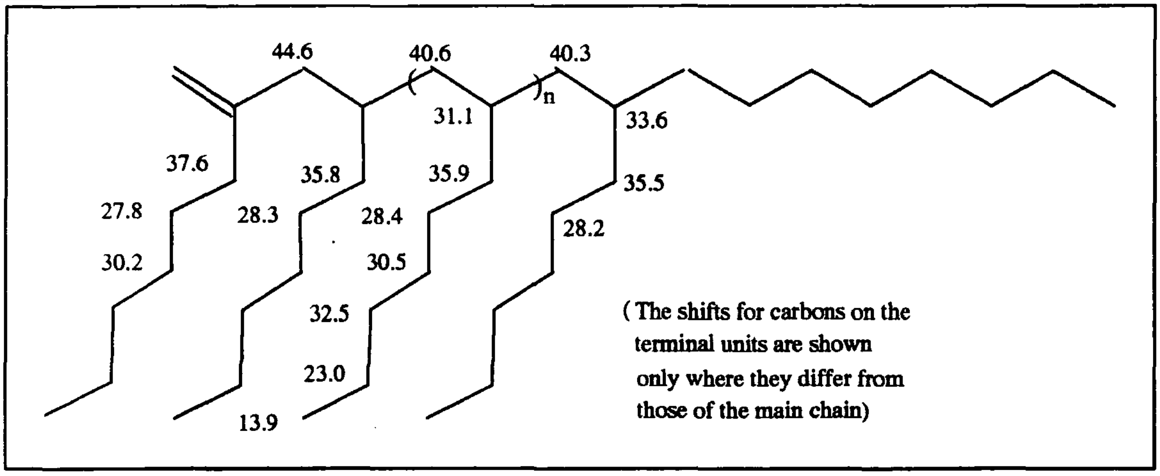


Although the exact role of the MAO in forming the active site is unknown, the overall effect is to methylate the zirconium. Evidence for this comes from short duration polymerizations of propene to low conversion[147] which allows the end due to the first insertion of monomer to be observed; for most polymerizations the number of chains initiated by insertion into the Zr-CH_3 will be very small compared to the number initiated during chain transfer. The vast majority of polymer chains will therefore contain one alkenyl end and one n-alkyl end.

The expected chemical shifts for the carbons in the end groups of poly(1-octene) predicted by this mechanistic rationalization calculated using the Grant and Paul parameters are shown in Figure 3.7, unfortunately they did not show a close correlation with the observed minor peaks in the product obtained in this work and so we are unable to confirm that Tsutsui's rationalization holds for this case.

Figure 3.7

Expected Chemical Shifts for Poly(octene) Calculated Using Grant and Paul Parameters



(The shifts for carbons on the terminal units are shown only where they differ from those of the main chain)

For poly(octene) the n-alkyl end group is very similar to the pendant alkyl groups of the main chain, and therefore it is unlikely to be observed in the ^{13}C spectrum.

3.2.1.b.ii. Study of the Reproducibility of the Polymerization of 1-Octene Initiated by Bis(cyclopentadienyl)zirconium dichloride and Methylaluminoxane.

A triplicate set of polymerizations of 1-octene (32.2g, 0.287mol) were carried out in toluene (67.5ml), initiated by bis(cyclopentadienyl) zirconium dichloride (1.03×10^{-5}mol) with methylaluminoxane prepared *in situ* from the reaction of trimethyl aluminium (0.45g, 6.25×10^{-3}mol) and water (0.111g, 6.17×10^{-3}mol), at 0°C for 96 hours. The polymers were isolated using the same procedure as described previously.

The peak molecular weights were determined by GPC, the chromatograms showed that a series of oligomers were obtained for each of the runs.

The average degree of polymerization was calculated for each run from the ^{1}H NMR spectrum, using the ratio of the vinylidene peak area to the total peak area. The results are summarized in Table 3.1

Table 3.1

Results for Triplicate Polymerizations of 1-Octene

Run	% Yield	Peak m.wt(GPC)	Dp(^{1}H NMR)
1	46.4	1240	7.1
2	61.3	1620	6.2
3	38.5	1140	5.7

The results demonstrate that there are considerable variations in the m.wt. and yield obtained from different runs under nominally the same conditions.

A major cause for the variation between runs was believed to be the method employed for the preparation of the MAO, in which water was added by syringe to a stirred solution of trimethylaluminium in toluene. The size of the water droplets cannot be controlled with any real precision, and as the trimethylaluminium reacts instantaneously with the surface of the droplets their size is likely to effect the final product. There was always some insoluble material formed when using this method of preparation.

The presence of significant numbers of unsaturated end groups due to the formation of oligomers make these products unsatisfactory for the intended use; for example the vinylidene end groups would be capable of undergoing cationically initiated polymerization, which would complicate the evaluation of crosslinking.

Clearly it was necessary to improve the reproducibility and produce higher molecular weight polymers. Several factors in the polymerization have been reported to affect the molecular weight obtained:-

a) Temperature.

In the original work by Sinn and Kaminsky the molecular weight of poly(ethene) could be increased from a series telomers, (essentially a set of α olefins) to greater than 1.5×10^6 by decreasing the polymerization temperature from 90^0C to 50^OC.

b) Monomer concentration.

The molecular weight increases with increasing monomer concentration

c) Aluminium:Zirconium ratio.

Increasing this ratio gives both higher molecular weight polymer and higher yield.

d) The degree of oligomerization of the methylaluminoxane.

(This factor was not studied during the current investigation.)

3.2.1.b.iii. Preparation of a Stock Solution of MAO Using Hydrated Copper Sulphate as the Source of Water.

The procedure described by Ewen[121] was employed. Trimethylaluminium (40ml, 0.417mol) was added over 40 minutes to a stirred slurry of copper sulphate pentahydrate (20.8g, 0.417mol H_2O) in toluene (350ml) cooled in an icebath. The mixture was allowed to gradually warm to room temperature then stirred for a further 16 hours before removing the solid by filtration.

3.2.1.b.iv. Study on the Effect of Variation in the Ratio of Al:Zr on the Polymerization of 1-Octene

Four polymerizations of 1-octene (45ml, 287mmol) in toluene (67.5ml) at 0°C for 42 hours initiated by bis(cyclopentadienyl)zirconiumdichloride (1.03×10^{-5}mol) and different amounts of MAO from a stock solution were carried out following the procedure described above. Polymerizations were terminated by the addition of methanol and isolated in the usual way before determining the molecular weight by GPC (1% solution, tetrahydrofuran eluent, 10^3Å and 100Å crosslinked polystyrene columns, RI detector). Four different ratios of Al:Zr were employed, the results are summarized in Table 3.2:

Table 3.2

Effect of Al:Zr Ratio on the Polymerization of 1-Octene

Al/Zr	%Yield	Peak m.wt.
510	6.3	832
1020	8.1	1245
1530	8.5	1400
2040	13.0	1988

The results show that increasing the Al:Zr ratio gives improved yields and increased molecular weights for the polymerization of octene. This is in agreement with previous findings for the polymerization of ethene and propene.[121,133b]

3.2.1.b.v. Comparison Between MAO Prepared as Stock Solution and MAO Prepared by the Direct Addition of Water for Use in Polymerization of 1-Octene.

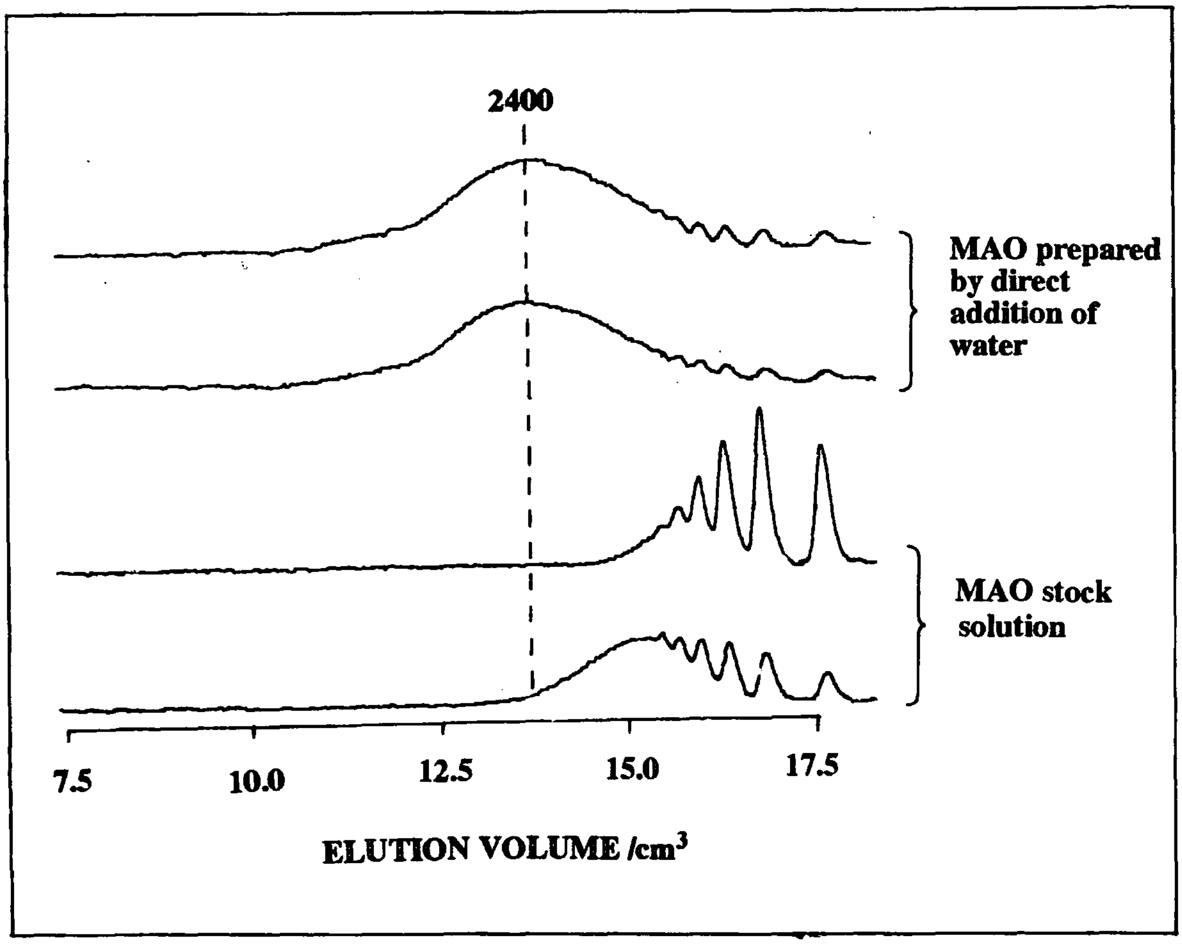
Polymerization of 1-octene (45ml,287mmol) in toluene (67.5ml) initiated with bis(cyclopentadienyl) zirconium dichloride ($3x10^{-3}$g, $1.03x10^{-5}$mol) with MAO cocatalyst ($6.24x10^{-3}$ mol Al) was carried out at 0°C for 86 hours, using two different sources of MAO. A pair of polymerizations using the stock MAO solution were compared with a pair in which water (0.112ml, $6.22x10^{-3}$mol) was added directly to the trimethylaluminium. The polymers were recovered by the usual method.

The yields using the direct addition of water were 57.8% and 49.9%, compared to 22.9% and 14.5% from the use of the stock MAO solution.

The GPC chromatograms are shown in Figure 3.8. The stock solution of MAO appeared much less satisfactory than the use of the MAO prepared by direct reaction of water with trimethylaluminium, and therefore the use of stock MAO solutions was not pursued.

Figure 3.8

GPC Chromatograms Showing the Effect of the Method of MAO Preparation on the Polymerization of 1-Octene



The result was the opposite to the expected behaviour, as the preparation using copper(II)sulphate pentahydrate appeared to be a much more controlled procedure. Gianetti[126] and Gross[148] had previously found that MAO prepared by the direct addition of water to trimethylaluminium was much less satisfactory than using a hydrated salt (preferably aluminium sulphate) as the water source. The procedure used was basically the same as that employed by Ewen, who achieved high yields of poly(propene). The degree of oligomerization of the MAO depends on the concentration of the solution, discussion with other workers[149] showed that the activity of the MAO also depends on the rate of addition of trimethylaluminium and on the rate of heating. In order to obtain maximum activity volatile components should be removed to give solid MAO which is then redissolved prior to use. In the current investigation the use of aluminium sulphate hexadecahydrate and removal of volatiles to give the solid MAO were tried, neither procedure gave activities as high as those obtained with MAO produced by the direct addition of water to solutions of trimethylaluminium in toluene. From the results obtained for the use of stock solutions of MAO it was decided to continue the preparation of MAO by the direct addition of water, until a more satisfactory practical alternative was obtained.

3.2.1.b.vi. Effect of Monomer Concentration on the Polymerization of 1-octene

Five batches of catalyst solution were prepared in the usual way from trimethylaluminium (1.22ml, 12.8mmol), water (0.224ml, 12.4mmol) and bis(cyclopentadienyl)zirconium dichloride (1.05×10^{-5}mol) in toluene (62.5ml). Different amounts of 1-octene were added to each batch, and polymerized for 118 hours at 0°C. The results are summarized in Table 3.3:

Table 3.3

The Effect of Monomer Concentration on the Polymerization of 1-Octene

[octene] (wt%)	Yield	Peak m.wt
6.2	45.6	970
11.8	51.5	1170
20.9	54.7	2200
34.5	45.8	2610
55.2	48.8	2790

The results are in agreement with the findings of other workers for detailed studies on the polymerization of propene[121] and ethene[133b]; namely, that the molecular weight increases with increasing monomer concentration. The molecular weight depends on the rate of the chain transfer reaction relative to the rate of the polymerization and that the accepted rationalization of these observations is that the rate of polymerization is dependant on the monomer concentration, while the rate of chain transfer by β-hydride elimination is unaffected by the monomer concentration.

3.2.1.b.vii. Homopolymerization of Propene

The polymerization was carried out in a thick walled glass reaction vessel, fitted with a double tap arrangement to allow addition of catalyst when the vessel was under pressure, a diagram of the vessel is shown in Appendix 4. The propene concentration used was intended to provide a saturated solution based on published solubility data for similar solvents.[150] this was intended to prevent the development of excessive pressure within the vessel. As an additional precaution all the manipulations of the apparatus were carried out behind a protective screen.

Water (0.33ml, 18.4mmol) was added, with stirring, to a solution of trimethylaluminium (1.80ml, 18.4mmol) in toluene (100ml) which had been cooled to 0°C in an icebath. After allowing the mixture to stir for 3.75 hours the vessel was cooled in liquid nitrogen, then propene (14.8g, 0.352mol) was added using standard gas handling techniques. The vessel was then transferred to the cooling bath and immersed in an acetone/carbon dioxide slush contained in the inner aluminium bath. The bath was warmed gradually by the addition of cold water, then drained and refilled with ice before allowing the temperature of the monomer solution to equilibrate with the bath temperature for 30 minutes. Bis(cyclopentadienyl)zirconium dichloride (6.28×10^{-3}g, 2.15×10^{-5}mol) in toluene (3.59ml) was added from the side arm then the mixture was stirred for 24hours.

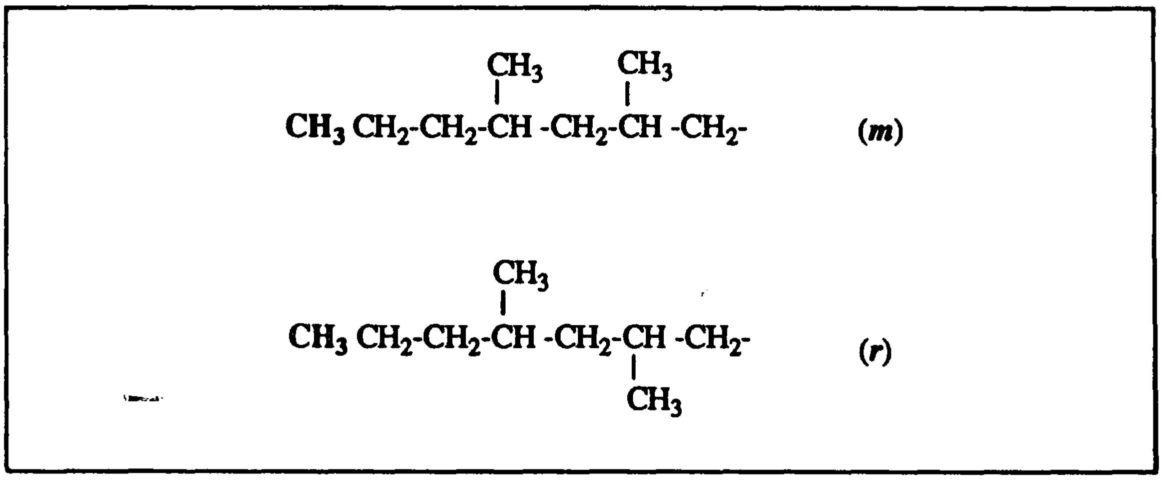
The polymerization was terminated by the addition of methanol (50ml), which caused a vigorous evolution of gas and the formation of a flocculant white precipitate. Volatile components were removed using a rotary evaporator to leave a white waxy solid, this was extracted with petroleum (b.pt.40-60°C)(4x100ml) volatile components were removed using a rotary evaporator followed by heating to 95°C at 0.1 torr, to give 8.71g (59%) of poly(propene).

The ^{13}C NMR (62.9MHz, $CDCl_3$) spectrum is shown in Figure 3.10.

A multiplicity of signals are observed, due to the main chain methylene carbons (44-46ppm), methine (ca 27ppm), and methyl groups (20.7ppm). Additional signals due to end groups were observed, assignments were made by comparison with results of Tsutsui and co-workers. The splitting of the signal due to the terminal methyl into a doublet has been assigned to the presence of two different stereoenvironments, as shown in Figure 3.9.

Figure 3.9

Stereoenvironments of Terminal Methyl Groups in Poly(propene)



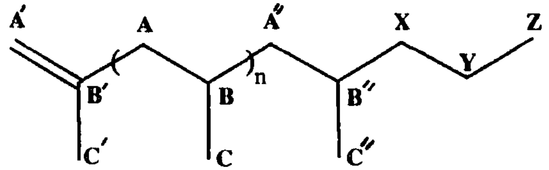
$$CH_3\,CH_2\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{C}H}\text{ -}CH_2\text{-}\overset{CH_3}{\overset{|}{C}H}\text{ -}CH_2\text{-} \qquad (m)$$

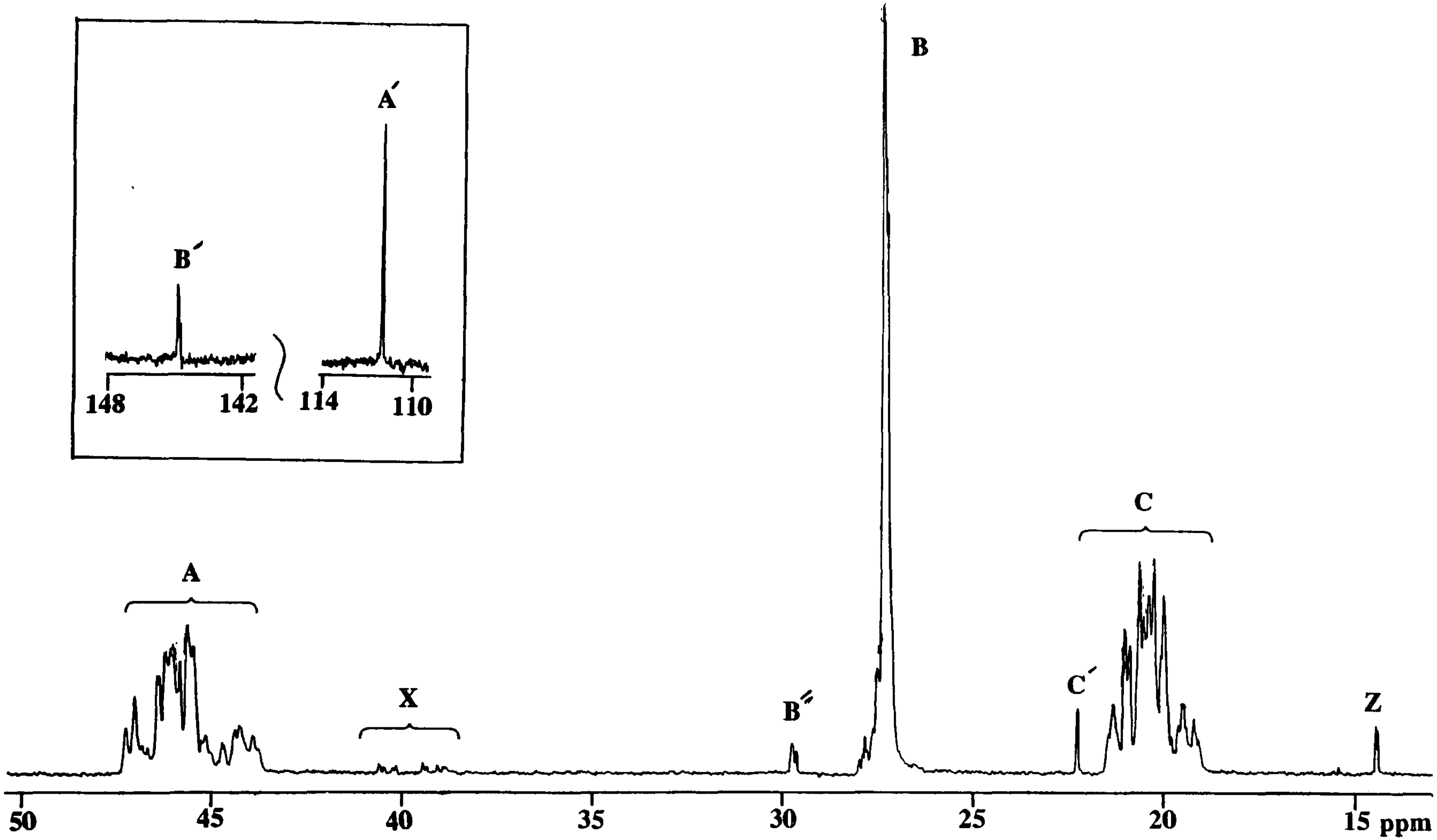
$$CH_3\,CH_2\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{C}H}\text{ -}CH_2\text{-}\underset{CH_3}{\underset{|}{C}H}\text{ -}CH_2\text{-} \qquad (r)$$

The similarity in intensities for the two signals shows that (*m*) and (*r*) units are formed with the same probability. The methyls adjacent to the terminal n-propyl end (C'') in polypropene have previously been shown to be sensitive to the arrangement of methyl groups up to five carbons distant.[151,152] In Figure 3.10 C''is obscured by the multiplicity of the signals due to C.

Figure 3.10

^{13}C NMR Spectrum of Atactic Poly(Propene)

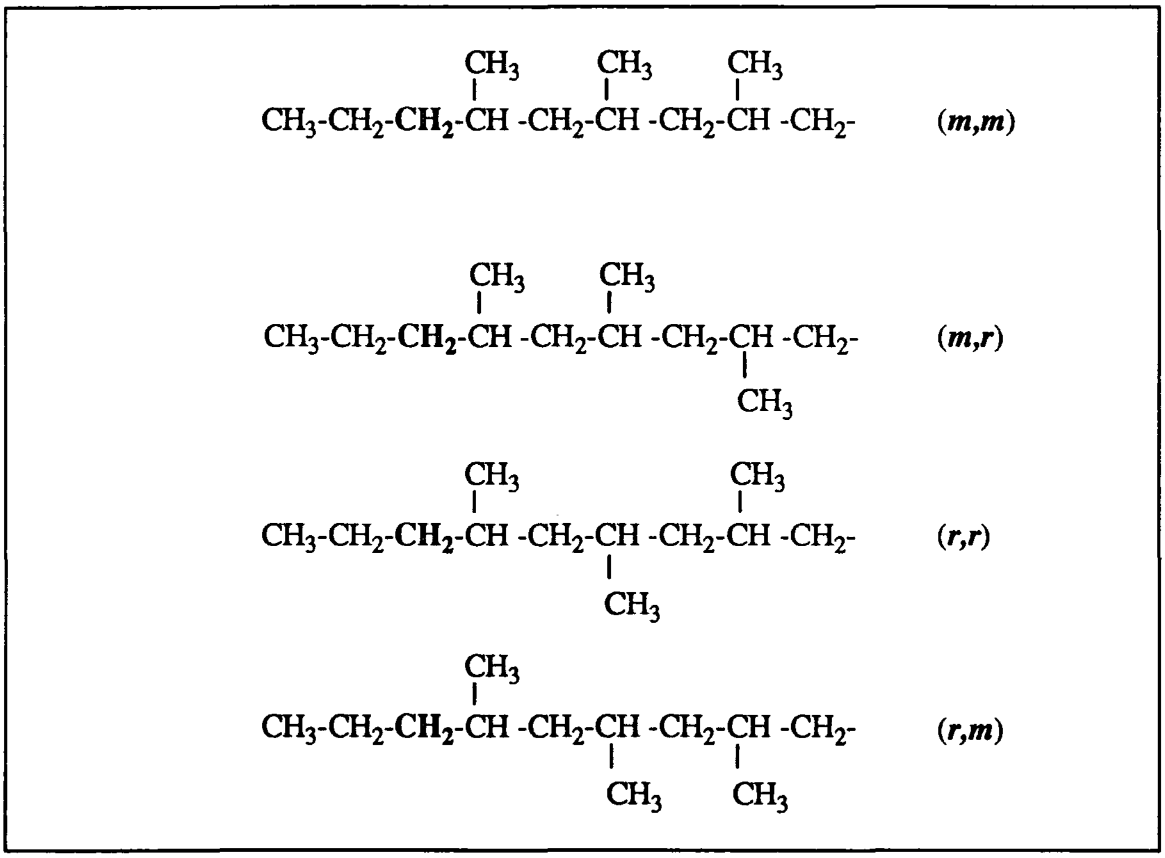




A series of eight relatively weak peaks with similar intensity are visible between 38.9-40.6ppm. Tsutsui concluded that four bands between 40.3-41.3ppm were due to the effect of differences in the stereochemistry of the three neighbouring repeat units on these methylene carbons(Figure 3.11).

