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The Synthesis of Some New Polymeric Materials as Potential Additives for Diesel Fuel

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A Thesis submitted in part fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Durham

1993

Andrei is seven. He lives in an army children's home in Siberia. He is an orphan but has heard the voice of his mother in his dreams. When asked if he has any toys, he says he has nothing of his own, they share everything in the home. Then his face lights up, "I have a pen."

Memorandum

The work reported in this thesis was carried out at the Interdisciplinary Research Centre in Polymer Science and Technology at Durham University between October 1990 and September 1993. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Statement of Copyright

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Abstract

Wax crystal formation in diesel and related hydrocarbon fuels during cold weather is a long standing problem. Current polymeric additives to diesel fuel modify the crystal habit of the wax, in a variety of ways, to improve its performance at low temperature. These wax crystal modifiers (WCM) have to operate at low concentrations (0.01-0.1%) to make their use economical, so it is critical that their structures are optimised for the application. The objectives of this work was to synthesise, characterise and test some new polymeric additives which are anticipated to effect the crystallisation of the wax from the fuel and to prepare a model ethylene vinyl acetate (EVA) polymer to gain insights into the mode of action of the EVA co-polymers which are currently in use as WCM. Ring opening metathesis polymerisation was chosen as the method of preparation for these new polymeric additives.

An introduction to wax crystallisation in diesel fuel and some proposals for the preparation of these new polymeric additives are given in Chapter 1. Chapter 2 discusses olefin metathesis and ring opening metathesis polymerisation reactions. The synthesis and characterisation of monomers and polymers are given in Chapters 3 and 4 respectively. Results from fuel tests are described in Chapter 5.

Acknowledgements

The work reported in this thesis would not have been possible without the support from family, friends and colleagues.

Many thanks to Professor W.J. Feast for his advice, encouragement and assistance, often above and beyond the call of duty, over the last three years.

I am very grateful to Dr. Brian Wilson and Dr. Ezat Khosravi for their patient and helpful discussions on all aspects of my work. I would also like to thank Dr. A. Kenwright and Mrs. J.M. Say for recording the NMR spectra and for their help with interpretation and presentation.

I would like to express my appreciation to all the members of the technical staff in the IRC and Chemistry Department for their assistance and to Rachel Grimditch who repeated the monomer synthesis to yield a useful stock of materials. Thanks go to Dr.Tuncel Ibrahim and her colleagues at Exxon for their enthusiastic support of this project.

A mention must go to colleagues (past and present) at Durham especially Patrique, Norman and Frank my badminton, squash and running partners.

Many thanks go to my friends in particular Ann, Helen, Sara, and Liz for providing an escape from science (and scientists) but most importantly for just being good mates.

Special thanks and all my love go to Mam, Dad and David for their love and support. This thesis is for them.

And thanks to Panagiotis, however far away.

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CHAPTER THREE Synthesis and characterisation of monomers

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Abbreviations

c	*cis*
CFPP	Cold filter plugging point
CP	Cloud point
CTA	Chain transfer agent
[CTA]	Concentration of CTA
2D	2 Dimensional
DEPT	Decoupled proton
DSC	Differential scanning calorimetry
EVA	Ethylene vinyl acetate
FTIR	Fourier transform infrared
FVA	Fumaric acid vinyl acetate
ΔG	Gibbs free energy change
GC	Gas chromatography
GCMS	Gas chromatography & mass spectroscopy
GPC	Gel permeation chromatography
H	Head
ΔH	Change in enthalpy
HPLC	High performance liquid chromatography
m	meso
[M]	Concentration of monomer
Mn	Number average molecular weight
Mw	Weight average molecular weight
MS	Mass spectroscopy
NBE	Norbornene
NMR	Nuclear magnetic resonance
PDI	Polydispersity index
PEG	Polyethylene glycol
PP	Pour point
r	racemic
ROM	Ring opening metathesis
ROMP	Ring opening metathesis polymerisation
ΔS	Change in entropy
SEM	Scanning electron micrograph
t	*trans*
T	tail
Tg	Glass transition temperature
Tm	Melting temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
UV	Ultra violet
WCM	Wax crystal modifier

Note to reader

The nomenclature in the literature for a metal carbon double bond is varied the most common terms being metal carbene, metal alkylidene and metallocarbene. A poster given by Professor R.H. Grubbs at The Tenth International Symposium on Metathesis (1993) proposed the use of metallaolefin as a general term, with nomenclature such as metallaethene for specific cases. This terminology is analogous to that currently in use for cyclic compounds which contain a metal for example metallacyclobutane.

The use of metallaolefin to describe an olefin which contains a metal will be used in this thesis.

CHAPTER ONE

WAX CRYSTALLISATION IN DIESEL FUEL

1.1 INTRODUCTION

Waxes are useful by-products from the petroleum industry. However problems can arise in cold weather due to unwanted crystallisation causing difficulties regarding the production, transportation and storage of "waxy crudes," that is oil fractions containing a high proportion of wax molecules and in the storage and operability of derived products such as diesel fuels, heavy fuels and lubricating oils. Such problems may be solved to some extent by refining processes and also by the action of additives, known as wax crystal modifiers (WCM). The use of WCM to alter the low temperature behaviour of waxy crudes and derived products is a preventative method and is often the most economical way in which to treat these materials in order to make them more commercially acceptable.

WCM have been used for a number of years to improve the low temperature properties of diesel fuel. They act either as nucleators or via the modification of the size and/or shape of the crystals which appear in the fuel when it is cooled below its cloud point (CP). The synthesis and study of the mode of action of additives, which improve the cold behaviour of waxes and wax containing products, represents a very important direction of research for the petroleum industry. Many investigations relating to wax crystallisation and additive action mechanisms have been performed in the laboratories of petroleum companies and academic institutions. This chapter highlights problems caused by wax crystallisation in diesel fuel, the use of additives to improve the behaviour of the fuel at low temperatures and proposals for the synthesis of some new polymeric materials as potential additives for diesel fuel.

1.2 DIESEL FUEL

Diesel fuel has always suffered from problems in cold weather due to wax crystallisation which can produce storage settling and line or filter plugging in diesel vehicles.

Diesel fuels are a complex mixture of hydrocarbon molecules 15-30wt-% being normal alkanes which are the least soluble, most abundant component in diesel fuel. When the fuel is cooled below the cloud point (CP), i.e. the point at which the wax crystals first appear, the bulk of the precipitated wax consists of n-alkanes with more than eighteen carbon atoms. The exact n-alkane composition of a particular diesel fuel is determined by the base stocks used in its formulation. A typical n-alkane distribution in diesel fuel together with the n-alkane content of the precipitated wax is illustrated in Figure 1.2.1.[1]

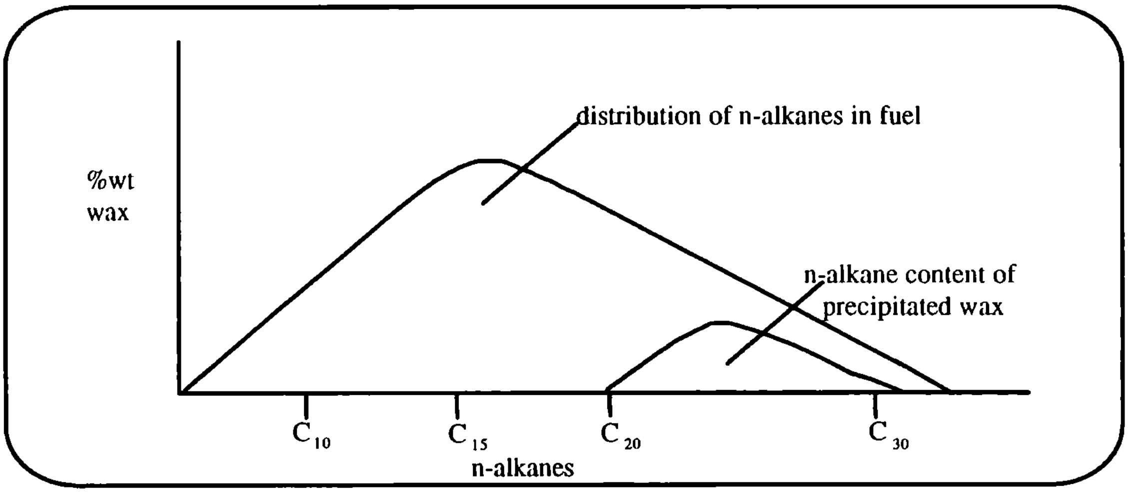


FIGURE 1.2.1 A typical distribution of n-alkanes in diesel fuel compared with n-alkanes in precipitated wax.

When untreated diesel fuel is cooled below its CP large flat rectangular plates with lateral dimensions typically in the range 100 to 1000 microns, and a thickness of 1 to 10 microns, appear and then grow to give an interlocking structure, which in the context of this work is referred to as a wax crystal gel.