Figure 3.11

Stereoenvironments of Methylene Groups in Poly(propene)



$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}CH_2\text{-} \qquad (m,m)$$

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}CH_2\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-} \qquad (m,r)$$

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}CH_2\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}CH_2\text{-} \qquad (r,r)$$

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}CH_2\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-}\underset{CH_3}{\underset{|}{CH}}\text{-}CH_2\text{-} \qquad (r,m)$$

The four peaks between 38.6-39.6ppm were ignored by Tsutsui, even though they have the same intensity as those assigned above. If they were due to a different end group arising from an alternative initiation or termination process then additional peaks should be observed elsewhere in the spectrum, no such peaks were observed. They occur in the correct region for the methylene carbon, which leads to the conclusion that all eight peaks are due to the methylene group which is affected by the stereoenvironment of the four adjacent repeat units, giving rise to eight triads, *mmm, mmr, mrm, mrr, rmm, rmr, rrm* and *rrr.* All the signals have similar intensities, implying a completely non selective polymerization.

The ^1H NMR (250MHz, $CDCl_3$) 4.7ppm(d), 1.6ppm(m), 1.3-0.8ppm (overlapping signals) and IR spectra (Thin film supported on a NaCl plate) 2950cm^{-1},2915cm^{-1},2860cm^{-1},2840cm^{-1}, 1455cm^{-1},1370cm^{-1}, no C=C str. observed at 1645cm^{-1}(Appendix 4.12) were in agreement with the assigned structure. GPC (1% solution, tetrahydrofuran eluent, 10^5Å, 10^3Å and 100Å crosslinked polystyrene columns, RI detector) showed that a low molecular weight polymer had been obtained, M_n=3016, M_w=6334, M_w/M_n=2.1.

The Use of Tributyl Tin Oxide to Prepare MAO

3.2.1.b.viii. Homopolymerization of 1-Octene at 0°C

Tributyl tin oxide (4.56g, 9.53mmol) was added to a solution of trimethylaluminium 91.22ml, 12.7mmol) in toluene (67.5ml), with stirring at room temperature. The mixture was stirred for 30 minutes then 1-octene (45ml, 287mmol) was added then the mixture cooled by immersion in an icebath for 30 minutes before injecting a solution of bis(cyclopentadienyl)zirconium dichloride (3mg, 1.02×10^{-5}mol) in toluene (0.43ml). The vessel was maintained at 0°C for 96 hours by immersion in ice, before the polymerization was terminated by the addition of methanol (50 ml). The polymer was purified by the removal of aluminium oxide arising from the catalyst followed by reprecipitation four times from petrol into methanol.

The effect of varying the ratio of tributyl tin oxide to trimethylaluminium was studied, the results (shown in Table 3.4) were in agreement with those of Porri for the polymerization of propene, where the optimum ratio was 1:0.75.[127]

Table 3.4

Effect of Variation of $AlMe_3:(Bu_3Sn)_2O$ on the Polymerization of 1-Octene

$AlMe_3:(Bu_3Sn)_2O$	%Yield
1 : 0.6	19
1 : 0.7	89
1 : 0.8	87
1 : 0.9	1.5
1 : 1.0	trace

Homopolymerization of Propene Using Improved Method of MAO Preparation.

3.2.1.b.ix. Polymerization at 0°C

The polymerization was carried out in the thick-walled glass reaction vessel described earlier. Tributyl tin oxide (8.97g, 15.1 mmol) was added, with stirring, to a solution of trimethylaluminium (1.80ml, 18.4mmol) in toluene (96.1ml) at room temperature. After allowing the mixture to stir for 30 minutes the vessel was cooled in liquid nitrogen, then propene (15.4g, 367mmol) was added using standard gas handling techniques. The vessel was transferred to an acetone/carbon dioxide slush bath at -78°C, the polymerization mixture was allowed to completely melt at -78°C before gradually warming to 0°C. The vessel was placed in a well insulated ice bath, the mixture was stirred for 1 hour before adding a solution of bis(cyclopentadienyl)zirconium dichloride (2.15×10^{-5}ml) in toluene (3.89ml). The reaction was allowed to continue at 0°C for 24 hours before adding methanol (50ml) to terminate the polymerization.

Volatile components of the mixture were removed using a rotary evaporator, then the crude product was washed with petroleum (b.pt.40-60°C)(3x100ml) and filtered through a fluted filter paper before removing the petroleum spirit using a rotary evaporator. The polymer was then purified by precipitation four times into methanol(200ml) from solution in petroleum (20ml) followed by removal of residual solvent at 95°C and 0.1 torr for 2 hours, to give 13.7g (89%) of poly(propene).

GPC (1% solution, tetrahydrofuran eluent, 10^3Å and 100Å crosslinked polystyrene columns, RI detector) showed that a higher molecular weight polymer had been obtained than was produced using the previous catalyst M_n=5300, M_w/M_n=4.82. The IR (Thin film supported on a NaCl plate)(Appendix 4.13), ^{1}H NMR ($CDCl_3$,400MHz) and ^{13}C NMR ($CDCl_3$,100MHz) spectra were essentially the same as for the previous sample, with a reduction in the intensity of signals due to vinylidene end groups.

3.2.1.b.x. Homopolymerization of Propene at -25°C

Polymerization of 14.7g(350mmol) propene initiated by bis(cyclopentadienyl)zirconium dichloride (2.15 x 10^{-5}mol),tributyl tin oxide (8.97g, 1.51x10-2mol) and trimethylaluminium (1.35g, 1.84x10^{-2}mol) at -25°C gave 13.5g (92%) of poly(propene).

GPC (1% solution, tetrahydrofuran eluent, 10^3Å and 100Å crosslinked polystyrene columns, RI detector) showed that the molecular weight was considerably higher than for the sample polymerized at 0°C (M_n=14060, M_w/M_n=3.42 relative to polystyrene standards), demonstrating that variation in polymer molecular weight could be achieved by control of the polymerization temperature. These results confirmed earlier reports, see 3.2.1.b.ii above.

3.2.1.b.xi. Copolymerization of Propene with 1-Octene

The procedure was basically the same as that employed in the homopolymerization of propene, with the addition of octene taking place just prior to cooling the vessel in liquid nitrogen for the addition of propene.

Polymerization of 1-octene (10.0g, 0.089mol) with propene (14.8g, 0.352mol) in toluene (100ml), initiated by a catalyst system of bis(cyclopentadienyl)zirconium dichloride (2.15x10^{-5}mol) and a methylaluminoxane prepared from the reaction of trimethylaluminium (1.80ml, 18.8mmol) with tributyltin oxide (8.97g, 15.1mmol), for 24 hours provided 8.75g, 90% of copolymer.

GPC (1% solution, tetrahydrofuran eluent, 10^3Å and 100Å crosslinked polystyrene columns, RI detector) M_n=5300, M_w/M_n=4.34

The polymerization demonstrated that a copolymer of propene and a higher 1-alkene could be obtained in good yield and with a similar molecular weight to propene homopolymer.

3.2.1.b.xii. Attempted Homopolymerization of 6-Cyclopropyl-1-Hexene

The procedure was the same as for the polymerization of octene described earlier. The catalyst was prepared from trimethylaluminium (1.22ml, 12.7mmol), tributyl tin oxide (6.07g, 10.2mmol) and bis(cyclopentadienyl)zirconium dichloride (3mg, 1.02×10^{-5}mol) in toluene (67.5ml). 6-Cyclopropyl-1-hexene (45ml, 284mmol) was added, and allowed to stir at 0°C for 144 hours. The polymerization was terminated by the addition of methanol (50ml), volatile components were then removed under reduced pressure to give a white paste. The crude mixture was extracted with petroleum (3x75ml) then the solvent was removed to leave a clear fluid. The fluid was diluted with petroleum (25ml) then poured, with stirring, into methanol (400ml) the mixture was completely soluble in methanol indicating no polymer had been obtained. (Several attempts to homopolymerize 6-cyclopropane-1-hexene using the homogeneous catalyst systems were carried out, none provided any polymer.) ***This surprising result is discussed later.*** Unreacted monomer was recovered from the mixture.

Model Studies on the Polymerization of Alkenylcyclopropanes using Zirconocene/MAO Catalysts.

3.2.1.b.xiii. Reaction of Bis(cyclopentadienyl)zirconium dichloride With Ethylcyclopropane

A solution of ethylcyclopropane(0.81g, 1.17x10^{-3}mol) and bis(cyclopentadienyl)zirconium dichloride (0.1703g, 5.83x10^{-4}mol) in toluene (25ml) was stirred at room temperature for 6 days. Volatile components were removed in vacuo, and gas chromatographic analysis showed that only ethylcyclopropane and toluene were present in the removed volatiles.

In a separate study ethylcyclopropane (1.03g,1.47x10^{-2}mol) was stirred with bis(cyclopentadienyl)zirconium dichloride (0.1766g, 6.05x10^{-4}mol) at room temperature for 6 days. An aliquot was filtered, then the IR spectrum was recorded for a capillary film between sodium chloride plates, the spectrum was correct for ethylcyclopropane.

The results did not provide evidence for any interaction between the cyclopropane group of the ethylcyclopropane with the bis(cyclopentadienyl)zirconium dichloride in the absence of MAO cocatalyst. It may not be valid to compare the behaviour in this test with the actual behaviour of the active catalyst.

3.2.1.b.xiv. Comparison Between the Effect of an Alkylcyclopropane and an Alkenylcyclopropane on the Polymerization of 1-Octene

Three polymerizations of 1-octene (45ml, 0.287mol) in toluene (67.5ml) initiated by a catalyst prepared by the reaction of trimethylaluminium (1.22ml, 12.7mmol) and water (0.224ml, 13.6mmol) with bis(cyclopentadienyl)zirconium dichloride (1.46x10^{-5}mol) were carried out.

A 1-octene only (control)

B 1-octene + ethylcyclopropane (mol ratio 1:0.25)

C 1-octene + hexenylcyclopropane (mol ratio 1:0.20)

The polymerizations were allowed to continue for 139 hours at 0°C, before terminating by the addition of methanol, the polymers were recovered by the usual procedure. The molecular weights were determined by GPC (1% solution, tetrahydrofuran eluent, 10^3Å and 100Å crosslinked polystyrene columns, RI detector)

A gave 73.9% yield, M_n 1630, M_w/M_n 2.48

B gave 59.6% yield, M_n 1250, M_w/M_n 2.98

C gave 26.0% yield, M_n 1030, M_w/M_n 1.63

The ^{1}H NMR ($CDCl_3$,250MHz) spectra of A and B showed the same resonances as previous samples of poly(octene). There was no evidence for the incorporation of ethylcyclopropane into B. The spectrum of polymer C contained additional signals at 0.67ppm(m), 0.4ppm(m), and 0ppm(m) characteristic of the ABX system of a mono alkyl cyclopropane. Polymer C was calculated to contain 18.5mol% 6-cyclopropyl-1-hexene, from the intergral of the signal for the cyclopropyl methylene protons. The spectra are shown in Appendices 3.1,3.2 and 3.3

The IR spectra (thin films supported on NaCl plates) of A and B showed absorption modes due to saturated aliphatic groups, and also maxima at 1645cm^{-1} and 890cm^{-1} due to C=C stretching and C-H out of plane bending of vinylidene end groups. The spectrum of C confirmed the incorporation of 6-cyclopropyl-1-hexene by the presence of a cyclopropyl skeletal mode at 1010cm^{-1}. The spectra are shown in Appendices 4.14, 4.15 and 4.16.

The ^{13}C NMR spectra ($CDCl_3$, 62.9MHz) of A and B were the same as those for poly(octene) obtained in earlier polymerizations. The spectrum of C contained additional signals at 4.4ppm and 10.9ppm due to cyclopropyl methylene and methine carbons. The spectra are shown in Appendices 3.5,3.6 and 3.7.

The combined analytical results clearly demonstrated that 6-cyclopropyl-1-hexene could be polymerized using the bis(cyclopentadienyl)zirconium dichloride/MAO catalyst. Copolymerization with octene gave a copolymer which had a similar composition to the monomer feed. The yield and molecular weight of the copolymer were lower than those of poly(octene) homopolymer. Because of the wide variation in the yields observed for earlier octene polymerizations it is difficult to decide whether the 6-cyclopropyl-1-hexene was responsible for Run C providing the lowest yield, or whether this was merely a reflection of the poor reproducibility of the method.

The presence of ethylcyclopropane appeared to have little or no effect on the yield, showing that the cyclopropane group does not destroy the catalyst activity.

The results from this series of polymerizations provide no explanation why 6-cyclopropyl-1-hexene should fail to homopolymerize in any of a series of 5 attempts. This failure was surprising, especially as an isotactic homopolymer had been obtained earlier using the heterogeneous titanium(III)chloride/triethylaluminium. Several possible causes were considered for the apparent inability of the monomer to homopolymerize.

The cyclopropane ring may interact with the transition metal centre of the active catalyst, interfering with the catalytic activity. The ability of octene to undergo polymerization in the presence of ethylcyclopropane showed that any interaction between the cyclopropane and the active catalyst is not strong enough to significantly effect the polymerization. The copolymerization of 1-octene with 6-cyclopropyl-1-hexene shows that the cyclopropyl monomer does not completely destroy the catalyst activity, although the yield of copolymer was less than the yield of octene homopolymer under the same conditions. This suggests that the monomer should homopolymerize, although possibly in lower yield than octene.

An alternative possibility is that the 6-cyclopropyl-1-hexene monomer contained an unidentified impurity, which was interfering with the catalyst. As only a very small amount of zirconium compound was used in the polymerizations the effect of even a trace impurity could be dramatic.

The 6-cyclopropyl-1-hexene monomer solution may act as a poorer solvent for the active catalyst species and may have led to the catalyst being precipitated from solution, however this seems unlikely in view of the similarity between octene and 6-cyclopropyl-1-hexene.

A tentative explanation is that the steric effect of the cyclopropyl group is greater than that for the linear alkyl group of 1-octene. For other alkenes it has been shown that chain branching causes a reduction in the reactivity in Ziegler-Natta polymerization, due to steric hindrance. The effect of chain branching diminishes with increasing distance from the double bond. For 6-cyclopropyl-1-hexene there are four methylene units between the cyclopropyl group and the double bond, and therefore one would expect very little steric effect. The copolymer with 1-octene had a lower molecular weight and was obtained in lower yield than the octene homopolymer, which further supports the suggestion that the problem is due to steric hindrance.

In summary, there appeared no satisfactory explanation for the failure of 6-cyclopropyl-1-hexene to homopolymerize, this merits further investigation.

Although the 6-cyclopropyl-1-hexene/octene copolymer contained pendant cyclopropyl groups it was not suitable for crosslinking studies because of the large number of vinylidene end groups which could undergo cationic polymerization. In order to provide polymers worth testing for network formation it would be necessary to produce higher molecular weight polymers. Clearly octene is not the best choice of comonomer to provide potentially useful coatings, and copolymers with propene were chosen for investigation on the basis of experimental convenience. If the preliminary investigations in this study were promising then it would probably be necessary to produce terpolymers containing ethene, propene and cyclopropyl monomer, however the facilities for the small scale copolymerization of ethene were not available to us.

3.2.1.b.xv. Copolymerization of Propene With 6-Cyclopropyl-1-hexene Using MAO Prepared by the Direct Addition of Water to Trimethylaluminium

The procedure was generally the same as for the homopolymerization of propene described earlier. Water (0.33ml, 18.4mmol) was added to a stirred solution of trimethylaluminium (1.80ml, 18.8mmol) in toluene (100ml) at $0^{o}C$. The mixture was stirred at $0^{o}C$ for 45 minutes, then allowed to warm to room temperature over 1 hour. 6-Cyclopropyl-1-hexene (11.2g, 0.0903 mol, 18.4mol% of monomer feed) was added prior to cooling vessel in liquid nitrogen. Propene (16.8g, 0.40 mol) was added, then the vessel was slowly warmed to $0^{o}C$ before adding a solution of bis(cyclopentadienyl) zirconium dichloride ($2.15x10^{-5}$mol) in toluene (3ml). The polymerization was terminated after 24 hours by the addition of methanol (50ml) before working up the polymer in the usual way to give 4.17g (14.9%) of low viscosity clear colourless fluid.

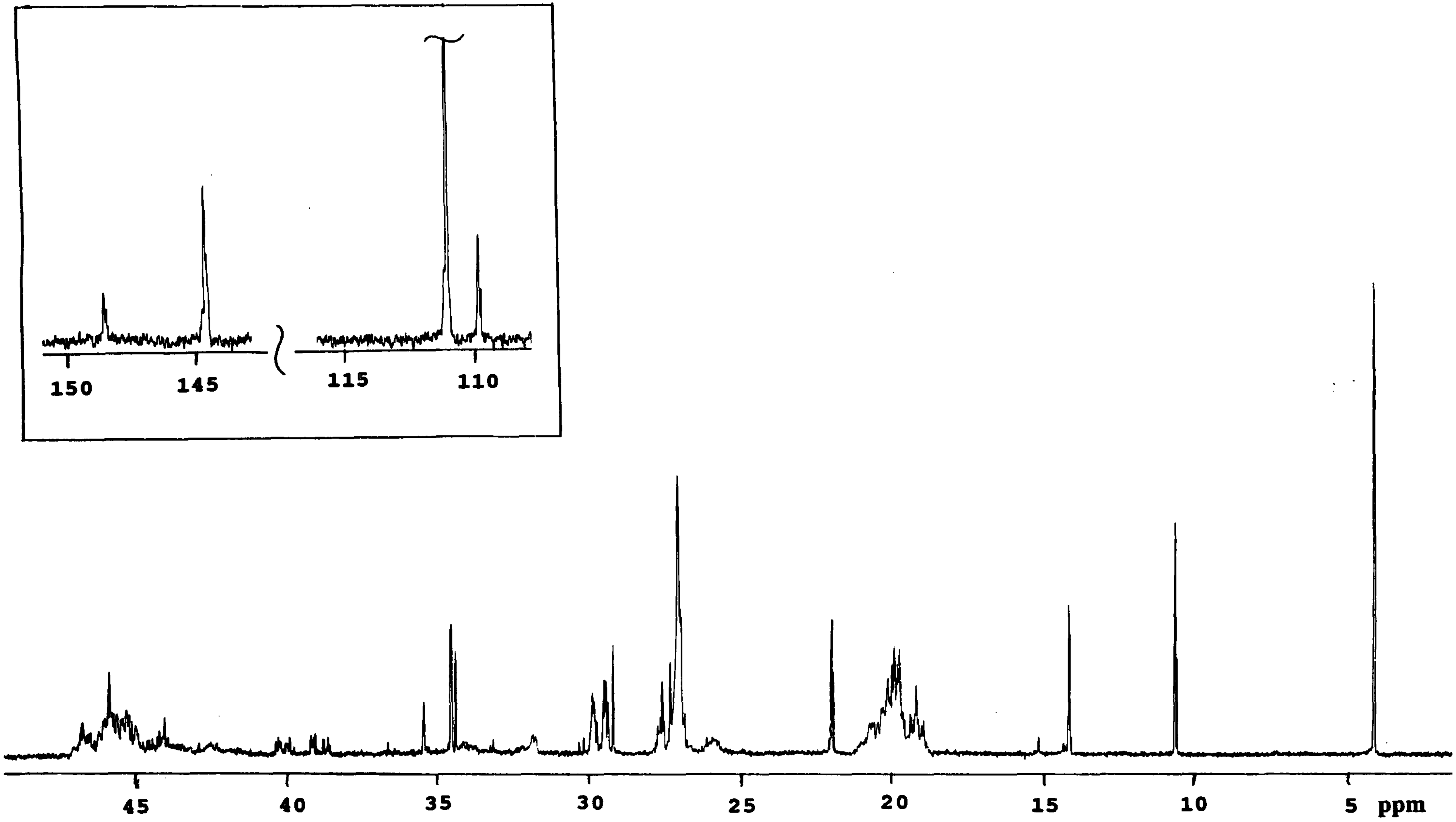
The ^{1}H NMR spectrum (250MHz, $CDCl_3$) 4.7ppm(d), 2.0ppm(m), 0.9ppm(m), 0.4ppm(m), 0.0ppm(m), 1.8-1.0ppm(series of overlapping signals), allowed the composition of the copolymer to be calculated from the intergrals of the cyclopropyl methylene protons at 0.4 and 0.0ppm. This showed that the copolymer contained 13.6 mol% of 6-cyclopropyl-1-hexene. The incorporation of 6-cyclopropyl-1-hexene into the polymer was confirmed by the ^{13}C NMR (62.9MHz, $CDCl_3$) and IR (thin film supported on a NaCl plate)(Appendix 4.17) 3060cm^{-1} (C-H str. cyclopropyl), 1645cm^{-1}(C=C str.), 1010cm^{-1}(cyclopropyl skeletal mode), 890cm^{-1}(C-H out of plane bend) spectra. GPC (1% solution, tetrahydrofuran eluent, 10^{3}Å and 100Å crosslinked polystyrene columns, RI detector) showed that a very low molecular weight polymer had been obtained M_n=440, M_w/M_n=1.6

In summary, the results showed that 6-cyclopropyl-1-hexene could be copolymerized with propene, however the molecular weight was too low to provide materials useful for crosslinking studies, and therefore higher molecular weight copolymers were required.

The short chain length of the copolymer was useful in allowing the chain ends to be observed in the ^{13}C NMR spectrum (Figure 3.13), and showed that vinylidene end groups were produced from each monomer. The end groups formed from propene units gave resonances at 144.9ppm and 111.4ppm, the end groups from the 6-cyclopropyl-1-hexene resonated at 148.7ppm and 109.8ppm. Although caution must be exercised when comparing the relative intensity of signals in ^{13}C NMR spectra, the spectrum appears to show that the ratio of monomers in the vinylidene chain ends is the same as the overall polymer composition.

Figure 3.13

^{13}C NMR Spectrum of Low Molecular Weight Propene/6-Cyclopropyl-1-Hexene Copolymer



3.2.1.b.xvi. Copolymerization of Propene With 6-Cyclopropyl-1-hexene Using MAO Prepared by the Reaction of Tributyltin oxide With Trimethylaluminium

The procedure was similar to the one described above, except for the method of preparation of the MAO. Tributyl tin oxide (8.97g, 15.1mmol) was added to a stirred solution of trimethylaluminium (1.80ml, 18.8mmol) in toluene (97ml). The mixture was stirred for 1 hour at room temperature, then 6-cyclopropyl-1-hexene (5.0g, 0.0403 mol) was added before cooling the vessel in liquid nitrogen. Propene was added using standard gas handling procedures, then the mixture was slowly warmed to the required temperature. A solution of bis(cyclopentadienyl) zirconium dichloride ($2.15\text{x}10^{-5}$mol) in toluene (3ml) was added to initiate polymerization. After 24 hours methanol (50ml) was added and the polymer was recovered in the usual way.

Two series of copolymers were prepared, one series of polymerizations at 0°C, and one at -25°C, the amount of 6-cyclopropyl-1-hexene was the same in each run, the level of propene was varied to control the composition of the monomer feed. The results for the two series are summarized in Table 3.5:

Table 3.5

Summary of 6-Cyclopropyl-1-Hexene / Propene Copolymers

Run	Temp °C	Mol% 6-cyclopropyl -1-hexene In Monomer	In Polymer	M_w	M_n	M_w/M_n	%Yield	$\overline{y}_w$
I	0	4.6	2.9	21800	6500	3.36	86	14
II	0	8.9	3.7	28000	5700	4.91	85	23
III	0	17.0	13.2	13200	5600	2.46	75	33
IV	0	26.9	17.0	10400	5200	2.00	65	32
V	0	42.0	20.0	11600	5600	2.08	30	40
VI	-25	10.3	5.7	67200	19600	3.43	67	82
VII	-25	21.0	9.2	37100	11600	3.20	41	69
VIII	-25	25.6	15.3	54400	15100	3.60	58	153
IX[a]	-25	38.4	22.8	23500	8200	2.86	40	88
X[b]	0	10.5	9.2	1850	950	1.95	26	4

notes: a) polymerization time 48 hours.

b) using aluminoxane prepared by the direct addition of water (included for comparison)

$\overline{y}_w$ is the average number of cyclopropyl groups per polymer chain calculated using the formula:

$$\overline{y}_w = \frac{\text{Weight fraction of 6-cyclopropyl-1-hexene}}{\text{Molecular weight of 6-cyclopropyl-1-hexene}} \times M_w$$

The compositions of the copolymers determined from the ^1H NMR spectra using the ratio of the cyclopropyl methylene resonances to the total peak area for the remaining hydrogens. A typical spectrum is shown in Figure 3.14.

All of the polymers showed very weak signals arising from vinylidene end groups, reflecting the higher molecular weights obtained compared to earlier experiments.

The ^{13}C NMR spectra of all of the copolymers were very similar, a typical spectrum is shown in Figure 3.15. The intensity of the signals due to vinylidene end groups was extremely weak compared to samples produced in earlier experiments, only the signal at 110ppm could be seen and this was barely visible.

The IR spectra (thin film supported on NaCl plate) 3075cm^{-1}(C-H str. cyclopropyl) 1010cm^{-1} (skeletal mode) were in agreement with the assigned structures. A typical spectrum is shown in Appendix 4.17.

The effect of temperature on the molecular weight of the copolymers is clearly shown by comparison between the two series.

There was no clear correlation between the level of 6-cyclopropyl-1-hexene in the monomer feed and the polymer molecular weights for either series. For the polymerizations at 0°C the yield decreased with increasing 6-cyclopropyl-1-hexene content of the feed, this was partly due to the low reactivity of the cyclopropyl monomer. The same weight of 6-cyclopropyl-1-hexene was used in each polymerization, and the amount of propene was varied to provide the required monomer feedstock composition. The monomer concentration was therefore lower for the runs containing the greatest amount of 6-cyclopropyl-1-hexene, which would tend to give lower yields.

The overall compositions of the polymers were found from the ^1H NMR data, however this did not provide any information on whether there had been any drift in the copolymer composition during the polymerization, or on the distribution of the monomers along the chain. The NMR results did not rule out the possibility that some homopolymerization of the two monomers may have occurred. If steric hindrance was

Figure 3.14

^{1}H NMR Spectrum of Propene/6-Cyclopropyl-1-Hexene Copolymer (VIII)

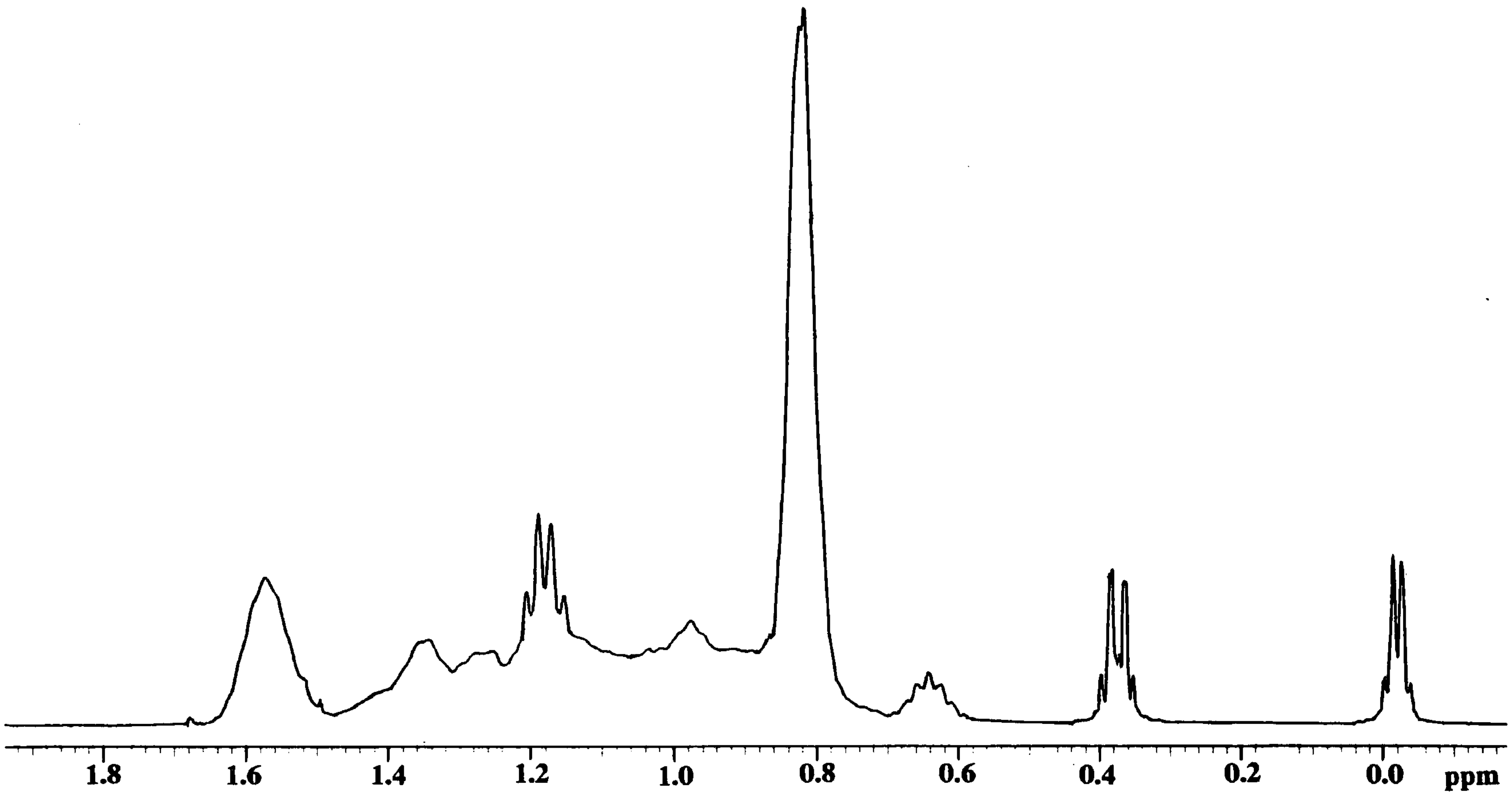
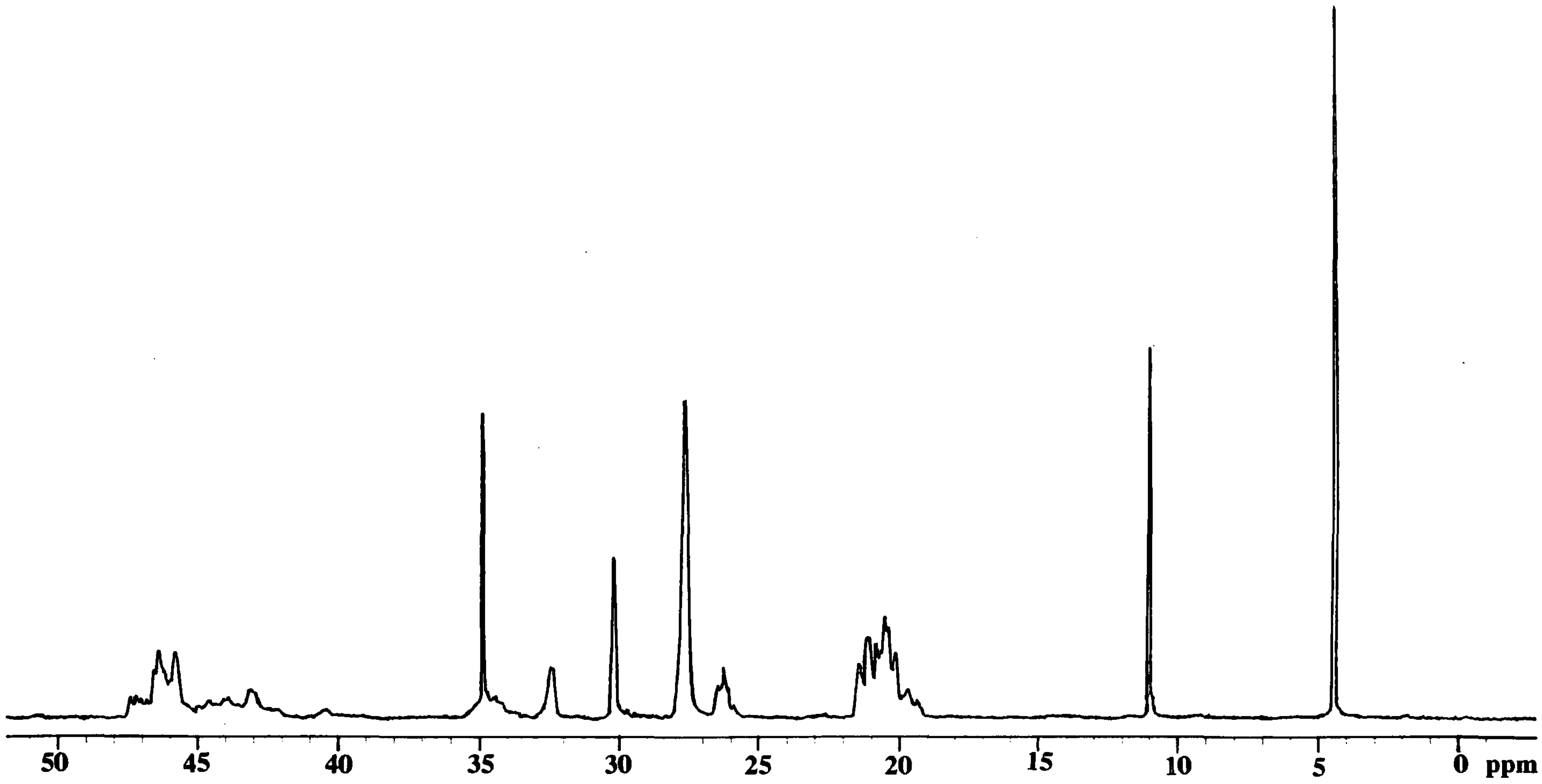


Figure 3.15

^{13}C NMR Spectrum of Propene/6-Cyclopropyl-1-Hexene Copolymer (VIII)



responsible for the failure of 6-cyclopropyl-1-hexene to homopolymerize using the zirconocene/MAO catalyst then it is unlikely that any blocks of this monomer will be formed. If the failure was due to a general deactivation of the catalyst then it might be possible that some poly(6-cyclopropyl-1-hexene) would be formed during the copolymerization.

^{13}C NMR is an extremely powerful technique for the elucidation of polymer microstructures, and has been applied to the determination of the sequences of comonomers for example in propene/butene[153] and ethene/1-alkene copolymers.[154-156] In the case of ethene copolymers, or of isotactic propene copolymers this is a relatively straightforward procedure due to the narrowness of the resonances. For example six lines were observed in the methylene region of the spectrum of an isotactic propene-butene copolymer, between 40.3ppm-47.1ppm, which were assigned to distinct dyad, triad and tetrad sequences. For the atactic copolymers obtained in the current study the multiplicity of the resonances prevents this approach.

Attempts were made to measure the composition of the copolymer produced at different times during a polymerization to determine whether there was any significant drift in the copolymer composition with time. No drift in composition was observed, however the results were inconclusive as it proved difficult to measure the extent of polymerization at each sample point.

In order to have the potential for producing networks from the copolymers it is clearly essential that the polymers contain sufficient cyclopropyl groups. Theories of network formation have been developed by Flory[157] and Stockmayer.[158] A polymer gel consists of an "infinite network" in which all the polymer chains have combined to form a single structure. Using the Flory-Stockmayer treatment the simplest case to consider is that of the gelation of a polymer with a monodisperse molecular weight distribution where each polymer contains y cyclopropyl groups.

The polymer chains are connected by v/2 crosslinks and it is assumed that no intramolecular reactions occur during crosslinking. The fraction of cyclopropyl groups which have reacted to form crosslinks is defined as ρ.

$$\rho = \quad = \frac{v}{N_o}$$

Where N_o is the total number of cyclopropyl groups in the polymer sample. For network formation to occur each polymer chain must be linked to more than one other chain. Another way of expressing this is that the probability that any one cyclopropyl group has formed a crosslink (ρ) multiplied by the total number of other cyclopropyl groups (y-1) must be greater than one. The critical condition at which the system is on the verge of forming a network is:

$$\rho_c = \frac{1}{y-1} \cong \frac{1}{y}$$

If the molecular weight of the polymer is large then the proportion of cyclopropyl groups required to react to ensure that on average each polymer chain is connected to more than one other polymer chain is very small. A similar treatment can be used for polymers with a polydisperse molecular weight distribution. The probability that any one polymer chain contains exactly y cyclopropyl groups is equal to the weight fraction of polymer containing y cyclopropyl groups. The critical condition for the onset of gelation therefore depends on the weight average number of cyclopropyl groups ($\bar{y}_w$) for the polymer:

$$\rho_c = \frac{1}{\bar{y}_w - 1} \cong \frac{1}{\bar{y}_w}$$

The values of $\overline{y_w}$ were calculated for each of the polymers based on the compositions determined by ^{1}H NMR, and the M_ws determined by GPC which are therefore relative to polystyrene standards, the calculations also assumed a random distribution of the comonomers. The results shown in Table 3.5 clearly show that the copolymers contain a sufficiently large number of cyclopropyl groups to make network formation feasible in principle. For example for copolymer (VI) to form a network only approximately 1/81 ($\cong$1-2%) of the cyclopropyl groups would be required to undergo crosslinking reactions.

3.3. Cationic Polymerization Studies

3.3.i. Polymerization of 2-Cyclopropylpropene Initiated by Tin(IV)chloride at -78°C

Tin(IV)chloride (0.32g, 1.22x10^{-3}mol) was added, with stirring at -78°C to 2-cyclopropylpropene (3.0g, 3.65x10^{-2}mol) under a nitrogen atmosphere, and the mixture was stirred for 5 hours. Methanol(10ml) was added which resulted in the formation of a white paste with some insoluble lumps. Diethylether (100ml) was added with stirring, the supernatant liquid was removed by decantation, then the residual solid was washed again with diethylether (100ml). Solvent was removed from the ether solution to give 1.28g (42.7%) of polymeric product, a further 0.25g (8.3%) of insoluble polymeric material was obtained.

^{1}The H NMR spectrum (CDCl$_3$, 250MHz) of the diethylether soluble product is shown in Appendix 3.4. The spectrum is more complex than would be expected for a polymer formed by 1,2 addition and indicates a mixture of 1,2 and 1,5 addition, with approximately 34mol% of units arising form 1,5 addition.

3.3.ii. Polymerization of 1-Octene Initiated by Aluminium Bromide at -78°C.

Aluminium bromide (0.4088g, 1.533x10^{-3}mol) and hexane (8.2ml) contained within an ampoule were cooled in liquid nitrogen, prior to the addition of 1-octene (3.72g,

3.32×10^{-2}mol) by vacuum transfer. The vessel was transferred to an acetone/carbon dioxide slush bath at-78°C and stirred for 90 minutes. Water (25ml) and hexane (25ml) were added, the organic phase was then separated and washed with saturated sodium bicarbonate solution (25ml) then water (3x25ml) before drying over magnesium sulphate and removal of solvent using a rotary evaporator at 50°C, to give 2.80g (75.3%) of a polymeric oil.

GPC (1% solution, tetrahydrofuran eluent, 10^3Å and 100Å crosslinked polystyrene columns, RI detector) M_n 2400, M_w/M_n 1.65 relative to polystyrene. The IR spectrum (capillary film between NaCl plates) showed no absorption maxima above 3000cm^{-1} or at ~1650cm^{-1} so that absorptions due to unsaturation were either not present or were too weak to observe. The ^{13}C NMR spectrum ($CDCl_3$,62.9 MHz) 35.6ppm(broad), 36.6ppm(broad), 34.1ppm(broad), 32.0ppm, 30.7ppm, 30.2ppm, 29.7ppm, 29.4ppm, 28.3ppm, 26.4ppm, 22.7ppm, 14.1ppm, showed that considerable rearrangement of the carbon skeleton had occurred during the polymerization. Such rearrangements generally occur during the polymerization of 1-alkenes,[159,160] leading to the formation of highly-branched, low-molecular-weight polymers.

3.3.iii. Reaction of Ethylcyclopropane With Alumiminium Bromide at -78°C

Reaction of aluminium bromide (0.1791g, 6.72×10^{-4}mol) with ethylcyclopropane (0.940g, 1.34×10^{-2}mol) in hexane (10ml) at -78°C for 130 minutes failed to provide any polymer. The monomer was recovered unaltered

3.3.iv. Polymerization of 6-Cyclopropyl-1-hexene Initiated by Aluminium Bromide at -78°C.

A solution of aluminium bromide (0.2116g, $7{,}93 \times 10^{-4}$mol) in dichloromethane (10ml) contained in an ampoule under a nitrogen atmosphere was cooled in liquid air. 6-Cyclopropyl-1-hexene was added by vacuum transfer, then the sealed ampoule was transferred to an acetone/carbon dioxide slush bath at -78°C. The mixture was stirred for

1 hour then allowed to stand for a further 15.5 hours at -78°C before adding methanol (50ml), then pouring the mixture into more methanol (250ml). The precipitated polymer was redissolved in refluxing pentane (100ml), the solution filtered, and solvent removed *in vacuo* at room temperature to give 1.06g (54%) of polymer. The IR, ^{13} NMR and ^{1}H NMR spectra showed that extensive ring opening of the cyclopropyl ring and rearrangement of the carbon backbone had occurred. IR (capillary film between NaCl plates) v3080cm^{-1}(cyclopropyl C-H str), v1010cm^{-1}(cyclopropyl skeletal mode), absorption maxima arising from unsaturated units were either absent or very weak. ^{1}H NMR.($CDCl_3$, 250MHz) 1.3-1.2ppm(m,broad)19H, 0.65ppm(m)1H, 0.4ppm(m)2H, 0.0ppm(m)2H. The intergrals indicated that 32% of the cyclopropyl groups had been lost during the polymerization, due to cationic ring opening. ^{13}C NMR ($CDCl_3$, 62.9MHz) 34.9ppm, 32.6ppm, 29.7ppm, 28.5ppm, 27.0ppm, 11.0ppm, 4.4ppm in addition there was a broad hump in the baseline between 20-45ppm, due to a multiplicity of overlapping signals.

The results showed that cationic polymerization of unsaturated cyclopropane monomers is not a satisfactory route to provide linear saturated polymers with pendant cyclopropyl groups.

3.4. Discussion

The feasibility of preparing hydrocarbon polymers containing cyclopropyl groups by the polymerization of 6-cyclopropyl-1-hexene with propene using a high activity homogeneous Ziegler-Natta catalyst has been clearly demonstrated. The polymers contained a sufficient number of cyclopropyl groups per chain to allow worthwhile crosslinking studies, the number of vinylidene groups was small and would not unduly interfere with the assessment of the network formation through ring opening polymerization of the cyclopropyl groups.

Considerable effort was required to establish the experimental conditions for the preparation of the MAO cocatalyst and for the copolymerization of propene, no local experience could be called on as these skills were new to the research group in Durham and the Company sponsoring these studies. Once the conditions had been optimized the polymerization was quite straightforward. The compositions and molecular weights of the polymers could be varied by modifying the polymerization conditions.

The failure of the 6-cyclopropyl-1-hexene to undergo homopolymerization initiated by the zirconocene/MAO was surprising and has been discussed earlier. No satisfactory explanation of this unexpected result is offered. Further experiments to study this phenomenon are required. The preparation of other alkenylcyclopropanes and the study of their polymerization behaviour would help to establish whether the difficulties were due to the presence of the cyclopropyl unit on the monomer, or due to the anomalous behaviour of 6-cyclopropyl-1-hexene.

Detailed structural information has not been obtained for the copolymers, it would be valuable to determine whether there was any drift in the composition during the polymerizations. The preparation of isotactic polymers using chiral homogeneous metallocene/MAO catalysts might give rise to simpler structures and consequently simpler ^{13}C NMR spectra, allowing the determination of the sequence distribution. It would also be interesting to compare the mechanical properties of networks obtained from isotactic polymers with those obtained from atactic polymers.

The possibility of using of cationic polymerization to provide polymers containing pendant cyclopropyl groups arose from the findings of Takahashi,[44] who reported that 2-cyclopropylpropene undergoes polymerization initiated by tin(IV)chloride to give 100% 1,2 polymerization, leaving the cyclopropyl groups intact. We were unable to repeat these results, and found that considerable 1,5 polymerization had occurred. This produced a polymer which contained a large proportion of double bonds, and which was therefore unsuitable for further study. The observation that ethylcyclopropane did not undergo polymerization initiated by aluminium bromide at -78°C, while 1-octene would polymerize under the same conditions suggested that it might be possible to cationically polymerize 6-cyclopropyl-1-hexene via the double bond while leaving the cyclopropyl group intact. In practice partial ring opening of the cyclopropyl groups occurred in addition to extensive rearrangement to give an ill defined polymer containing substantial amounts of unsaturation.

The preparation of polymers containing pendant cyclopropyl groups from the cationic polymerization of alkenyl cyclopropanes appeared to be less satisfactory than the use of Ziegler-Natta polymerization.

CHAPTER 4

CROSSLINKING STUDIES

Introduction

In Chapter Three the synthesis and characterization of a series of copolymers of 6-cyclopropyl-1-hexene and propene was described.

In order to produce networks from the linear polymers a practical procedure for the ring opening polymerization of the cyclopropyl groups was required. This chapter describes the investigation into the crosslinking of the copolymers. The preliminary studies on low molecular weight model compounds are considered first, before describing the crosslinking experiments involving the copolymers.

Experimental

4.1 Ring Opening Polymerization of Low Molecular Weight Model Compounds.

4.1.i. Polymerization of Ethylcyclopropane Initiated by Aluminium Bromide.

The polymerization was carried out in an ampoule equipped with a magnetic stirrer, a nitrogen inlet and a septum seal. Aluminium bromide (0.1934g, 7.3×10^{-4}mol) was stirred rapidly under a nitrogen atmosphere until it was broken down into a fine powder. Ethylcyclopropane (1.0g, 1.43×10^{-2}mol) was injected with rapid stirring, resulting in an immediate exothermic reaction. The mixture was stirred for 2 hours then water (10ml) was added. The aqueous layer was extracted with pentane (3x10ml), the combined organic layer was dried over magnesium sulphate prior to the removal of solvent to give 0.51g (51%) of a pale yellow oil.

The IR spectrum (capillary film between NaCl plates)(Appendix 4.18) was consistent with the product being a saturated hydrocarbon, no peaks arising from cyclopropyl groups were observed at 3080cm^{-1} or 1010cm^{-1}. The ^{13}C NMR ($CDCl_3$,62.9MHz)(Appendix 3.8) spectrum showed a large number of overlapping peaks between 10-50ppm, indicating a structure with a multiplicity of carbon environments. The ^{1}H NMR ($CDCl_3$,250MHz) spectrum showed broad peaks at 0.9ppm, 1.29ppm, 1.56ppm and 1.72ppm, which was consistent with the formation of a hydrocarbon with a complex irregular structure. There was no evidence in any of the spectra for the presence of unsaturation. GPC (1% solution, tetrahydrofuran eluent, 10^3Å and 100Å crosslinked polystyrene columns, RI detector) showed a series of peaks assigned to oligomers of ethylcyclopropane.

4.1.ii. Polymerization of Hexylcyclopropane Initiated by Aluminium Bromide.

Polymerization of hexylcyclopropane (1.22g, 9.69×10^{-3}mol) initiated by aluminium bromide (0.163g, 6.1×10^{-4}mol) following the above procedure gave 0.52g (43%) of an oily product. The analytical data were essentially the same as for the product from the polymerization of ethylcyclopropane.

4.1.iii. Polymerization of 1,1-Diethylcyclopropane Initiated by Aluminium Bromide

Polymerization of 1,1-diethylcyclopropane (0.878g, 8.08×10^{-3}mol) initiated by aluminium bromide (0.118g, 4.44×10^{-4}mol) as above gave 0.228g (26%) of oil. The analytical data were essentially the same as for the polymer from ethylcyclopropane.

4.1.iv. Attempted Polymerization of 1,4-Dicyclopropylbutane Initiated by Aluminium Bromide.

1,4-dicyclopropylbutane (1.82g, 1.32×10^{-2}mol) and aluminium bromide (0.2106g, 7.9×10^{-4}mol) were stirred together at room temperature for 2 hours. Water (10ml) was added, then the mixture was extracted with pentane (4x10ml) and solvent was removed from the organic phase to give 1.07g (80.8%) of a clear liquid.

The IR (capillary film between NaCl plates) and ^{13}C NMR spectra ($CDCl_3$,62.9MHz) 34.84ppm, 29.54ppm, 10.93ppm, and 4.39ppm, appeared the same as for the starting material, and showed that the recovered material was essentially unreacted 1,4-dicyclopropylbutane.

4.1.v. Polymerization of 1,4-Dicyclopropylbutane Initiated by Aluminium Bromide in Dichloromethane.

To a stirred solution of aluminium bromide (0.4358g, 1.63×10^{-3}mol) in dichloromethane (10ml) was added 1,4-dicyclopropylbutane (4.50g, 3.26×10^{-2}mol), an exothermic reaction occurred during the addition, the temperature was not recorded. Water (10ml) was added after 2 hours, and the mixture was extracted with dichloromethane (4x10ml). The combined organic phase was washed with water (2x25ml) before drying over magnesium sulphate and removing solvent to give 3.14g (70%) of pale yellow liquid.

The IR spectrum (capillary film between NaCl plates) showed strong absorptions at 3080cm^{-1} and at 1010cm^{-1} due to residual cyclopropyl groups. The presence of a small amount of oligomeric material was revealed by GPC (1% solution, tetrahydrofuran eluent, 10^3Å and 100Å crosslinked polystyrene columns, RI detector).

4.1.vi. Polymerization of 1,2-Bis(1-methylcyclopropyl)ethane Initiated by Aluminium Bromide in Dichloromethane.

Reaction of 1,2-bis(1-methylcyclopropyl)ethane (2.76g, 2.0×10^{-2}mol) with aluminium bromide (0.267g, 1×10^{-3}mol) in dichloromethane (10ml), using the same procedure as described above, gave 1.87g (68%) of pale yellow liquid. The IR spectrum (capillary film between NaCl plates) was very similar to that for the monomer. GPC (1% solution, tetrahydrofuran eluent, 10^3Å and 100Å crosslinked polystyrene columns, RI detector) showed that only small amounts of oligomers, mainly dimers and trimers, had been obtained.

4.1.vii. Reaction of Ethylcyclopropane With Trifluoromethanesulphonic acid.

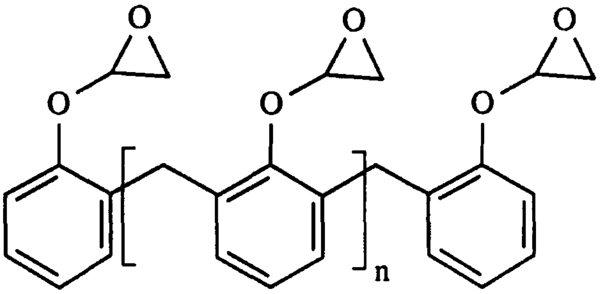
Trifluoromethanesulphonic acid (3 drops) was added to ethylcyclopropane (2.0g, 0.0286 mol) with stirring under nitrogen. There was an immediate exothermic reaction which caused an increase in temperature from 21.9°C to 25.4°C and the formation of a yellow colour. The mixture was stirred for 2 hours before adding water (30ml) then leaving the mixture overnight. The bulk of the upper organic phase evaporated leaving only a trace of oil, this was not characterized.

4.2. Crosslinking Studies on 6-Cyclopropyl-1-hexene Copolymers.

4.2.i. Attempted Crosslinking of Copolymer (VI) Initiated by Diphenyliodonium hexafluorophosphate.

Copolymer (VI) (0.5224g) and diphenyliodonium hexafluorophosphate (0.0105g, 2 parts by weight per hundred parts of resin (phr)) were dissolved in dichloromethane (3.29ml) to give a clear homogeneous solution. The solution was applied to a glass slide, the film thickness being defined by four layers of Sellotape giving a nominal wet film thickness of 200μm. The film was allowed to stand overnight before irradiating with UV light using a Hannovia medium pressure mercury lamp at a distance of 10cm. The appearance of the film was unchanged after irradiation for 180 minutes, it remained opaque due to the incompatibility of the polymer and photoinitiator and was completely soluble in dichloromethane. To test whether the phase separation was responsible for the failure to crosslink an aliquat of the original solution was irradiated in a borosilicate glass flask for 180 minutes. No increase in viscosity was observed.

A control experiment was carried out using a commercially available epoxy resin (Ciba-Giegy LY558);



A solution of LY558(0.50g) and diphenyliodonium hexafluorophosphate(0.0100g, 2 phr) in dichloromethane (2.0ml) was used to prepare a film which was irradiated using the procedure described above. The film was completely clear initially and after irradiation for 10 minutes it became tough and insoluble in dichloromethane.

4.2.ii. Attempted Crosslinking of Copolymer (VI) Using Borondifluoride-Acetoacetanilide Chelate.

Borondifluoride-acetoacetanilide chelate (0.0175, 6.2 phr) was added to a solution of copolymer (VI) (0.2817g) in xylene. The mixture was stirred for 60 minutes before removing most of the solvent under reduced pressure to leave a hazy solution containing some solid particles. The mixture was poured onto a microscope slide then placed in an oven at 180°C for 1 hour. The film remained soluble in petrol.

A control experiment was carried out using 1% weight of borondifluoride-acetoacetanilide chelate with LY558. After 1 hour at 180°C the mixture was a hard glassy solid which was insoluble in dichloromethane.

4.2.iii. Attempted Polymerization of 6-Cyclopropyl-1-Hexene Initiated by Borondifluoride-Acetoacetanilide Chelate.

A mixture of borondifluoride-acetoacetanilide chelate (0.1118g) and 6-cyclopropyl-1-hexene (2.84g) were placed in a round bottom flask fitted with a reflux condenser and magnetic stirrer bar. The mixture was refluxed at 150^{O}C for 6 hours then allowed to cool, giving a small amount of solid residue from the catalyst, covered by unreacted liquid monomer.

4.2.iv. Radical Initiated Crosslinking of Copolymer (VI).

The method was based on examples given in a patent application,[69] but with the omission of carbon black which was used in the reference. A mixture of sulphur (0.010g, 0.87 phr), dicumyl peroxide (0.2132g, 18.5 phr), copolymer (VI) (1.1451g) and petroleum spirit (b.pt. 40-60^{o})(25ml) was stirred together in an ampoule until the polymer and peroxide had fully dissolved. The solvent was removed under reduced pressure, with stirring to keep the sulphur finely dispersed. A sample was applied to a microscope slide using a spatula, then placed in an ampoule and purged with nitrogen for 1 hour before heating at 180^{0}C for 30 minutes. The film, which had initially been opaque, had became clear. It was immersed in petroleum spirit and became grossly swollen but did not dissolve. The result was in agreement with the claims described in the patent, that crosslinked materials could be obtained from polymers containing 6-cyclopropyl-1-hexene.

4.2.v. Radical Initiated Crosslinking of Poly(propene).

Poly(propene) (0.5135g), dicumyl peroxide (0.9125g, 18.6 phr) and sulphur (0.0044g, 0.86 phr) were stirred together in petroleum spirit (17ml). The mixture was treated the same way as described above, producing a gel which was insoluble in petroleum spirit.

4.2.vi. Thermally-Initiated Crosslinking of Copolymer (VI).

Aliquots from a solution of copolymer (VI) (0.1005g) and p-toluenesulphonic acid (5.04×10^{-3}g, 5phr) in diethylether (2.5ml) were poured onto a series of microscope slides. The solvent was allowed to evaporate before placing the slides in an oven. Heating a sample at 240°C for 1 hour gave a hard glossy brown film which was insoluble in petroleum spirit.

Heating a thin film of copolymer (VI) without any added p-toluenesulphonic acid at 240°C for 1 hour produced an even harder film which was also insoluble in petrol. The same procedure was used with a sample of poly(propene) this gave a mainly glossy, hard and insoluble film. Part of the original film was thicker than the rest, this portion remained tacky and soluble in petrol.

The results suggested that the crosslinking was due to oxidation of the samples, which would result in the thinner parts of the film crosslinking more rapidly. Elemental analysis of the brown film obtained from copolymer (VI) without any p-toluenesulphonic acid provided further evidence that extensive oxidation of the polymer had occurred. (Found for cured film: C 72.47%, H 8.71% compared to C 85.79%, H 14.56% initially).

The effect of heating copolymer in air was studied using a Stanton-Redcroft TGA 760 thermobalance. Maintaining the polymer at 100°C for 4 hours produced a 1% weight loss, while at 240°C for 3 hours another sample steadily lost approximately 4% of its weight each hour. The samples removed from the crucible after the thermal studies were soft tacky solids.

The results show that crosslinking was not achieved through simple thermally-initiated ring-opening polymerization of the cyclopropyl groups.

4.2.vii. Crosslinking Reactions Initiated by Aluminium Bromide.

The reactions were carried out in a small rectangular cross-sectioned ampoule, with a side-arm to allow attachment to a nitrogen inlet, equipped with a magnetic stirrer and a septum seal. A stock solution of aluminium bromide (7.2746g, 2.728×10^{-2}mol) in n-heptane (124.5ml) was prepared.

The polymer (typically 0.5g) was weighed into the ampoule under a nitrogen atmosphere, then n-heptane (enough to provide a 10% $^{w}/_{v}$ solution) was added and the mixture was stirred until the polymer had fully dissolved. An aliquot of the aluminium bromide solution was added with rapid stirring, causing an exotherm of 1-2°C. The mixture was stirred until an increase in the viscosity was observed then the ampoule was placed on its side and allowed to stand, giving a slab of gel with an approximately rectangular cross section. Methanol (approx. 25ml) was added to fill the ampoule, this generally caused the gel to shrink away from the walls of the vessel and allow its easy removal. The product was then extracted successively with methanol and petroleum spirit (b.pt. 40-60°C) for 24 hours using a soxhlet apparatus before drying to constant weight.

The results obtained using different ratios of aluminium to cyclopropyl groups are shown in Table 4.1 for copolymer (VI).

Table 4.1

Crosslinking of Copolymer (VI) Using Different Levels of Aluminium Bromide.

Ratio Cyclopropyl / Aluminium	Gel time/ mins.	%sol	M_n of sol.
40	no gel	-	28500
20	10	11	29300
10	9	30	29800
5	7	28	30400
10[a]	6	30	31700

a) 25% w/v solution used

The gel time refers to the point where the solution no longer appeared fluid by visual inspection. The sol content was determined from the weight of petrol soluble material recovered by soxhlet extraction. Small amounts of copolymers were available so only 0.5g of polymer was used in each of the tests, as a result any small losses of material would lead to relatively large errors in the sol content. The apparently low sol content for the experiment using a 20:1 ratio of cyclopropyl to aluminium may reflect the poor reproducibility of the method.

The molecular weights of the sols were approximately the same each time (M_n between 28500 and 31700) and were higher than those of the copolymer (M_n 19700). Increasing the amount of aluminium bromide used to crosslink the copolymer gave more rigid gels, which were swollen less when immersed in solvent, which suggests that an increase in crosslink density was obtained.

The characterization data for the gel and the sol fractions of a typical sample are given below.

Characterization of the gel fraction.

The ^1H NMR (swollen in $CDCl_3$, 400MHz) spectrum (Figure 4.1) was similar to that of the original polymer, although peak broadening was observed due to the reduced mobility of the sample. Cyclopropyl methylene protons were observed resonating at 0.4ppm and 0ppm, the cyclopropyl methine at 0.65ppm was partially obscured by the broadened signal due to the propene methyl protons. Attempts to estimate the amount of unreacted cyclopropyl groups from the ratio of the peak areas for the cyclopropane methylene resonance at 0ppm to the total signal area were unsatisfactory. The broadening of the methyl signal caused sloping of the baseline in the region of the cyclopropyl methylene resonances, preventing accurate measurement of the peak areas. No signals were observed arising from vinylidene end groups, which would be expected to resonate at approximately 4.5ppm.

Figure 4.1

^{1}H NMR Spectrum Of The Gel Fraction From The Crosslinking Of A Solution Of 6-Cyclopropyl-1-Hexene/Propene Copolymer (VI) Initiated By Aluminium Bromide

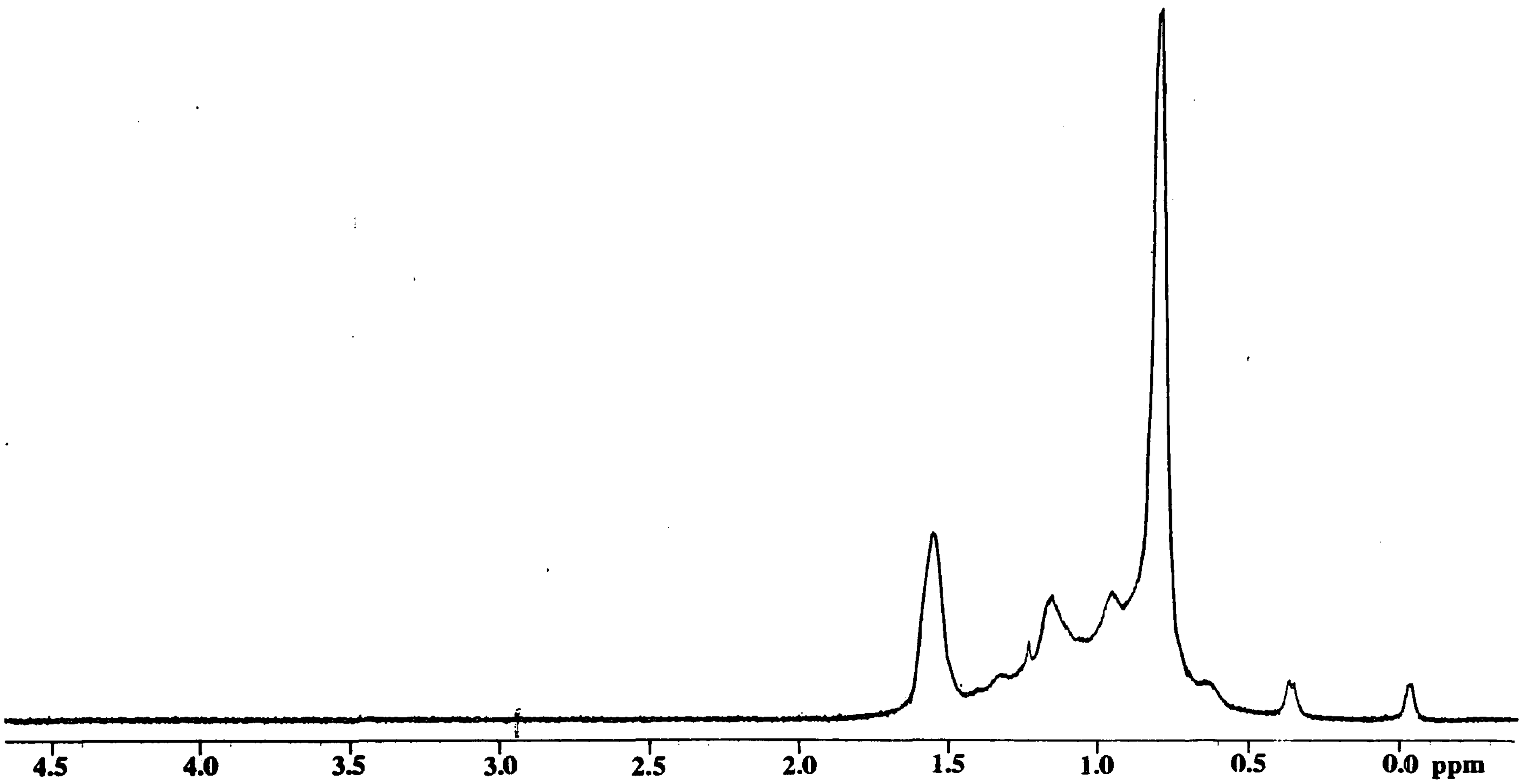
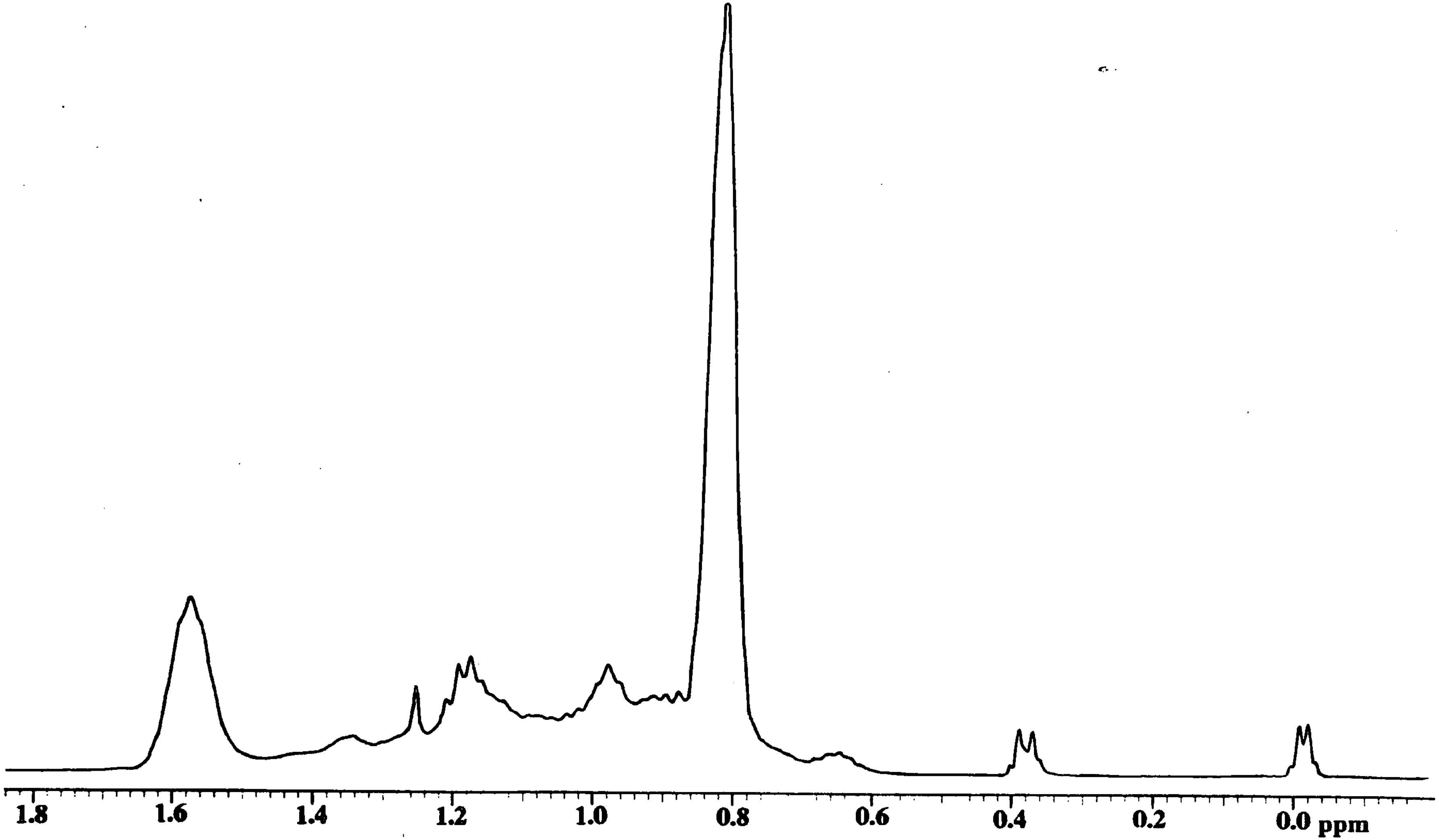


Figure 4.2

^{1}H NMR Spectrum Of The Sol Fraction From The Crosslinking Of A Solution Of 6-Cyclopropyl-1-Hexene/Propene Copolymer (VI) Initiated By Aluminium Bromide



The ^{13}C NMR spectrum (swollen in $CDCl_3$, 100MHz)(Appendix 3.9) appeared to be similar to that of the linear polymer, however there was a poor signal to noise ratio due to the small amount of polymer within the swollen gel. Strong resonances were observed at 10.91ppm and 4.37ppm due to residual cyclopropyl methine and methylene carbons. IR spectroscopy (unsupported film) confirmed the presence of cyclopropyl groups from the maxima at 3060cm^{-1} (cyclopropyl C-H str.) and 1010cm^{-1} (cyclopropyl skeletal mode).(Appendix 4.19).

Characterization of the sol fraction

The IR (thin film supported on NaCl plate)(Appendix 4.20) and ^{1}H NMR ($CDCl_3$, 400MHz)(Figure 4.2) spectra appeared similar to those of the starting material. The intensities of the cyclopropyl methylene resonances at 0.4ppm and 0ppm in the ^{1}H NMR spectrum were unaltered. The ^{13}C NMR spectrum ($CDCl_3$, 100MHz)(Appendix 3.10) contained peaks at 10.90ppm and 4.32ppm due to residual cyclopropyl methine and methylene carbons. The rest of the spectrum appeared similar to that of the original polymer, however the signal to noise ratio was low due to the small amount of sol available, so that any minor differences would be undetectable.

Similar results were obtained for the other copolymers. The concentrations of cyclopropyl groups in the gel fractions were estimated from the ^{1}H NMR spectra. The results were unsatisfactory due to the excessive peak broadening, but appeared to be broadly similar to the concentration in the original polymers. For record the results are summarized in Table 4.2.

TABLE 4.2

Treatment of 6-Cyclopropyl-1-Hexene Copolymers With Aluminium Bromide in Solution.

Polymer	Cyclopropyl/ Aluminium Ratio	Gel time / mins.	%sol	M_n	M_w/M_n
(III)	20	6	29	not measured	
(III)	10	no gel	-	3400	3.15
(IV)	20	37	21	35600	3.36
(IV)	10	no gel	-	4000	3.41
(VII)	20	2	5	20800	2.24
(VII)	10	3	6	22800	2.25
(VIII)	20	1	12	32400	3.45
(VIII)	10	26	25	41300	3.32
(IX)	20	26	21	28200	3.27
(IX)	10	4	12	20200	3.71

The crosslink density of the gel obtained from copolymer (VI) using 20:1 molar ratio of cyclopropyl groups to aluminium was estimated using a solvent swelling technique. The procedure is described in Appendix 2.

The number average molecular weight (M_c) between crosslinks was found to be 2100000. The are several factors which may lead to a large error in the calculated crosslink density, as discussed in Appendix 2, however the figure gives an approximate indication of the molecular weight between crosslinks. M_c was approximately one hundred times greater than the M_n of the linear polymer. In order to achieve such a large value for M_c it would be necessary for most of the polymer chains to react through only one functional group, with only 1% acting as polyfunctional crosslinking species. The molecular weight of the sol fraction was considerably higher than the initial molecular weight of the copolymers, showing that some reaction of the polymers forming the sol had occurred, but not enough to provide network formation.

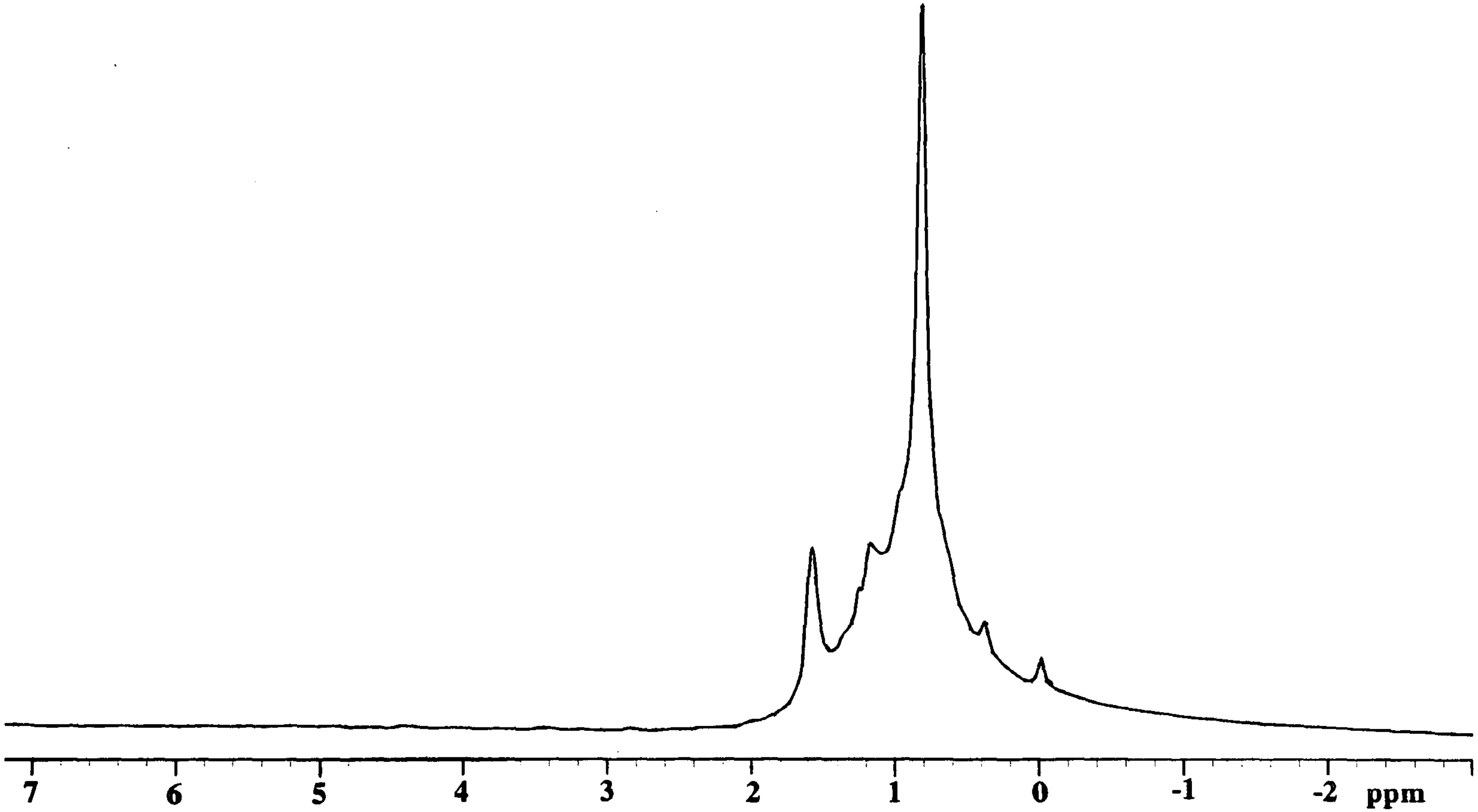
The results clearly demonstrated that the conditions used had given only lightly crosslinked networks, and that increased crosslink densities were required. The solutions contained only approximately 10% $^{w}/_{v}$ of polymer, the concentration of cyclopropyl groups was therefore much lower than this, for copolymer (VI) the concentration of cyclopropyl groups was approximately 1.7% $^{w}/_{v}$. In order to increase the amount of crosslinking it would be necessary to use more concentrated polymer solutions, but the higher viscosities of such solutions would prevent thorough mixing with the aluminium bromide before the mixture gelled. Clearly alternative procedures for the crosslinking of the polymers were required.

4.2.viii. Treatment of 6-Cyclopropyl-1-Hexene Copolymer Films With Aluminium Bromide.

The details for a typical experiment are given. A solution of copolymer (VI) in heptane (approximately 10% w/v) was applied to a glass microscope slide between strips of Sellotape as described previously, then allowed to stand overnight. The weight and area of the film were measured, and as the density of the polymer was known (see Appendix 2) the average film thickness (106μm) could be calculated. The microscope slide was immersed in a solution of aluminium bromide in n-heptane (10ml of solution from Section 4.2.vii) inside a Schlenk tube under nitrogen. After 5 minutes the film was removed, then placed in methanol (approximately 50 ml) for approximately 60 minutes. The orange colour which had developed at the edges of the film while it was immersed in the aluminium bromide solution rapidly disappeared, and the film became detached from the glass slide. Immersion in petroleum spirit (b.pt. 40-60^{o}C) caused the film to swell, but it appeared to be mainly insoluble. The polymer was then extracted with methanol using a soxhlet apparatus for 24 hours before drying under reduced pressure to a constant weight, to give greater than 93% recovery of polymer.

Figure 4.3

^{1}H NMR Spectrum Of The Gel Fraction From The Crosslinking Of A Film Of 6-Cyclopropyl-1-Hexene/Propene Copolymer (VI) Initiated By Aluminium Bromide



The ^{1}H NMR spectrum (sample swollen in $CDCl_3$, 400MHz) (Figure 4.3) was similar to that of the original polymer, although there was considerable broadening of the peaks due to the restricted mobility of the gel. Resonances due to cyclopropyl methylene protons were observed at 0.4ppm and 0ppm, however these signals were partially obscured by an overlapping intense peak centred at 0.8ppm. All the protons

resonated between 0ppm and 2ppm, with no evidence for the presence of alkyl bromides due to the addition of bromine to the cyclopropyl groups (expected resonances at 2.7ppm for primary or 4.1ppm for the more likely secondary bromide), or of unsaturation arising from termination of the cationic polymerization by hydride transfer. The IR spectrum (unsupported film) showed a strong broad peak between 2500cm^{-1} and an additional broad peak centred at 1620cm^{-1}, possibly due to adsorption of moisture by the sample. The presence of cyclopropyl groups was confirmed by the peaks at 3060cm^{-1} and 1010cm^{-1}.

The same procedure was used for copolymers (VII)(containing 9.2 mol% 6-cyclopropyl-1-hexene),(VIII)(containing 15.3 mol% 6-cyclopropyl-1-hexene) and (IX)(containing 22.8 mol% 6-cyclopropyl-1-hexene). The results were similar for all the polymers using film thicknesses of approximately 100μm and 50μm. Elemental analysis of the product from copolymer (VII) showed that there was a small amount of bromine present (C 78.72%, H 13.66%, Br 1.43%), there was 6.19% unaccounted for, which may have been due to oxygen or to trapped aluminium. The halogen content corresponds to the incorporation of one bromine atom to 11% of the cyclopropyl groups originally present. The analysis of the product from copolymer (IX) showed this contained a greater amount of bromine (C 75.64%, H 12.79% Br 9.98%), corresponding to the addition of a bromine to 37% of the cyclopropyl groups, however the ^{1}H NMR showed no evidence for the presence of alkyl bromides. The extraction with methanol should have removed any aluminium bromide, however some may have been trapped within the film and be responsible for the high bromine content.

A film of poly(propene) treated in the same way rapidly dissolved when it was immersed in the aluminium bromide solution, leaving a bare glass plate. This demonstrated that it was the reaction of the cyclopropyl groups which was responsible for insolubility of the copolymer.

4.2.ix. Treatment of 6-Cyclopropyl-1-Hexene Copolymer Films With Trifluoromethanesulphonic Acid.

A film of copolymer(VI) supported on a glass plate was immersed in trifluoromethanesulphonic acid for 5 minutes. When the plate was removed the film was found to have completely dissolved.

4.3. Discussion.

The feasibility of the system was demonstrated in principle from the crosslinking of hydrocarbon polymers with pendant cyclopropyl groups, initiated by aluminium bromide. Clearly a more practical method for crosslinking the polymers would be required if they were to be used for coatings. Preliminary experiments to test whether the cyclopropyl copolymers could be crosslinked using "masked" cationic initiators which have been employed in the crosslinking of epoxy resins were carried out. The results showed that there were considerable problems involved in the use of such initiators with the cyclopropyl copolymers and that further investigations would be required.

Aluminium bromide has been widely employed in the cationic polymerization of alkenes.[161,162] Inspite of its widespread use the exact nature of the initiating species has not been established, and the need for HBr as a co-initiating species has not been unambiguously established. The addition of HBr is often employed and it has been reported that HBr is essential,[163] in the absence of deliberately added water it was assumed that slight traces of moisture present, even after thorough drying of the system, was involved.[164] Aluminium bromide has been reported to initiate polymerization of isobutene even under the most stringently anhydrous conditions, this observation has been used to argue that water is not required, and that initiation may occur through self-ionization of the metal halide.[165] Tipper and Walker[38] found that the polymerizationof cyclopropane initiated by aluminium bromide required the presence of HBr as a co-catalyst. The polymerization of 1,1-dimethylcyclopropane and isopropylcyclopropane by $AlBr_3$ in the absence of added HBr was reported by Pines *et al.*[40] The careful control of the amount of co-initiator employed, and the presence of traces of moisture are critically important for kinetic studies. Our aim was to establish whether crosslinked polymers could be obtained, therefore less rigorous conditions were required. The solvents were anhydrous and equipment was dried under nitrogen, but monomers and polymers were not dried before use to allow a source for traces of water to form HBr co-catalyst. This procedure may have caused some irreproducibility in the crosslinking of the polymer solutions, but appeared generally satisfactory. Aluminium bromide is very soluble in hydrocarbons, solutions containing up to 20% by weight have been obtained in heptane,[33] and therefore should not cause problems with incompatibility.

he results for the cationic polymerization of the low molecular weight cyclopropyl compounds were similar to those of previous workers, who also obtained low molecular weight oils.[38,40,42] The polymerization of 1,1-diethylcyclopropane which would be expected to involve a tertiary cation intermediate, which would be more stable than the secondary cation intermediate involved in the polymerization of the monoalkylcyclopropanes, did not provide either higher yields or increased molecular weight polymers.

The dicyclopropyl compounds gave only low yields of oligomers, however there is no reason why they should fail to polymerize under the same conditions as monocyclopropyl materials. The addition of 1,4-dicyclopropylbutane to finely divided aluminium bromide produced a vigorous exotherm and so clearly some reaction was taking place. There was only partial recovery of the starting materials, so it is possible that higher conversions to oligomers occurred, but the oligomers were lost during the isolation procedure. An alternative explanation for the low yield of oligomers is that the cyclopropyl groups may have reacted rapidly with the aluminium bromide, to form a crosslinked shell which prevented further reaction.

The bulk polymerization of ethylcyclopropane initiated by aluminium bromide gave approximately 50% yield of oligomers. The level of aluminium bromide used (1:20 molar ratio of aluminium:cyclopropyl groups) was higher than the levels of initiator likely to be employed in a practical network forming system. The extent of reaction of cyclopropyl groups attached to a polymer is unlikely to be as high as that for a low molecular weight cyclopropyl compound, due to the limited mobility of groups attached to polymer. The weight average number of cyclopropyl groups ($\bar{y}_w$) per chain for the 6-cyclopropyl-1-hexene copolymers (determined by GPC relative to polystyrene) was between 14 and 153, for copolymer (VI) which was used in most of the studies $\bar{y}_w$ was 82. The fraction of cyclopropyl groups which are required to react in order to form a network is $1/(\bar{y}_w-1)$ (as discussed in Section 3.2.1.b.xvi.). For the copolymers (I) to (IX) in table 3.5 between 7% (for copolymer I)and 0.6% (for copolymer VIII)of the cyclopropyl groups would be required to react to form crosslinks. The extent of ring opening polymerization of the cyclopropyl groups during crosslinking of the copolymers could therefore be much lower than that observed in the polymerization of the simple alkylcyclopropanes and still provide a satisfactory route for the formation of a crosslinked system.

The reaction of aluminium bromide with the 6-cyclopropyl-1-hexene copolymers was rapid and strongly exothermic, and therefore it was impossible to form a film containing the two reagents without the mixture immediately gelling. In order to overcome this difficulty the preliminary reactions were carried out in solution. The experiments showed that crosslinked networks could be obtained, however the crosslink density, as expected under these conditions of formation, was very low and the materials obtained proved difficult to characterize. The low concentration of the polymer in the solutions did not provide the best conditions to allow crosslinking. In dilute solutions there is a greater probability of intramolecular reactions, or of termination reactions occurring before crosslinking can occur.

Quantitative analysis of the gel by ^{1}H NMR to determine the amount of unreacted cyclopropyl groups was not possible due to the overlapping of resonances, although qualitatively there appeared to be similar amounts of cyclopropyl groups as there had been in the polymer prior to reaction (see Figure 4.1). The ^1H NMR spectra of the sol fractions also indicated that the concentration of cyclopropyl groups was similar to that of the starting polymers (see Figure 4.2). This showed that the sol fractions appeared to contain high enough concentrations of cyclopropyl groups to allow them to undergo crosslinking if more effective reaction conditions could be found.

The crosslinking of copolymer films by immersion in aluminium bromide solution showed that the polymers were capable of rapidly undergoing network formation. The crosslinking was carried out in a solvent for the linear polymer, and polypropene rapidly dissolved under the same conditions, showing that crosslinking was due to the cyclopropyl groups. The apparently higher crosslink density of the samples crosslinked as a film compared to the gels prepared from crosslinking in solution meant that the polymers were only slightly swollen by chloroform. Characterization of the swollen gels by ^1H NMR, or ^{13}C NMR was not completely satisfactory, although the presence of some residual cyclopropyl groups could be seen, detected in peaks at 0.4ppm and 0.0ppm in the ^1H NMR spectrum overall quality of the spectra was not good (see Figure 4.3)

In order to provide a practical curing system it is necessary to obtain an initiator for the ring opening polymerization of the cyclopropyl groups which is compatible with the polymer and shows a reactivity towards cyclopropyl groups which would provide both an acceptable pot life and rate of curing of the applied film. It would be desirable to have a "masked" initiator which could be stored with the polymer and not start to react until after the solution had been applied to the substrate. Photocationic initiators or masked Lewis acids such as those employed with epoxy resins appeared to be obvious candidates for investigation.

The photocationic initiator used, diphenyliodonium hexafluorophosphate is part of a class of highly efficient photoinitiators, the diaryliodonium salts. These initiators have been widely studied for use with epoxy resins.[16,168] Irradiation with UV light causes the homolytic cleavage of the Ph-I bond to give a highly reactive cation radical:

$$\mathrm{Ph_2I^+PF_6^-} \xrightarrow{h\upsilon} \mathrm{PhI^{+\cdot}PF_6^-} \quad + \mathrm{Ph\cdot}$$

The cation radical undergoes a complex series of further reactions, including the abstraction of a hydrogen from the substrate or the solvent, leading to the formation of a strong Bronsted acid $H^+PF_6^-$ which initiates the polymerization. The cyclopropyl group is known to undergo ring opening when treated with acids, for example in the alkylation of benzene by alkylcyclopropanes in the presence of hydrofluoric or sulphuric acid.[39] Cyclopropane has also been shown to undergo protonation and ring opening if added to a large excess of concentrated sulphuric acid to give propyl sulphate.[169,170] As there is generally a correlation between the strength of an acid and its ability to initiate cationic polymerization it would be very surprising if $H^+PF_6^-$ was not capable of initiating the ring opening polymerization of alkylcyclopropanes.

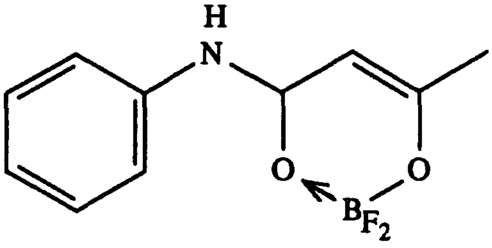
Another photoinitiator in the same class is diphenyliodonium hexafluoroantimonate, which gives rise to $H^+SbF_6^-$ when irradiated by UV light. Ethylcyclopropane has been shown to undergo protonation and isomerization to form the t-amyl cation when reacted with an excess of HF/SbF_5 in solution,[171] and therefore under suitable conditions this would also be expected to be capable of initiating the ring opening polymerization of alkylcyclopropanes.

The failure of the homogeneous solution of copolymer (VI) and diphenyliodonium hexafluorophosphate in dichloromethane to crosslink appeared to suggest that the problem was not due solely to the incompatibility of the two components in the films. The relatively low concentrations of cyclopropyl groups in the sample may have been partially responsible. The commercial epoxy resin used as a control had an epoxy equivalent weight of approximately 162 (The epoxy equivalent weight is the weight in grams of the resin containing 1 mol of epoxy groups). The corresponding 'cyclopropyl equivalent weight' for copolymer (VI) was 820. It would be valuable to use polymers with a higher cyclopropylcontent to thoroughly test the feasibility of crosslinking the cyclopropyl polymers by a

practical method. Clearly the use of 6-cyclopropyl-1-hexene homopolymer would have been very valuable in these studies, unfortunately this was not available, due to the unexpected failure of the monomer to homopolymerize using the homogeneous Ziegler-Natta catalyst system.

In order to provide a potentially useful system a photoinitiator which is compatible with the hydrocarbon polymer is required. The most important classes of photocationic initiators, such as onoium salts or mixed ligand arene cyclopentadienyl salts are unlikely to be compatible with a hydrocarbon copolymer.

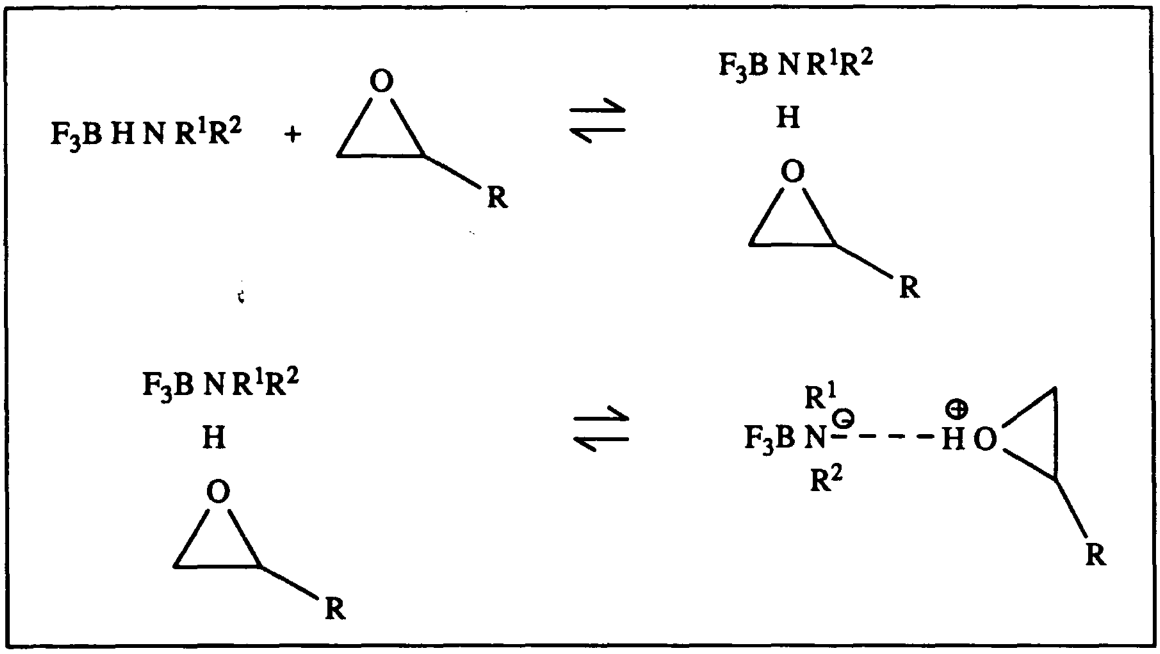
The use of thermal cationic initiators suffered from incompatibility problems, similar to those above. Boron trifluoride complexes such as BF_3-ethylamine, or boron difluoride chelates such as the chelate with acetoacetanilide:



have been used in thermally cured epoxy systems. The chelate has been reported to offer improved mechanical properties compared to the amine adducts.[172] The BF_3-amine complexes were originally assumed to dissociate upon heating to liberate the Lewis acid which then initiated the polymerization. Harris and Temin[173] found that there was no correlation between the curing temperature required and the decomposition temperature of the curing agent. They proposed an initiation reaction involving protonation of the epoxy by the amine as shown in Figure 4.1:

Figure 4.1

Initiation of the Polymerization of Epoxides by BF_3.Amine Adducts

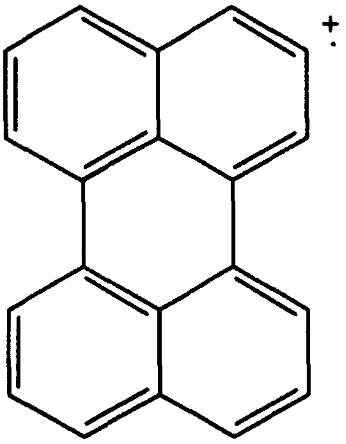


The acetoacetanilide chelate is more soluble in non-polar solvents than the ethylamine adduct, and so it appeared to offer the best prospect to achieve crosslinking of the cyclopropyl polymers. Unfortunately the initiator was not compatible with the polymer and did not give observable crosslinking. Prolonged heating of a mixture of the initiator with 6-cyclopropyl-1-hexene also failed to provide any polymer. It was therefore extremely unlikely that the initiator would be capable of crosslinking the copolymers which contained a maximum of slightly less than 23 mol% 6-cyclopropyl-1-hexene.

Ketley[41] and Aoki *et al*[42] reported that $BF_3.Et_2O$ failed to polymerize 1,1-dimethylcyclopropane, as these initiators have been widely employed to polymerize alkenes and are used commercially for the polymerization of isobutene, this demonstrates the low reactivity of the cyclopropyl ring. The failure of the cyclopropyl polymers to crosslink may therefore be because the thermal cationic initiators are not reactive enough to initiate the polymerization rather than solely because of their incompatibility with the polymer.

Had more time been available it may have been possible to determine which of these factors was responsible, however for the current study the fact that the monomer failed to polymerize, for whatever reason, showed the unsuitability of the initiator for the crosslinking of 6-cyclopropyl-1-hexene copolymers.

An alternative approach to the crosslinking of the polymers would be to incorporate an organic compound which was capable of being subsequently converted to a cationic species which could then initiate the crosslinking. A candidate for further investigation would be the perylene radical cation;



this has been used to initiate the polymerization of styrene and isobutene.[174] The radical cation generated by the irradiation of perylene with UV light in the presence of 9,10-dicyanoanthracene (DCA) as an electron acceptor has also been used to polymerize cyclohexeneoxide.[175] Polyaromatics including perylene and anthracene are widely used as Photosensitizers in conjunction with onium salt photocationic initiators.[15] Pappas *et al*[176] have shown that the radical cation formed from the sensitizer is capable of initiating the polymerization of cyclohexene oxide. It would therefore be interesting to carry out further studies using perylene or other polyaromatic compounds in conjunction with photoinitiators.

The possibility of using an acid would be compatible with the polymer and be able to initiate crosslinking was tested using trifluoromethanesulphonic acid (triflic acid). This is one of the strongest of the monoprotic acids known,[177] and has been used to initiate the polymerization of p-methoxy-α-methyl styrene[178] and styrene.[179] Trimethylsilyl triflate has been used as part of an initiating system for the polymerization of styrene[180] and it was suggested that it might be compatible with the 6-cyclopropyl-1-hexene copolymers[181] preliminary experiments were undertaken. The addition of a small amount of trifluoromethanesulphonic acid to ethylcyclopropane gave a low yield of oil which was not characterized. The reaction of a large excess of the acid with a film of 6-cyclopropyl-1-hexene copolymer caused the film to dissolve. The results were inconclusive and the use of triflic acid would require further study.

A further possibility for the incorporation of a latent initiator was to incorporate phenols into the polymer film. There is a dramatic increase in the acidity of phenols upon photoexcitation, for example the pK_a of 2-naphthol decreases from 9.46 in the ground state to 2.82 in the excited state.[198] However even in the excited state they are unlikely to be strong enough acids to initiate the polymerization of the cyclopropyl groups, therefore this approach was not pursued.

The radical crosslinking of hydrocarbon copolymers containing 6-cyclopropyl-1-hexene by heating with dicumyl peroxide has been claimed in a patent application.[165] Our results confirmed this claim, but demonstrated that polypropene would also crosslink under the same conditions. There is considerable evidence in the literature for the low reactivity of the cyclopropyl ring to direct attack by radicals, although cyclopropane has been shown to undergo free radical polymerization upon irradiation with UV light in the presence of mercury vapour.[37,182,183] Substituted cyclopropanes have been shown not to undergo direct attack by radicals to form polymers,[44,45,184] while (as discussed in Section 1.3.c.i.) vinyl cyclopropanes undergo initial radical attack at the double bond leading to 1,5 addition polymerization. Further evidence for the low reactivity of the cyclopropyl ring to opening by radicals comes from the observations that chlorine radicals attack cyclopropane by hydrogen abstraction rather than by ring opening,[185] while methylcyclopropane reacts with chlorine radicals by abstraction of a hydrogen from the methyl group rather than at the tertiary site of the cyclopropyl ring.[186] A feature of polypropene which has important implications in it's practical applications, is that it is less stable towards photo-oxidative degradation than polyethene due to the large number of tertiary hydrogens on the polymer backbone. The degradation process involves auto-oxidation (as described for the crosslinking of drying oils in Section 1.1.b.i.). Unstabilized polypropene is therefore rapidly degraded if left exposed out of doors and must be stabilized by the addition of radical scavengers. These slow down the rate of degradation by reacting with the peroxide radicals involved in the auto-oxidation,[187,188] so reducing the kinetic chain length for the propagation reaction in the degradation. (The mode of action of these antioxidants was likened by Taylor to "...a warden caring for a hundred lunatics. The warden would be powerless were all the lunatics simultaneously violent. Only at intervals does an occasional lunatic become a candidate for the padded cell. The warden cares for him, the gentler ninety nine do not require attention.")[189]

The crosslinking of polypropene and polyethene is carried out deliberately for some applications, using dicumyl peroxide as an initiator.[97] The photografting of monomers onto polypropene and polyethene has also employed dicumyl peroxide as an initiator.[190] In both processes the formation of radicals by abstraction of hydrogen from the polymer backbone is involved. The grafting of monomers can be carried out by irradiation of the polymer under vacuum, at a temperature below the glass transition temperature. The mobility of the polymer chains is then too low to allow combination of the radicals to form crosslinks. Monomer is then introduced to the irradiated polymer, which can then react to form the grafted product.

The crosslinking of the cyclopropyl polymer when heated with dicumyl peroxide was therefore not surprising, but the use of a 6-cyclopropyl-1-hexene copolymer claimed in the patent literature appears to be an expensive option compared to the use of polypropene homopolymer!

The possibility of using other reactions of the cyclopropyl group were considered, for example thermal ring-opening polymerization. Cyclopropane and alkylcyclopropanes have been found to undergo thermal rearrangement to give the corresponding alkenes without polymerization,[191,192] and therefore this approach did not appear to be very attractive. In order to test the possibility of obtaining a thermally curing system a sample of one of the 6-cyclopropyl-1-hexene copolymers was heated in air. Initially p-toulenesulphonicacid was added to the sample, with a view to using the acid-catalysed ring-opening polymerization to provide a crosslinking route. The acid chosen is soluble on diethylether and gave a homogeneous solution with the copolymer, which therefore allowed thorough mixing of the polymer and initiator. Heating the film for 1 hour at 240°C produced a hard film which was insoluble in petroleum spirit, which initially appeared to suggest that the acid-catalysed thermal crosslinking of the copolymers might be worthy of further investigation. Heating a sample of the polymer without the acid catalyst gave an even harder film. Treating polypropene in the same way also gave an insoluble film, showing that the crosslinking was not dependant on the presence of the cyclopropyl groups, but was perhaps instead due to oxidation rather than due to ring-opening of the cyclopropyl group.

The use of ionizing radiation to initiate crosslinking was also considered. Isobutene[193] and ethene[194] have been polymerized by γ-irradiation with. A proposed mechanism involves the ejection of an electron to give a radical cation which initiates polymerization,[199] as shown i

n Figure 4.2.

Figure 4.2

Polymerization of Ethene Initiated By γ Radiation

$$(CH_2{=}CH_2) \xrightarrow{\gamma\ \text{irradiation}} (CH_2{=}CH_2)^{\oplus\cdot} + e$$

$$(CH_2{=}CH_2)^{\oplus\cdot} \quad n(CH_2{=}CH_2) \longrightarrow \cdot\, CH_2CH_2(CH_2CH_2)_{n-1}CH_2\overset{\oplus}{C}H_2$$

Unfortunately it has been found that 1,1-dimethylcyclopropane was not polymerized by ionizing radiation,[48] and therefore there seems no possibility of using γ irradiation to achieve curing of the cyclopropyl copolymers. (Cyclopropane has been polymerized by exposure to α radiation from radon,[195] but this does not appear to provide a practical method for the crosslinking of the current system.

Alternative reactions of the cyclopropyl group might be employed to achieve crosslinking, for example 1,1-dimethylcyclopropane reacts with toluene in the presence of aluminium bromide to give 40% yield (based on the cyclopropane) of alkylated toluene after 1 minute. It might be possible to use toluene as a reactive diluent which could be reacted with the cyclopropyl polymer to provide crosslinked material through a Friedel-Crafts reaction. There would probably be similar problems in finding a suitable catalyst with controlled reactivity as were encountered in the ring opening polymerization route. An additional disadvantage would be the increased absorption of U.V. light as a result of incorporation of aromatic groups.

The cyclopropyl group is able to undergo $\pi^2+\sigma^2$ cycloaddition reactions with alkenes or alkynes.[196,197] The thermal cycloaddition reaction does not occur for simple cyclopropyl rings and they must generally posses electron donating groups, and react with alkenes bearing electron withdrawing groups, for example with tetracyanoethene.[197] The use of cycloaddition reactions do not therefore appear to provide a practical method for the crosslinking of the polymers.

In summary, the feasibility of the proposed network forming system has been demonstrated in principle. In order to have the potential of providing a practically useful network forming system, the copolymers studied require a cationic initiator which is compatible with the polymer and which has a controlled reactivity. In this experimental study and literature survey the author has been unable to identify a satisfactory initiator although the initial theoretical analysis implied that strong protic acids (e.g. $H^+PF_6^-$) ought to be satisfactory, and the practically unacceptable Lewis acid $AlBr_3$ does cure solid films.

APPENDIX 1

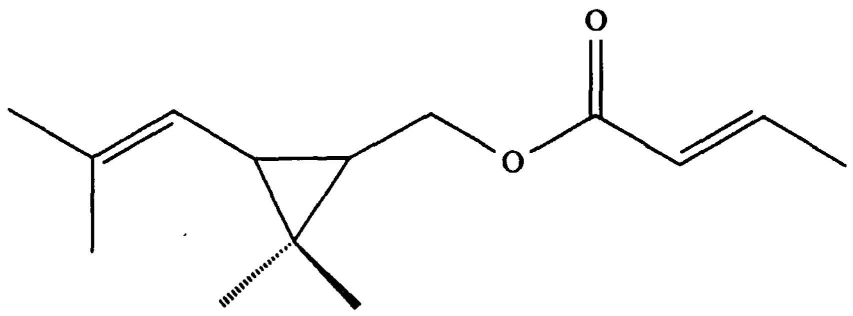
Investigation into the use of Cyclopropyl Acrylates as Potential Network Forming Materials

A1.1 Previous Investigations into Cyclopropyl Acrylates

In view of the vast range of studies reported for both acrylic acid derivatives and of cyclopropane derivitives there is a scarcity of references relating to compounds containing both cyclopropane and acrylate groups.

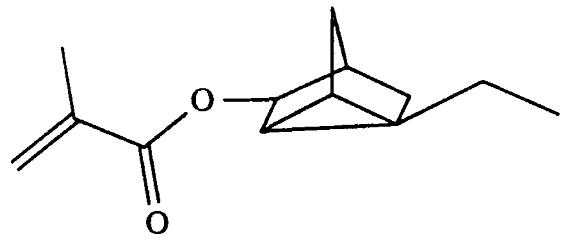
Ito and co-workers[199] reported the synthesis of cyclopropyl methylacrylate and it's anionic polymerization as part of a study into stereospecific polymerizations of methacrylic esters having hetero atoms in their pendant alkyl groups. Tanimoto *et al*[200] reported the synthesis and free radical polymerization of dicyclopropylmethylacrylate and 2,2-dicyclopropylethylacrylate. The synthesis and polymerization of cyclopropyl derivatives of acrylamide and methacrylamide were reported by Blaschke and Donow[201], the monomers were prepared by the reaction of the corresponding amine with acrylic anhydride. Esters of cyclopropyl methanol derivatives have been patented for use in perfumes[202] for example esters of chrysanthic acid as shown in Figure A1.1

Figure A1.1



In a patent covering norbornyl esters and their use in enhancing the aroma or taste in consumable materials, Sprecker[203] claimed that the ester shown in Figure A1.2 gave a salad dressing "a fresh, dandelion leaf, raw spinach nuance."

Figure A1.2



The reasons for the decision to study the polymerization of the acrylate esters prepared from cyclopropanecarboxylic acid were discussed in Chapter 3.

A.1.2. Monomer Synthesis

A.1.2.i. (2-Cyclopropyloxy carbonyl) ethyl propenoate (I)

The procedure was based on that of Hassner and Vazker.[204] To a three-neck round-bottom flask equipped with reflux condenser protected with a calcium chloride guard tube, thermometer and a dropping funnel, were charged cyclopropanecarboxylic acid (17.20g, 0.20mol), hydroxyethylacrylate (23.20g, 0.20mol), 4-pyrolidinopyridine (2.96g, 0.02mol), 2,6-di t-butyl-4-methyl phenol (0.107g, 4.86×10^{-4}mol) and dichloromethane (200ml). A solution of dicyclohexylcarbodiimide (41.3g, 0.20mol) in dichloromethane (50ml) was added from the dropping funnel over 66 minutes, with stirring and cooling by immersion of the flask in a cold waterbath. Dicyclohexylurea was removed by filtration, the filtercake was washed with dichloromethane (50ml), then the combined filtrate was washed successively with water (3x50ml), 5% acetic acid (3x50ml), saturated sodium bicarbonate (50ml), and finally water (3x50ml) before drying over magnesium sulphate. Excess solvent was removed using a rotary evaporator prior to distillation at reduced pressure to give 20.21g (55%) of (2-cyclopropyloxy carbonyl)ethyl propenoate (b.pt 76-78°C at 0.01mmHg). The purity of the monomer was determined by gas chromatography (5'10% SE 30 column , nitrogen carrier gas, oven temperature 200°C) and found to be greater than 99% pure.

The IR (capillary film between NaCl plates)(Appendix 4.21), ^1H NMR ($CDCl_3$, 250MHz) 5.7ppm(dd)1H, 5.5ppm(dd)1H, 5.2ppm(dd)1H, 3.7ppm(m)4H, 1.0ppm(m)1H, 0.2ppm(m)4H; ^{13}C NMR ($CDCl_3$, 62.9MHz) 173.6ppm, 165.2ppm, 130.7ppm, 128.1ppm, 62.2ppm, 62.1ppm, 12.3ppm, 8.0ppm; and MS (EI)M^+ not observed, m/e 99,69,55,43,41, were in agreement with the assigned structure.

A.1.2.ii. (2-Cyclopropyloxy carbonyl)ethyl-(2-methyl propenoate) (II)

Reaction of hydroxylethylmethacrylate (65.07g, 0.50mol), with cyclopropanecarboxylic acid (43.05g, 0.50mol) in dichloromethane (600ml), using dicyclohexylcarbodidimide (103.16g, 0.50mol) as a coupling agent with 4-pyrolidinopyridine (3.70g, 0.025mol) catalyst in the presence of 2,6-di t-butyl-4-methylphenol (0.107g, 4.86×10^{-4}mol) as a polymerization inhibitor gave 84.4g (85.1%) yield of (2-cyclopropyloxy carbonyl)ethyl-(2-methyl propenoate), b.pt. 76-78°C at 0.03mmHg. The purity of the monomer was determined by gas chromatography (Hewlett-Packard 5890A chromatogram, crosslinked methyl silicone coated capillary column, nitrogen carrier gas, FID detector, oven temperature 250°C) and found to be greater than 99% pure.

The IR (Capillary film between NaCl plates)(Appendix 4.22); ^1H NMR ($CDCl_3$, 250MHz) 5.42ppm(s)1H, 4.94ppm(s)1H, 3.67ppm(s)4H, 0.97ppm(s)3H, 0.74ppm(m)1H, 0.20ppm(m)4H; ^{13}C NMR ($CDCl_3$, 62.9MHz) 173.7ppm, 156.2ppm, 136.2ppm, 125.1ppm, 62.4ppm, 61.9ppm, 17.6ppm, 12.2ppm, 7.7ppm; and MS (EI) M/E 113, 69, 41 (CI) M+1 199 were consistent with the assigned structure.

A.1.2.iii. (4-Cyclopropyloxy carbonyl) butyl propenoate (III)

Reaction of hydroxylbutylacrylate (75.53g, 0.50mol), with cyclopropanecarboxylic acid (43.05g, 0.50mol) in dichloromethane (600ml), using dicyclohexylcarbodidimide (103.16g, 0.50mol) as a coupling agent with 4-pyrolidinopyridine (1.85g, 0.0125mol) catalyst in the presence of 2,6-di t-butyl-4-methylphenol (0.107g, 4.86x10^{-4}mol) as a polymerization inhibitor gave 84.4g (85.1%) of (4-cyclopropyloxy carbonyl) butyl propenoate,(b.pt. 76-78°C at 0.03mmHg). The purity of the monomer was determined by gas chromatography (Hewlet-Packard 5890A chromatogram, crosslinked methyl silicone coated capillary column, nitrogen carrier gas, FID detector, oven temperature 250°C) and found to be greater than 99% pure.

The IR (Capillary film between NaCl plates)(Appendix 4.23); ^{1}H NMR ($CDCl_3$, 250MHz) 5.75ppm(dd)1H, 5.48ppm(dd)1H, 5.18ppm(dd)1H,3.45ppm(d)4H, 1.08ppm(s)4H, 0.97ppm(m)1H, 0.20ppm(m)4H; ^{13}C NMR ($CDCl_3$, 62.9MHz) 173.7ppm, 165.2ppm, 130.1ppm, 128.5ppm, 63.7ppm, 63.6ppm, 25.3ppm, 12.4ppm, 7.7ppm; and MS (EI) m/e 113, 69, 41 (CI) M+1 199 spectra were in agreement with the assigned structure.

A.1.3. Synthesis of Homopolymers

A.1.3.i. Free radical initiated homopolymerization of (I)

A solution of (I) (2.00g, 0.0109mol) and 4,4'-azobisisobutyronitrile (0.0200g, 1.22x10^{-4}mol) in toluene (16g) were maintained at 80°C for 5 hours, then cooled in an icebath. An aliquot (15g) was poured, with stirring into hexane (100ml), the polymer which precipitated was recovered by filtration and redissolved in toluene (10ml)and poured into hexane, after a further reprecipitation the polymer was dried *in vacuo* at room temperature for 24hours, to give a tacky white resin. GPC (tetrahydrofuran eluent, mixed gel polystyrene column, RI detector) indicated a peak molecular weight of 8500 relative to polystyrene standards.

The IR (thin film supported on NaCl plate)(Appendix 4.24);^{1}H NMR ($CDCl_3$, 250MHz); and ^{13}C NMR ($CDCl_3$, 62.9MHz) 174.3ppm, 173.9ppm, 62.2ppm, 61.8ppm, 60.9ppm, 31.7ppm(broad), 12.4ppm,8.4ppm; spectra were in agreement with the assigned structure. The ^{1}H NMR spectrum contained a series of overlapping resonances between 1-2ppm, due to the main chain methylene and methine protons, and the cyclopropyl methine proton. The broadening of the resonance at 31.7ppm in the ^{13}C NMR due to the main chain methylene demonstrated that this carbon experienced multiple environments. The ^{13}C and ^{1}H NMR spectra were consistent with an atactic polymer, as would be expected for a free radical polymerization.

A.1.3.ii. Free radical initiated homopolymerization of (II)

A solution of (II) (2.05g, 0.0104mol) and 4,4'-azobisisobutyronitrile (0.0208g, 1.27×10^{-4}mol) in toluene (38.95g) were maintained at 80°C for 4.5 hours, then cooled in an icebath. An aliquot (10g) of the polymer solution was poured into hexane (100ml), giving a white precipitate of polymer. The polymer was redissolved in toluene (5ml)and precipitated by pouring into hexane (100ml), the precipitation procedure was repeated before drying the polymer *in vacuo* at room temperature for 24hours. GPC (tetrahydrofuran eluent, mixed gel polystyrene column, RI detector) indicated a peak molecular weight of 12600 relative to polystyrene standards. The IR (thin film supported on NaCl plate)(Appendix4.25);^{1}H NMR ($CDCl_3$, 250MHz) 4.1ppm(s)4H, 1.6-2.2ppm(s+overlapping multiplet)6H, 0.9ppm(m)2H, 0.6pm(m)2H; and ^{13}C NMR ($CDCl_3$, 62.9MHz) 177.1ppm, 176.8ppm, 175.9ppm, 174.2ppm, 62.7ppm, 61.3ppm, 54.7-52.7ppm(broad) 44.8ppm, 44.5ppm, 18.8ppm(broad), 16.3ppm(broad) 12.4ppm, 8.4ppm were in agreement with the assigned structure. The multiplicity of resonances between 177.1-175.9ppm(due to the carbonyl adjacent to the polymer backbone), the broadening of the signal between 54.7-52.7ppm (arising from the main chain methylene), and the multiplicity of the methyl signal (~18.8-16.3ppm) were consistent with an atactic polymer.

A.1.3.iii. Free radical initiated homopolymerization of (III)

A solution of (III) (2.00g, 0.9.43x10^{-3}mol) and 4,4'-azo bis isobutyronitrile (0.0200g, 1.22x10^{-4}mol) in toluene (16g) were maintained at 80°C for 5 hours, then cooled in an icebath. An aliquot (15g) was poured, with stirring into hexane (100ml), then redissolved in toluene (10ml)and poured into hexane, after a further reprecipitation the polymer was dried *in vacuo* at room temperature for 24hours, to give a viscous white fluid. GPC (tetrahydrofurn eluent, mixed gel polystyrene column, RI detector) indicated a peak molecular weight of 5000 relative to polystyrene standards.

The IR (thin film supported on NaCl plate)(Appendix 4.26) and ^{13}C NMR ($CDCl_3$,62.9MHz) 174.6ppm, 174.1ppm, 64.0ppm, 63.7ppm, 41.3ppm, 35.3ppm, 25.1ppm, 12.7ppm, 8.2ppm spectra were in agreement with the assigned structure. The broadness of the main chain methylene resonance in the ^{13}C NMR may indicate an atactic polymer was obtained.

The ^{1}H NMR spectrum ($CDCl_3$, 250MHz) 4.07ppm(s)4H, 1-2.2 ppm(series of overlapping peaks)(12H) was of limited value due to the multiplicity of overlapping resonances.

A.1.4. Crosslinking Studies

A.1.4.i. Attempted crosslinking of poly(III) by irradiation with UV light in the presence of diphenyliodonium hexafluorophosphate

The polymer was thoroughly mixed with solvent and photoinitiator to give a formulation containing poly(CP-HBA)(87.8%), toluene(8.6%) acetone(1.2%) and diphenyliodionium hexafluorophosphate(2.4%). A film was prepared from the mixture by coating the solution onto a nylon block, between a double thickness of Sellotape to give a nominal film thickness of 100μm. The film was then irradiated using a Hannovia 100W medium pressure mercury vapour lamp, for 5 minutes at a distance of 15cm. The film remained very soft, and completely soluble in acetone after irradiation.

A.1.4.ii. Crosslinking of Ciba-Giegy epoxy resin CY177 by irradiation with UV light in the presence of diphenyliodonium hexafluorophosphate

A formulation containing CY177(97%), diphenyiodonium hexafluorophosphate(2%) and acetone(1%) was coated onto a nylon block as described above. After irradiation for 5 minutes the surface had wrinkled and the film appeared to have cured to approximately half its depth.

A.1.4.iii. Irradiation of cyclopropyl methyl ketone with UV light in the presence of diphenyliodonium hexafluorophosphate.

Cyclopropyl methyl ketone (98%) and diphenyliodonium hexafluoropphosphate (2%) were stirred together in a 25 ml round bottom borosilicate glass flask. The solution was irradiated with UV light from a 100W Hannovia medium pressure mercury lamp, at a distance of 2cm, for 2 hours. The solution, which had initially been colourless became yellow during the irradiation. The IR spectrum (Capillary film between NaCl plates)showed no reduction in the intensity of the characteristic cyclopropyl absorption maximum at 3085cm^{-1}.

A.1.4.iv. Irradiation of ethylcyclopropanecarboxylate with UV light in the presence of diphenyliodonium hexafluorophosphate

Irradiation of ethylcyclopropanecarboxylate (99%) with diphenyliodionium hexafluorophosphate (1%) under the same conditions as above led to no reduction in the intensity of the characteristic maximum at 3080cm^{-1} due to cyclopropyl groups.

A.1.4.v. Irradiation of α-methyl cyclopropanemethanol acetate with UV light in the presence of diphenyliodonium hexafluorophosphate

Irradiation of α-methyl cyclopropane methanol acetate (85%) with diphenyliodionium hexafluorophosphate (2%) and acetone (13%) under the same conditions as above led to no reduction in the intensity of the characteristic maximum at 3080cm^{-1} arising from cyclopropyl groups in the IR spectrum.

A.1.4.vi. Irradiation of ethylcyclopropane with UV light in the presence of diphenyliodonium hexafluorophosphate

Irradiation of ethylcyclopropane (38%) with diphenyliodionium hexafluorophosphate (1%), ethyl acetate (48%), acetone (13%) and cyclohexane (1.63g) under the same conditions as above led to no reduction in the intensity of the characteristic maxima at 3080cm^{-1} and 1010cm^{-1} in the IR spectrum.

APPENDIX 2

Estimation of the Crosslink Density of a Network by Using a Solvent Swelling Technique.

A model describing the swelling of networks by solvents was developed by Flory and Huggins, leading to the Flory-Huggins theory.[157] The theory has been subject to modifications however it remains the basic explanation of this phenomenon. A network is swollen by solvent if there is a favourable free energy for the process. As the network swells the polymer chains have to adopt an extended conformation this leads to a force opposing the uptake of more solvent. At some stage the energy required to extend the chains further is equal to the energy of solvation, and the gel reaches its equilibrium volume. The degree of swelling is related to the crosslink density, as shown in equation A.2.1:

$$\ln(1-\upsilon_r) + \upsilon_r + \chi_1\upsilon_r^2 = -Vp\,\rho\,M_c^{-1}\left(\upsilon_r^{1/3} - \frac{2\upsilon_r}{Z}\right) \quad \text{A.2.1}$$

Where $Z =$ The number of functionalities at the junctions (in this case $Z=3$)

$Vp =$ Molar volume of the solvent

$\rho =$ Polymer density

$M_c =$ Number average molecular weight between crosslinks

$\upsilon_r =$ Equilibrium volume fraction of polymer in the swollen network

$\chi_1 =$ The solvent-polymer interaction parameter

The solvent-polymer interaction parameter arises from the Flory-Huggins model for the dissolution of a polymer, and accounts for different interaction energies between solvent and polymer molecules. The value of χ_1 is dependant on temperature and on the polymer concentration,[205] the determination of χ_1 for a polymer-solvent pair is not a trivial matter and requires considerable time. The value of χ_1 would have to be calculated for each of the copolymers if a thorough study of the crosslink densities was to be undertaken. The determination for each copolymer would require a lot of time, which was not available to us, it was therefore necessary to employ literature values for similar polymer-solvent pairs. For polyheptene/toluene at 30°C χ_1=0.49,[206] for polypropene/benzene χ_1=0.496-0.498.[207] The effect of simple alkyl groups on the value of χ appeared to be small, so it was presumed that the behaviour of 6-cyclopropyl-1-hexene would similar to that of heptene. The values of χ_1 above are close to the value for ideal behaviour (0.5), it was therefore decided to use this value in the calculation of the crosslink density of copolymer (VI). The value of v_r for the copolymer was small, and so the $\chi_1 v_r^2$ term is tiny, any error caused by the assumption for the value will be very small.

Method

The procedure was carried out in triplicate. A weighed sample of the crosslinked polymer, which had previously been extracted with petroleum spirit(40-60°C b.pt.) and dried to constant weight, was placed in a stoppered tube with toluene (5ml) and maintained at 25°C. The sample was taken out periodically, excess solvent was removed from the surface before weighing the swollen gel in a sealed flask. After approximately 24 hours the samples had reached approximately constant weight. The weighings were repeated at 2-hourly intervals and ν_r was calculated. The average was then used to calculate M_c.

The results are tabulated below.

	A	B	C
Weight of Sample/g	0.0388	0.0522	0.0407
ν_r 24hrs	0.0352	0.0314	0.0348
ν_r 26hrs	0.0364	0.0341	0.0360
ν_r 28hrs	0.0352	0.0299	0.0342
ν_r 48hrs	0.0333	0.0279	0.0336
Average value of $\upsilon_{re} = 0.0335$			

There was considerable difficulty in obtaining samples free of excess solvent on the surface without losing solvent from the bulk of the gel. The difficulty in obtaining accurate values for the weight of swollen gels is the main source of error in the calculation of M_C. All the samples were highly swollen, and therefore mechanically weak. Sample B broke in two while being removed for weighing after 26 hours.

M_C was calculated using the following values

$V_p = 106.3$

$\chi_1 = 0.5$

$\rho = 0.857$

Substituting these values into equation A.2.1. gave M_c= 2100000.

The value of M_c appeared to be very large, and clearly demonstrated that the gel was only lightly crosslinked. Because of the difficulty experienced in obtaining reproducible values for the weights of the swollen gel, and hence in the value of υ_r there is likely to be a relatively large error in the experimentally determined value of υ_r. Inspite of the shortcomings of the results they clearly demonstrated that the gels obtained by the reaction of the 6-cyclopropyl-1-hexene copolymers with aluminium bromide in solution had a very low crosslink density, and that an alternative crosslinking procedure was required.

APPENDIX 3

NMR Spectra

1. ^{1}H NMR of poly(octene)
2. ^{1}H NMR of poly(octene) synthesised in the presence of ethylcyclopropane
3. ^{1}H NMR of octene/6-cyclopropyl-1-hexene copolymer
4. ^{1}H NMR of poly(2-cyclopropylpropene)
5. ^{13}C NMR of poly(octene)
6. ^{13}C NMR of poly(octene) synthesised in the presence of ethylcyclopropane
7. ^{13}C NMR of octene/6-cyclopropyl-1-hexene copolymer
8. ^{13}C NMR of poly(ethylcyclopropane)
9. ^{13}C NMR of gel fraction from propene/6-cyclopropyl-1-hexene copolymer crosslinked by the addition of aluminium bromide
10. ^{13}C NMR of sol fraction from propene/6-cyclopropyl-1-hexene copolymer crosslinked by the addition of aluminium bromide

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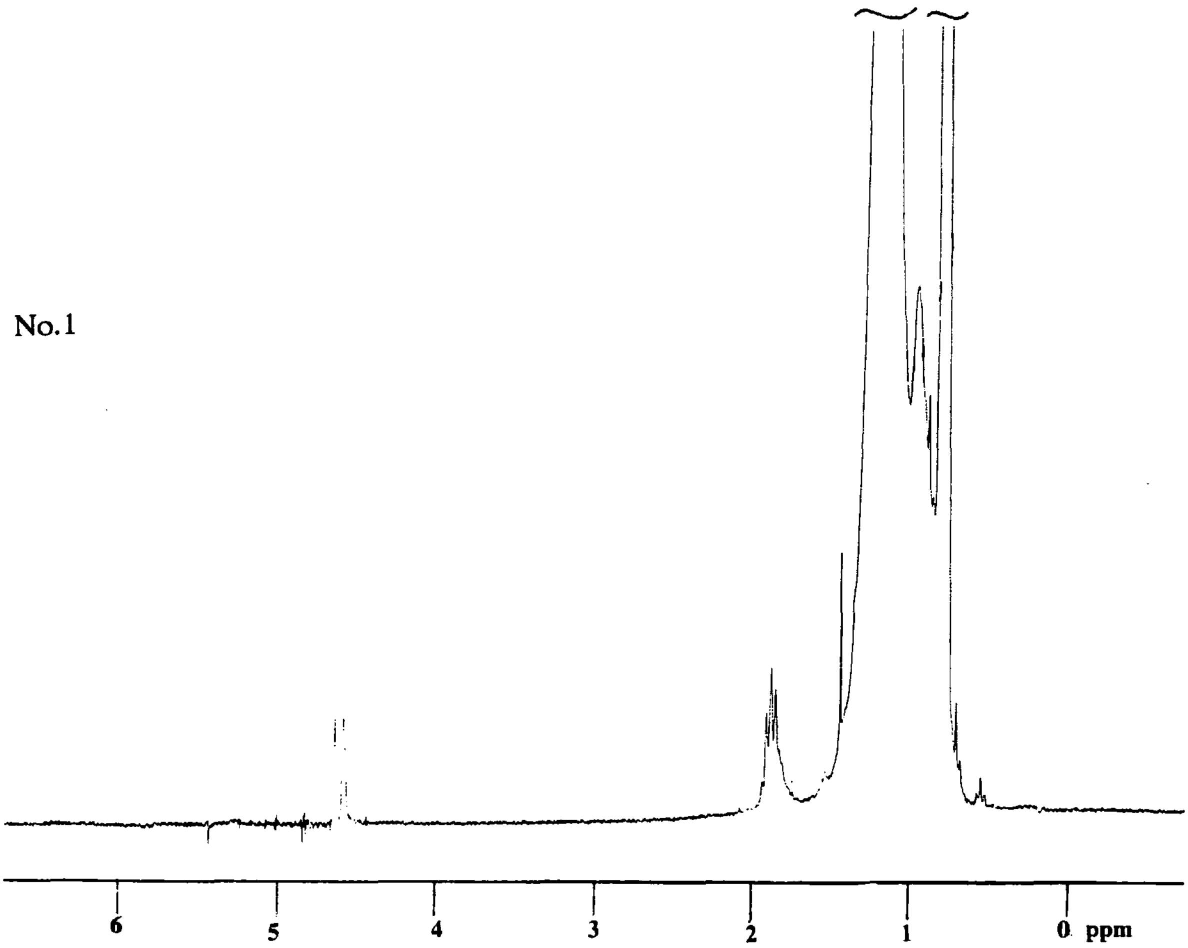

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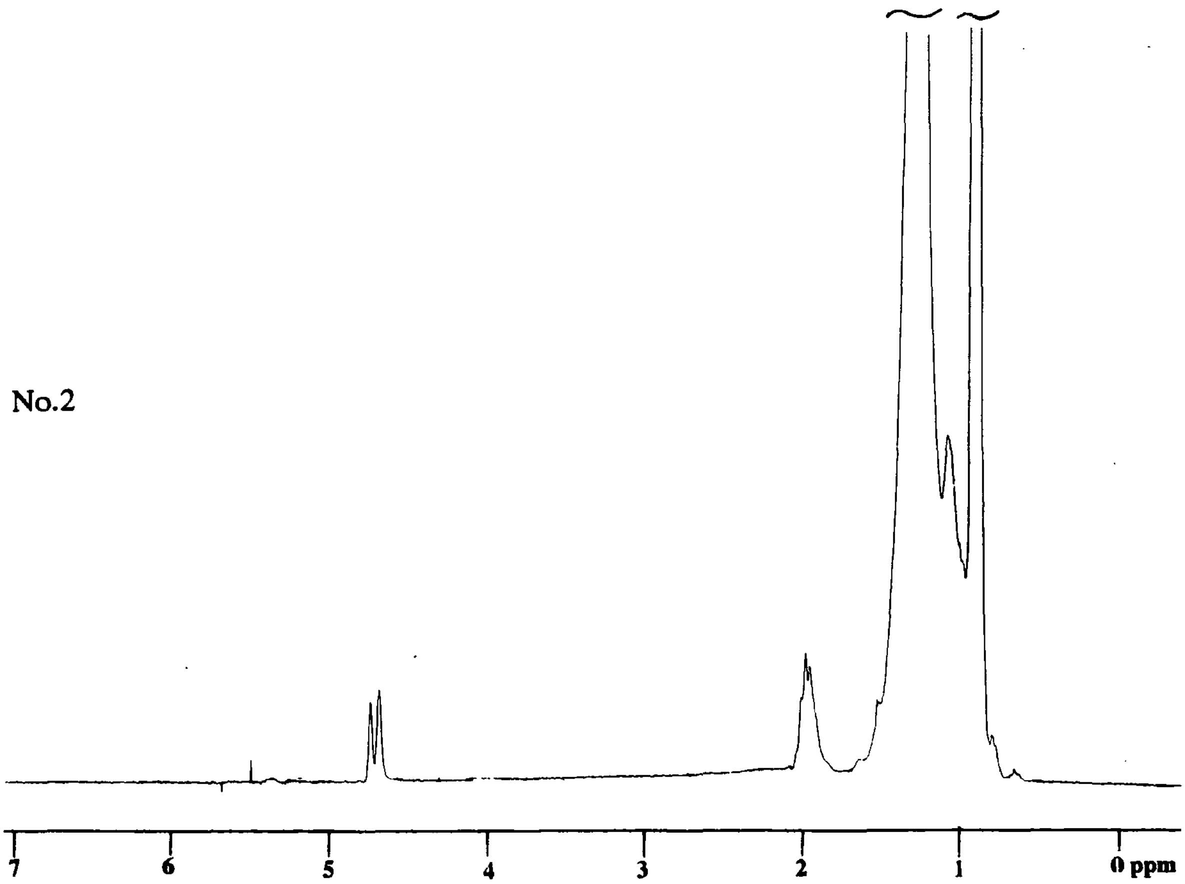

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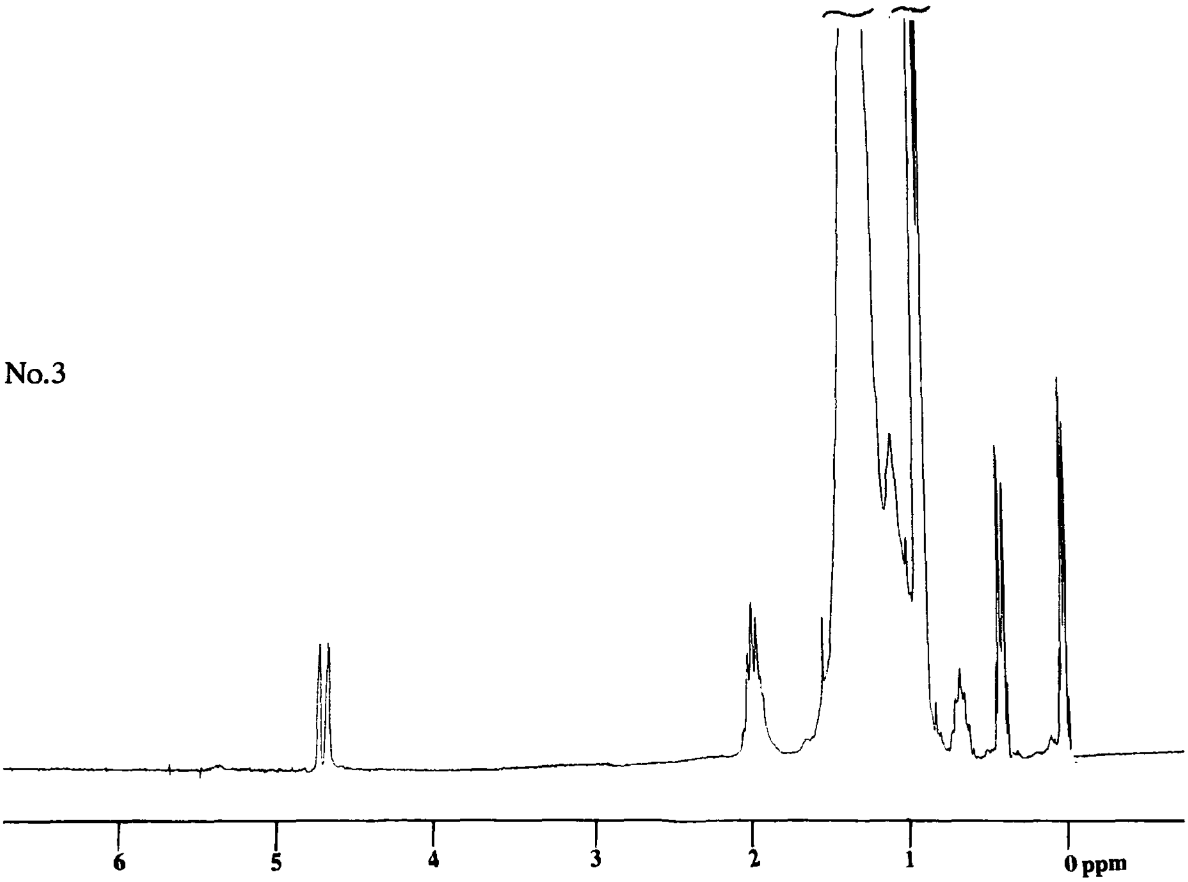

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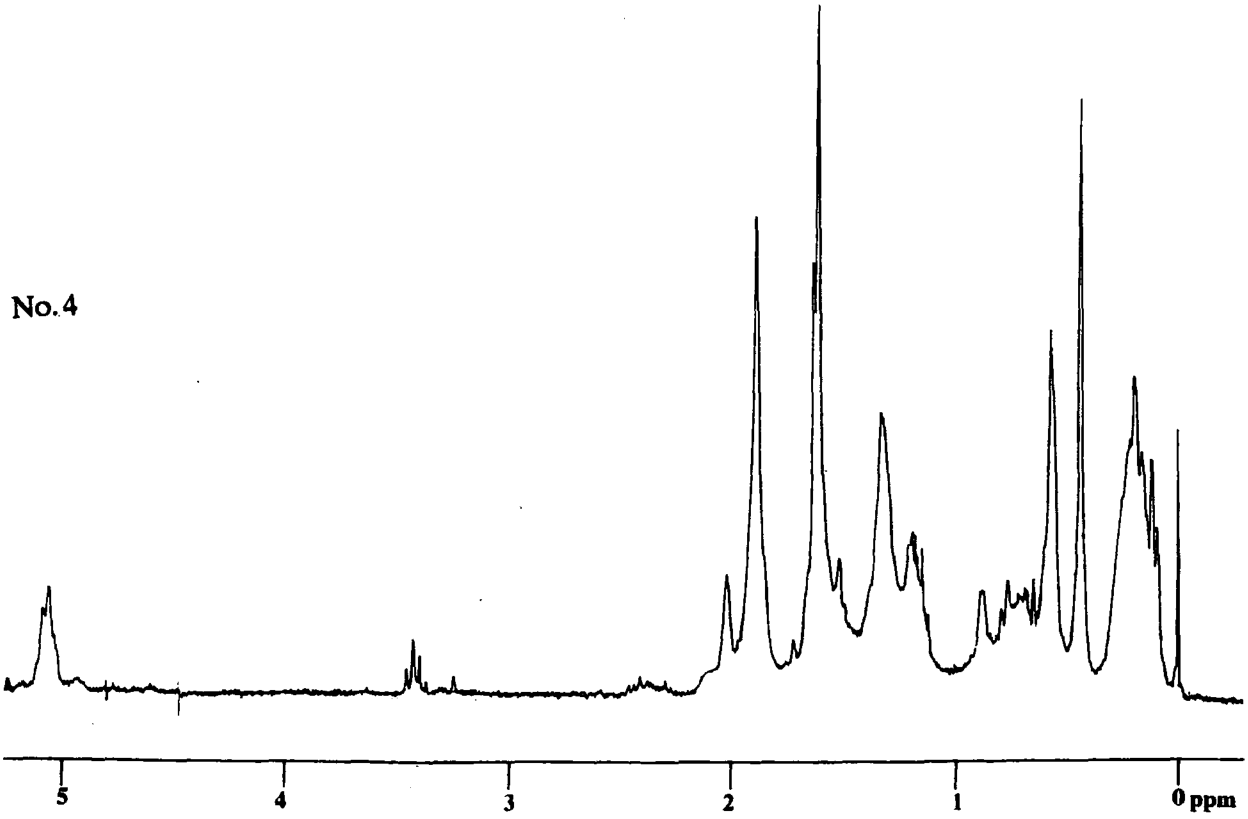

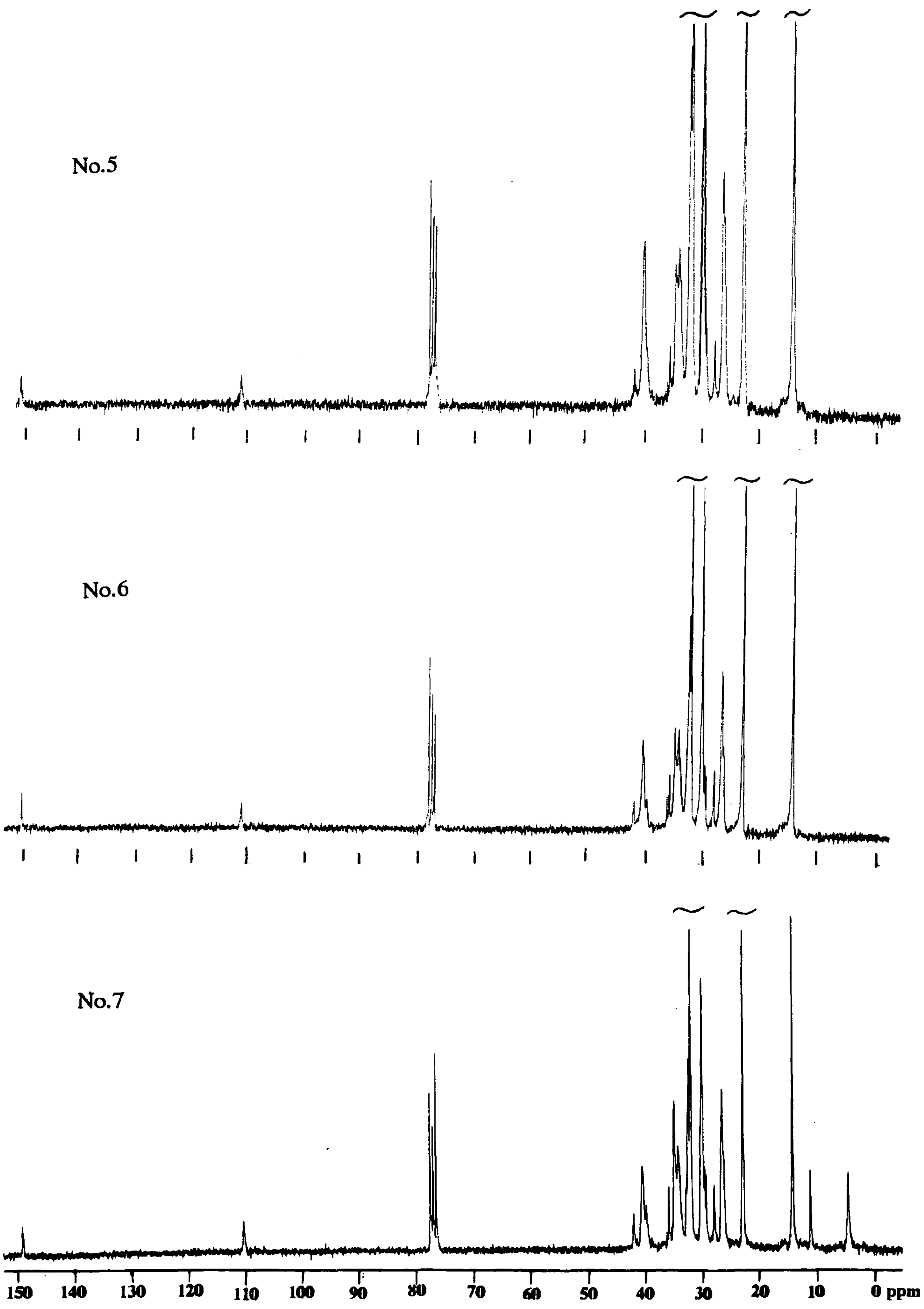
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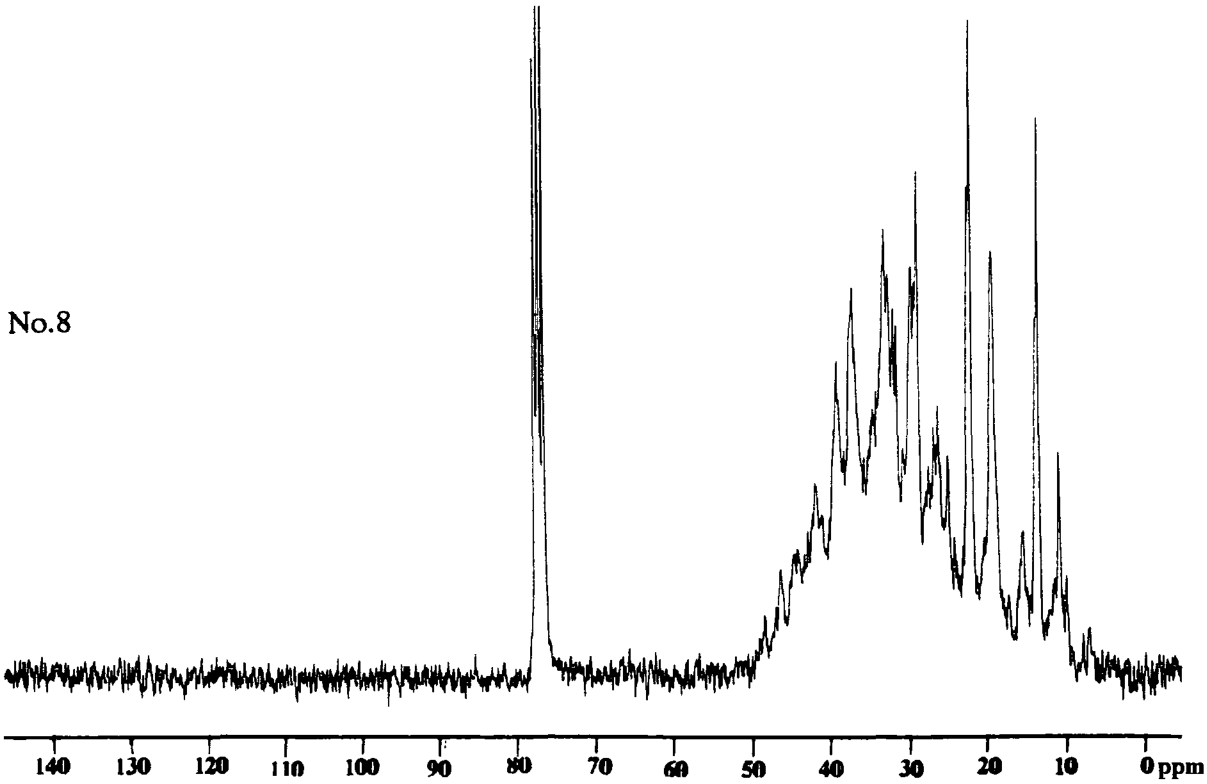
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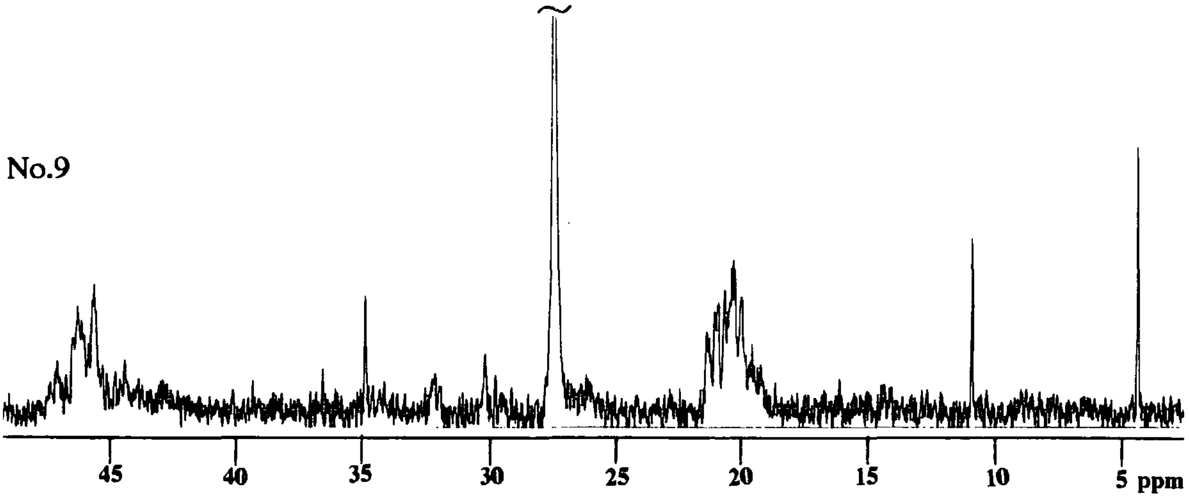
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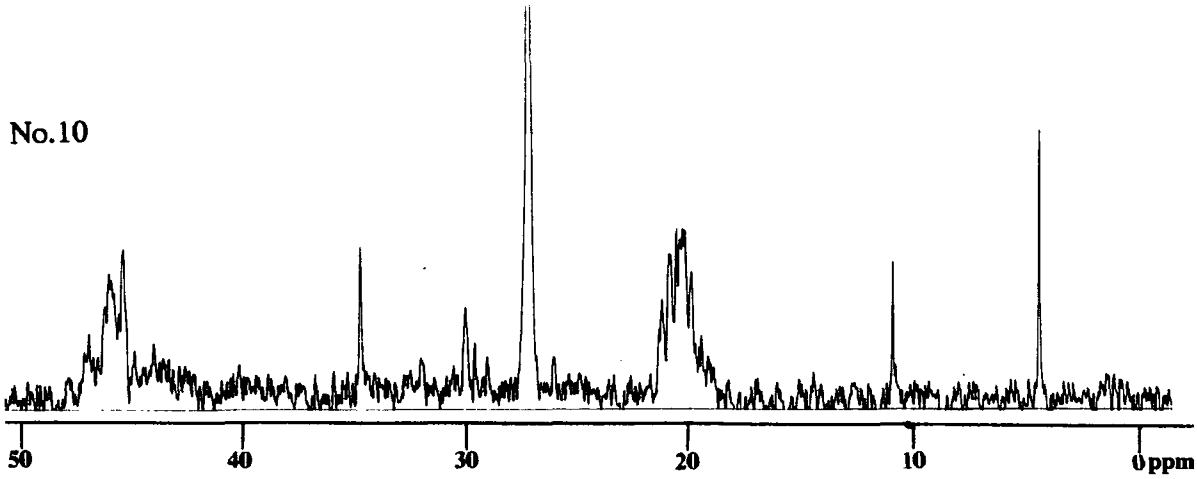
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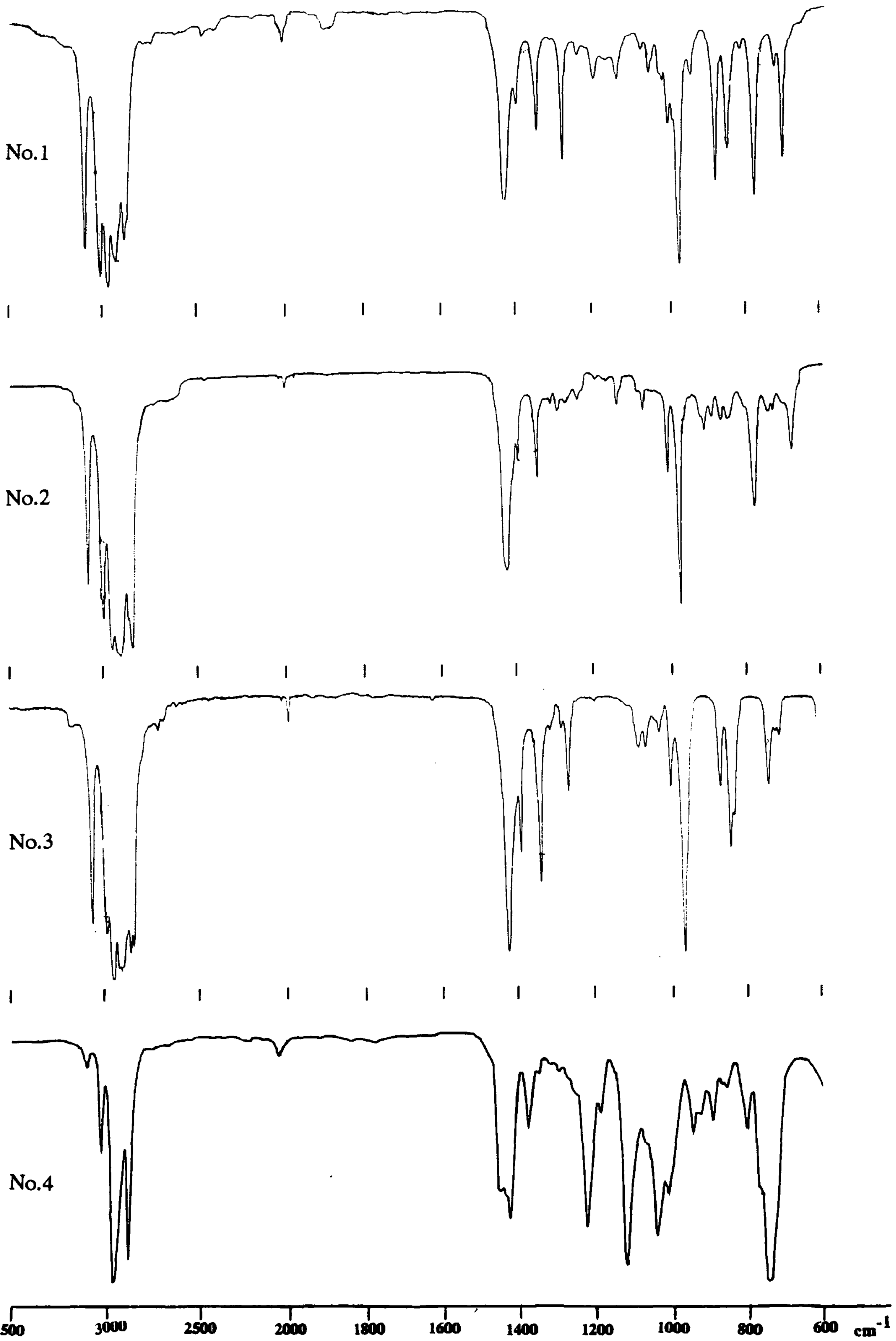
APPENDIX 4

IR Spectra

1. Ethylcyclopropane
2. Hexylcyclopropane
3. 1,1-Diethylcyclopropane
4. 1,4-Bis-(2,2-dichlorocyclopropyl)butane
5. 1,1-dichloro-2-hexylcyclopropane
6. 1,2-Bis-(1-methylcyclopropyl)ethane
7. 2-Cyclopropylpropene
8. 6-Cyclopropyl-1-hexene
9. Isotactic poly(octene)
10. Isotactic poly-(6-cyclopropyl-1-hexene)
11. Atactic poly(octene)
12. Atactic poly(propene) (M_n~3000)
13. Atactic poly(propene) (M_n~5300)
14. Atactic poly(octene)
15. Atactic poly(octene) prepared in the presence of ethylcyclopropane
16. Octene/6-cyclopropyl-1-hexene copolymer
17. Propene/6-cyclopropyl-1-hexene copolymer
18. Poly(ethylcyclopropane)
19. Gel fraction from propene/6-cyclopropyl-1-hexene copolymer crosslinked by the addition of aluminium bromide
20. Sol fraction from propene/6-cyclopropyl-1-hexene copolymer crosslinked by the addition of aluminium bromide
21. (2-Cyclopropyloxy carbonyl)ethyl propenoate
22. (2-Cyclopropyloxy carbonyl)ethyl(methyl propenoate)
23. (4-Cyclopropyloxy carbonyl) butyl propenoate
24. Poly-[(2-cyclopropyloxy carbonyl)ethyl propenoate]
25. Poly-[(2-cyclopropyloxy carbonyl)ethyl(methyl propenoate)]
26. Poly-[(4-Cyclopropyloxy carbonyl) butyl propenoate]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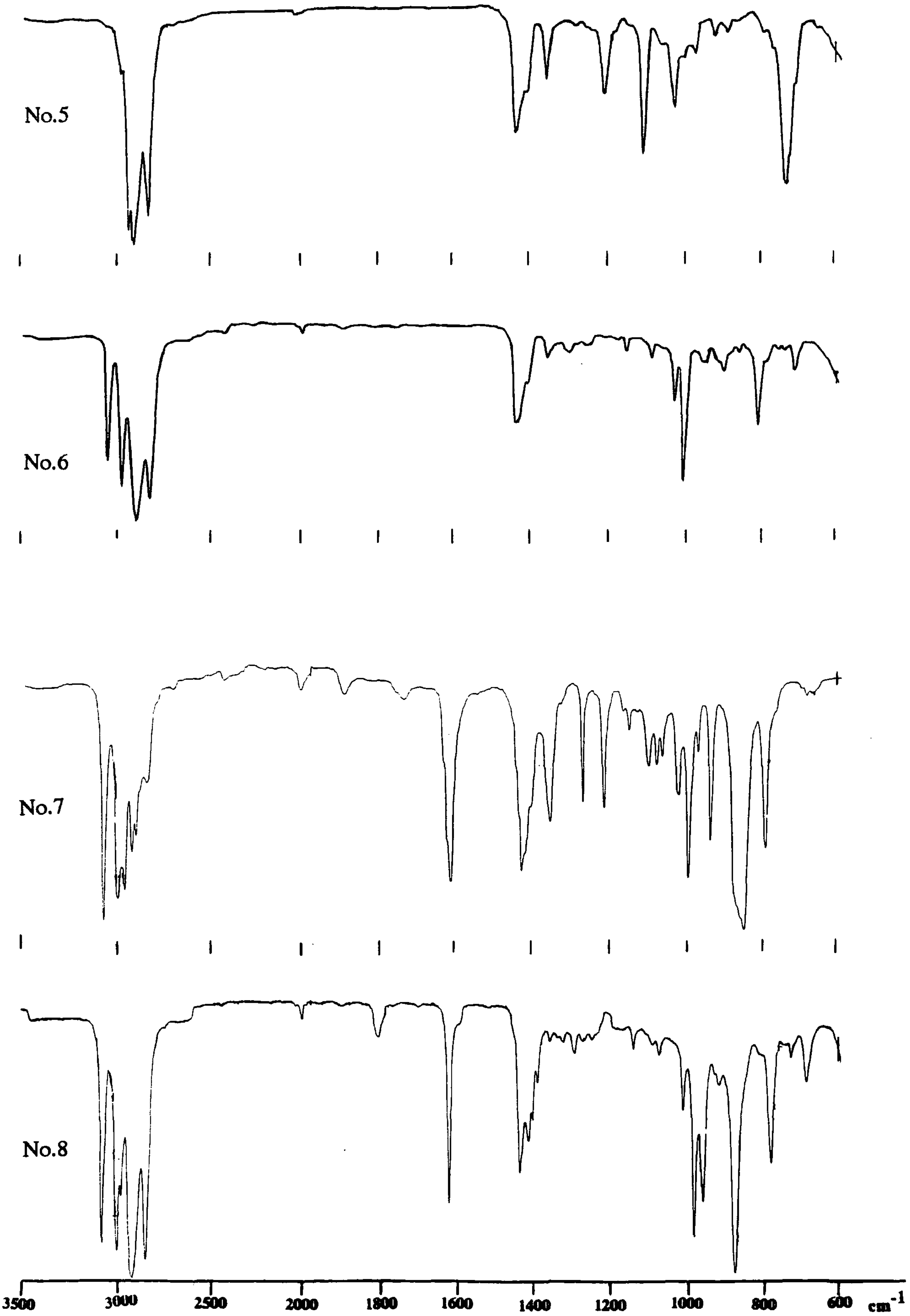
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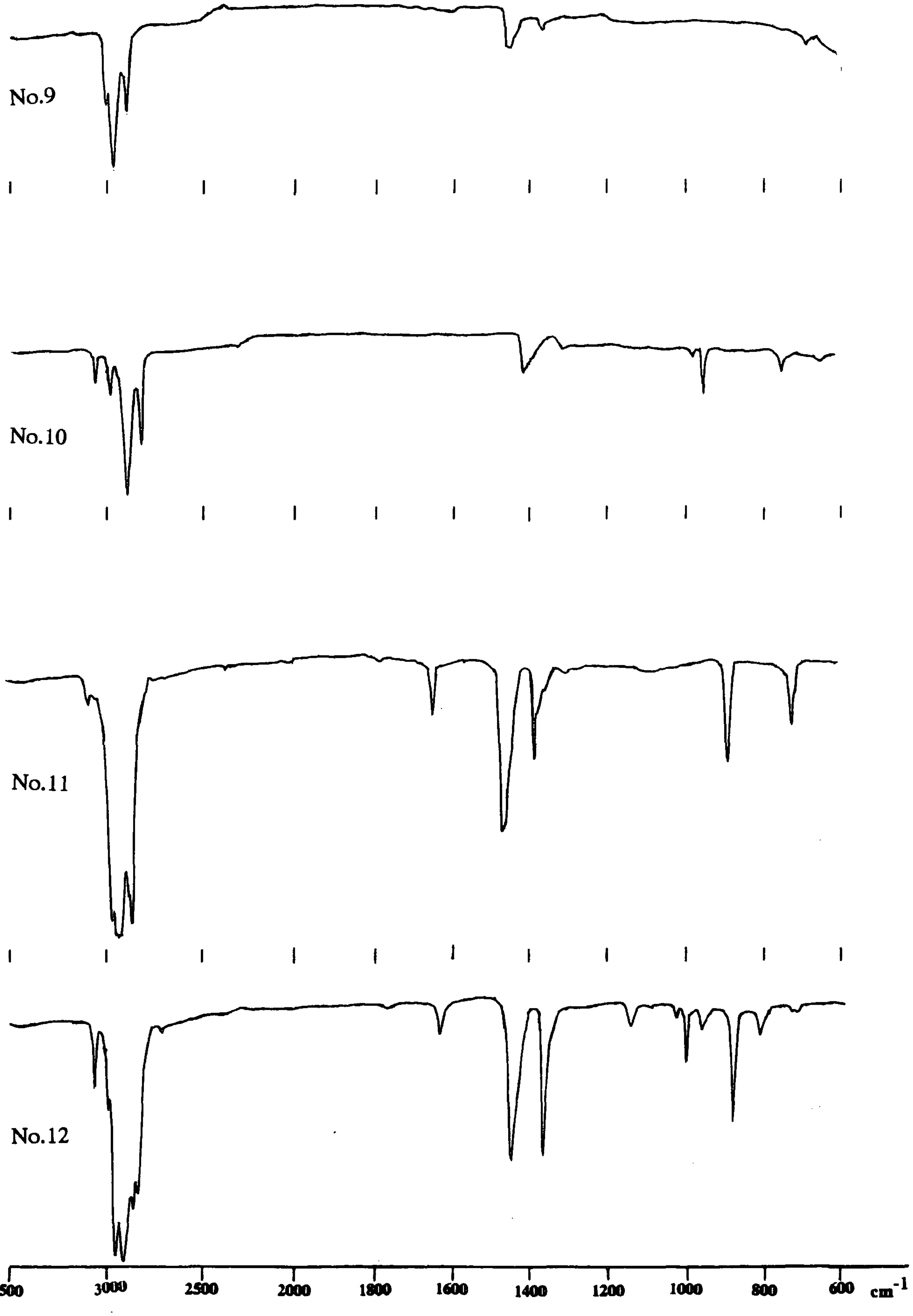
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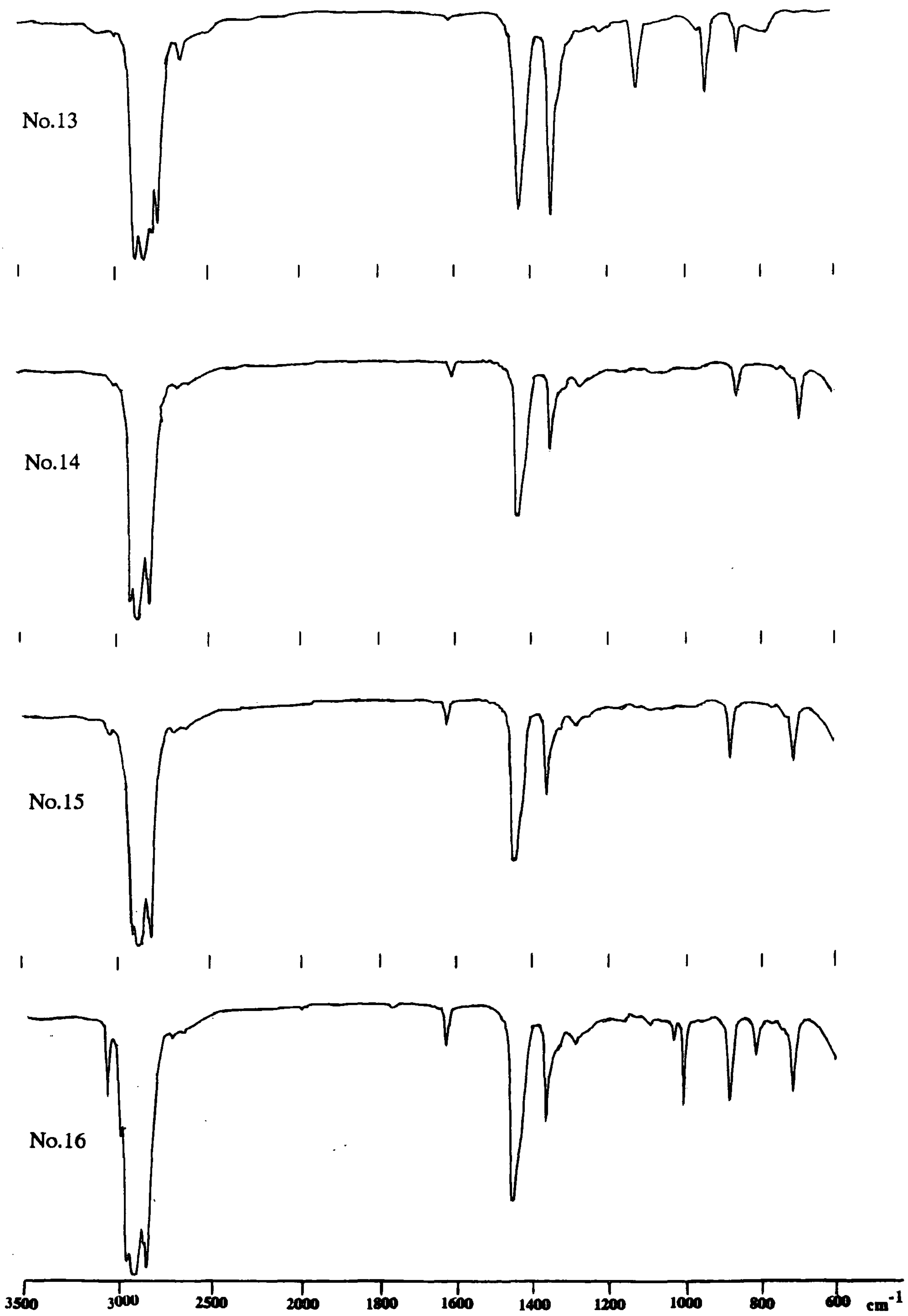
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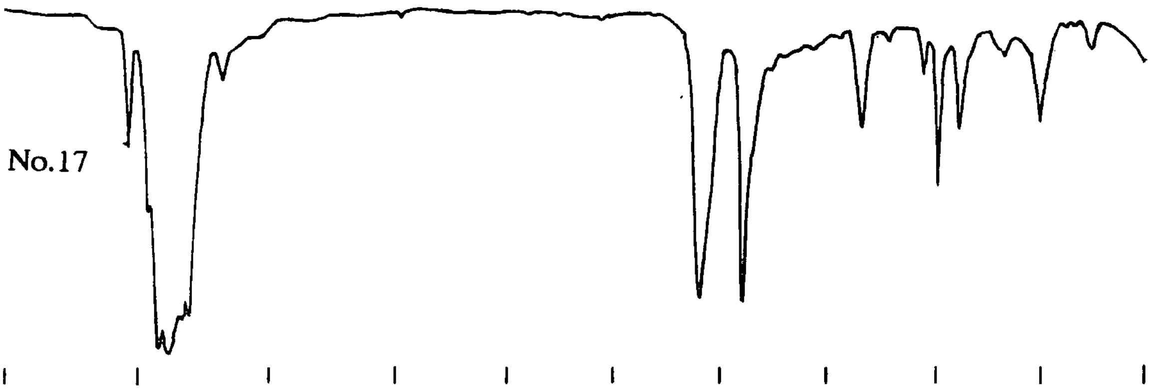

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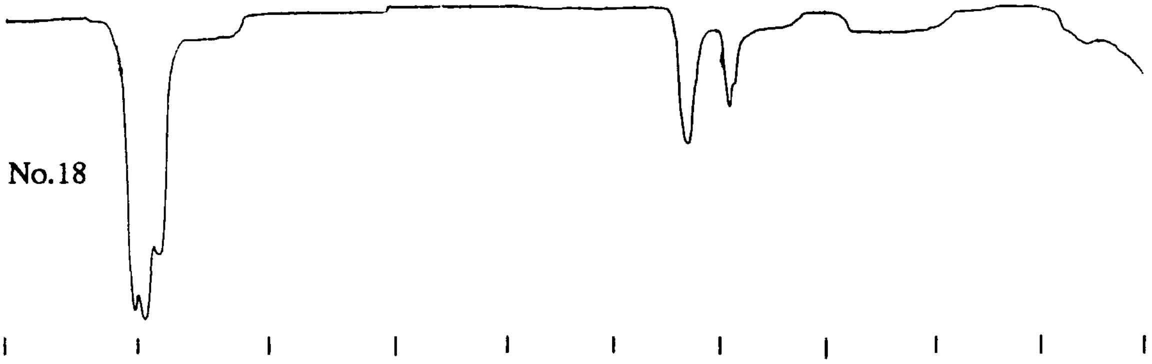

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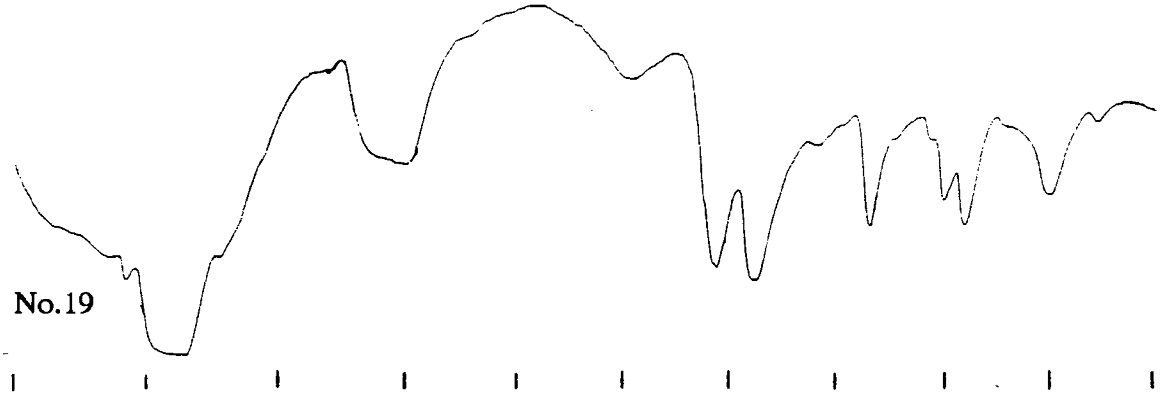

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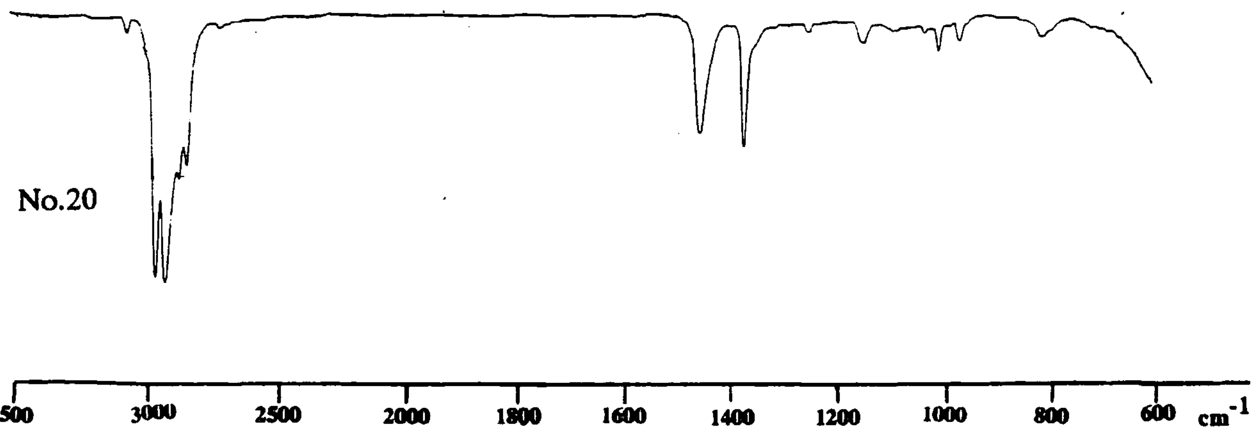
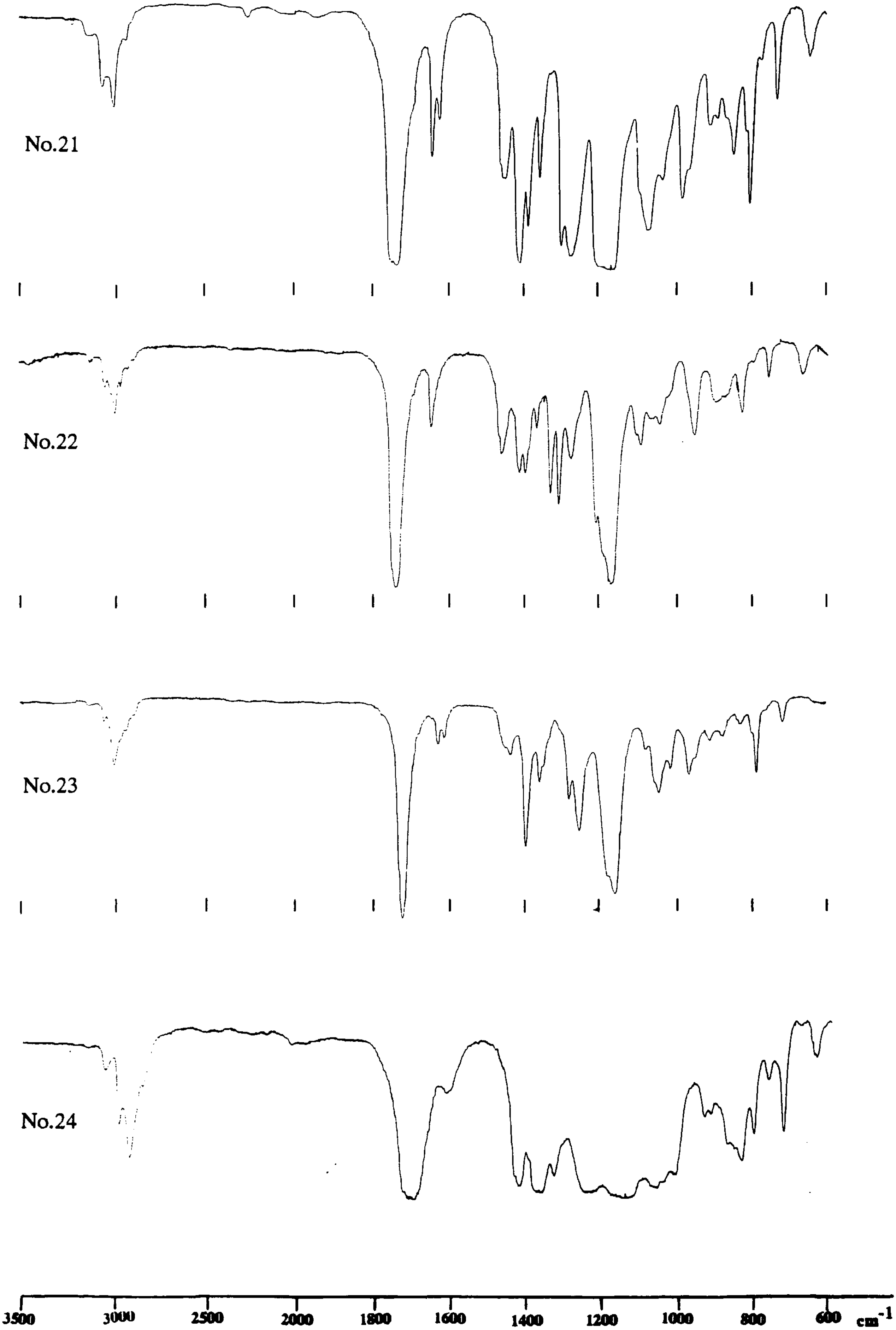
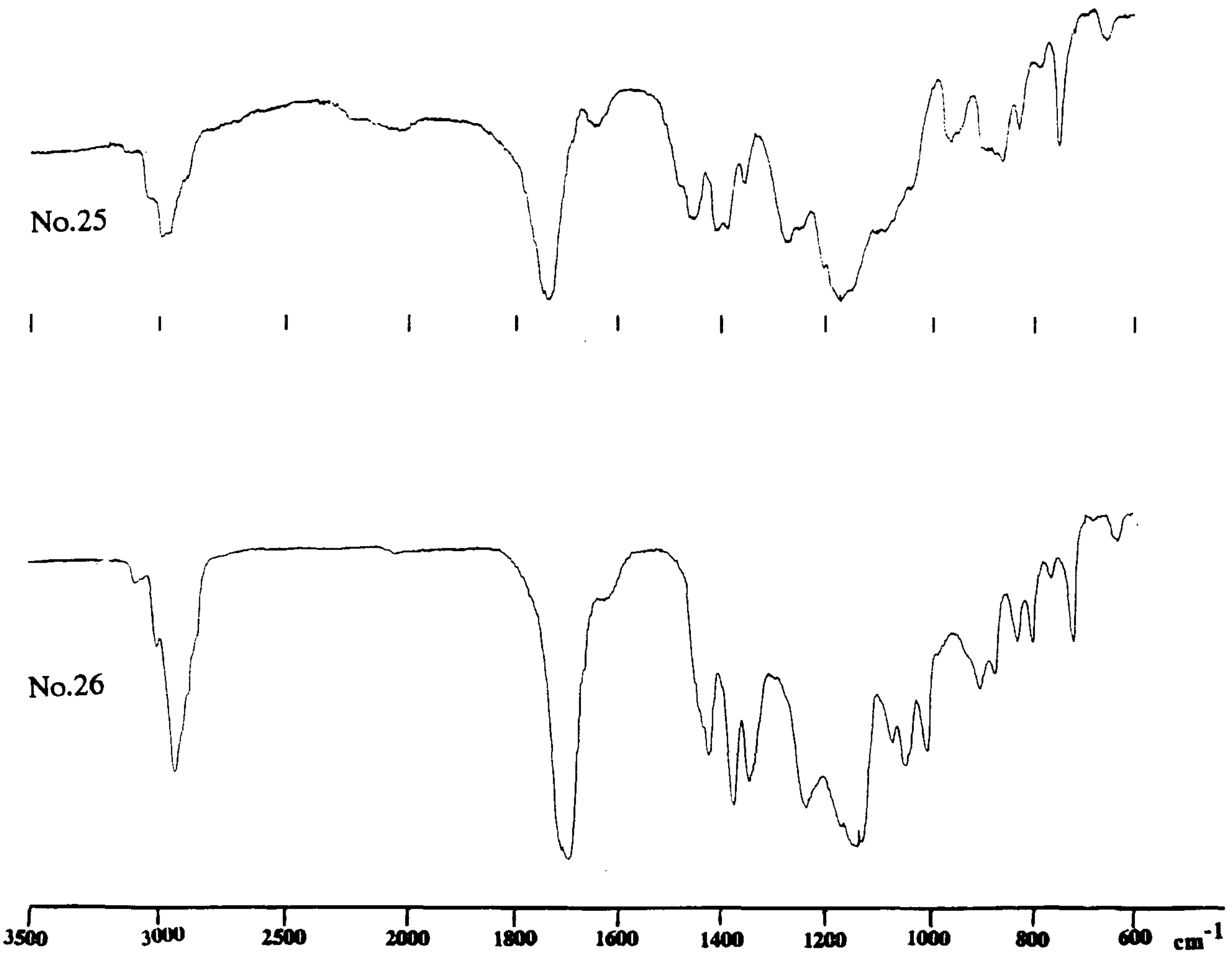


No.20


No.21
No.22
No.23
No.24
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
cm-1


No.25
No.26
3500
3000
2500
2000
1800
1600
1400
1200
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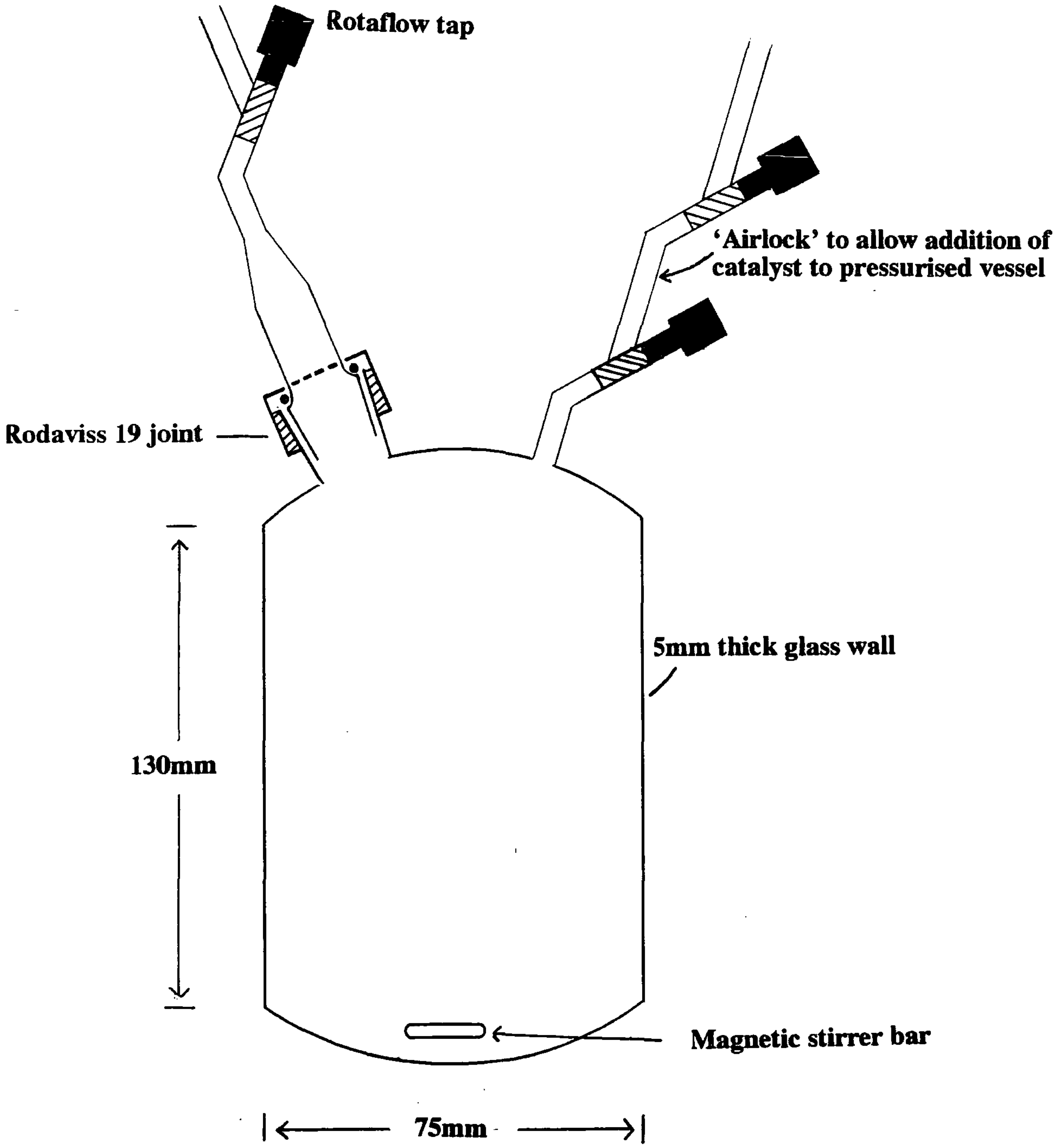
600
cm^{-1}

APPENDIX 5

APPARATUS, EQUIPMENT AND REAGENTS

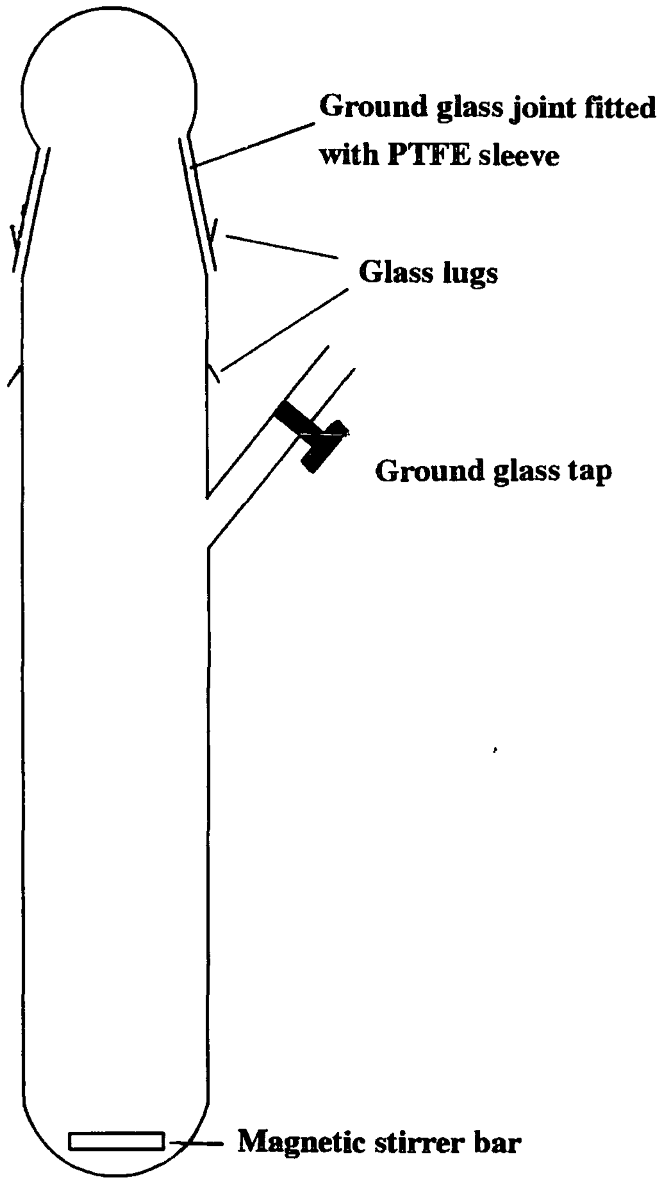
5.1 Apparatus

Vessel used for the Polymerization of Propene



Note: The ground glass cone of the Rodaviss 19 joint is held in place by a rubber 'O' ring which is compressed by tightening the screw fitting between the flange and the ground glass socket

Schlenk-Type Reaction Vessel used for the Polymerization of 1-Octene



5.2 Equipment

^{1}H NMR

Spectra were recorded on a Bruker AC250, or Varian VXR400 NMR spectrometers.

^{13}C NMR

Spectra were recorded on Bruker AC250 (62.9MHz), Bruker WH360 (90.56MHz), or Varian VXR400 NMR spectrometers.

GPC

Chromatograms were obtained using a Waters Model 590 pump, Waters ModelR401 Differential Refractometer detector, Polymer Laboratories PLgel 5 m 300x7.5mm crosslinked polystyrene columns,, equipped with a SIC Chromacorder12 computing intergrator.

Elemental Analysis

Results were obtained from a Carlo-Erba Model 1106 elemental analyser.

IR

Spectra were recorded using a Perkin-Elmer 577, or Perkin Elmer 1310 grating Infrared Spectrophotometers.

Mass Spectra

Spectra were obtained from a VG Analytical Model 7070E Mass spectrometer.

Gas Chromatography

Chromatograms were obtained using a Perkin-Elmer 5980 Chromatogram,equipped with a Hewlett-Packard HP-1 25mx0.2mmx0.33 m capillary column, and a FID detector linked to a Spectra-Physics SP4200 computing intergrator.

5.3 Reagents

Diethyl ether, BDH Anhydrous grade was dried over sodium wire; toluene May and Baker Analar grade was dried by refluxing over sodium/benzophenone;1-octene was dried over lithium aluminium hydride; aluminium bromide was sublimed twice before use in crosslinking copolymers. Tributyl tin oxide, Albright and Wilson commercial grade; boron difluoride-acetoacetanilide chelate and BF_3.ethylamine, Ciba-Giegy commercial grade; hydroxyethylacrylate, hydroxyethylmethacrylate, and hydroxybutylacrylate, Sartomer commercial grade; were used without further purification.

Diphenyliodonium hexafluorophosphate was prepared by Dr. S. Matuszczak, Copper(I)chloride was freshly prepared by a standard procedure.[208] Propene, Aldrich 99+% or Air Products 98+%, was used without further purification. Other reagents were obtained from Aldrich, solvents were obtained from May and Baker, and were used without further purification unless otherwise stated.

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