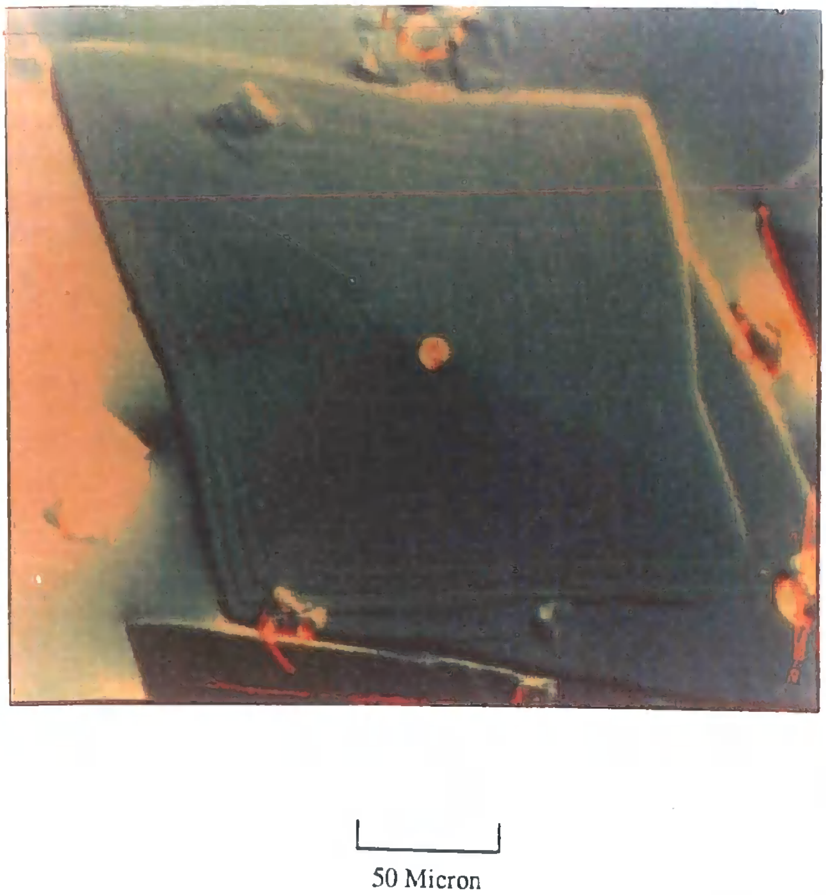


FIGURE 1.2.2 Plate-like wax crystals precipitated from untreated fuel

Figure 1.2.2 shows a photomicrogram of such crystals illustrating their plate-like morphology. Even prior to this wax crystal gel formation, at a wax solid concentration of less than 1%, these wax platelets will coat any filter or small opening hindering the passage of fuel. Ultimately these platelets will form a continuous sheet over a vehicle's main filter preventing the passage of fuel and leading to engine failure.

The formation of this wax crystal gel is dependent upon size, shape and number of crystals present as well as the total wax concentration. The action of WCM alters the size and shape of these crystals in such a manner so that a permeable layer is formed over the filter. The fuel will then still be able to pass through and excess fuel, which will be warmed by the action of the engine before being returned to the main fuel supply, will eventually melt the accumulated wax before vehicle performance is impaired to any great extent. Figure 1.2.3 shows a scanning electron micrograph (SEM) of an example of crystals with a needle like morphology which have the effect outlined above.

FIGURE 1.2.3 Needle-like crystals precipitated from fuel to yield a permeable cake.

At temperatures just below the cloud point this process is rapid and the WCM are fully effective. However as the temperature falls further below the CP the warming and dissolving processes are less effective and wax deposition occurs faster. More additive can be used and the operability will be sustained to approximately 10°C below the CP but as the operating temperature drops even further the wax will eventually block the filter cutting off the fuel supply to the engine. The foregoing comments refer to needle-like morphologies, other WCM can give a further significant reduction in crystal size and form producing a more compact blocky crystal with sizes confined to the micron range. Figure 1.2.4 shows a SEM of a fuel after treatment with such additives illustrating the cubic morphology of the resultant crystals. Crystals of this type have several advantages; a larger quantity of wax may be tolerated on the filter before it becomes plugged; because of their size and shape some of these crystals are able to pass straight through the filter; they also give antisettling properties to the fuel preventing the formation of wax layers at the bottom of storage tanks and vehicle fuel tanks; and the wax dissolves faster when the temperature rises.

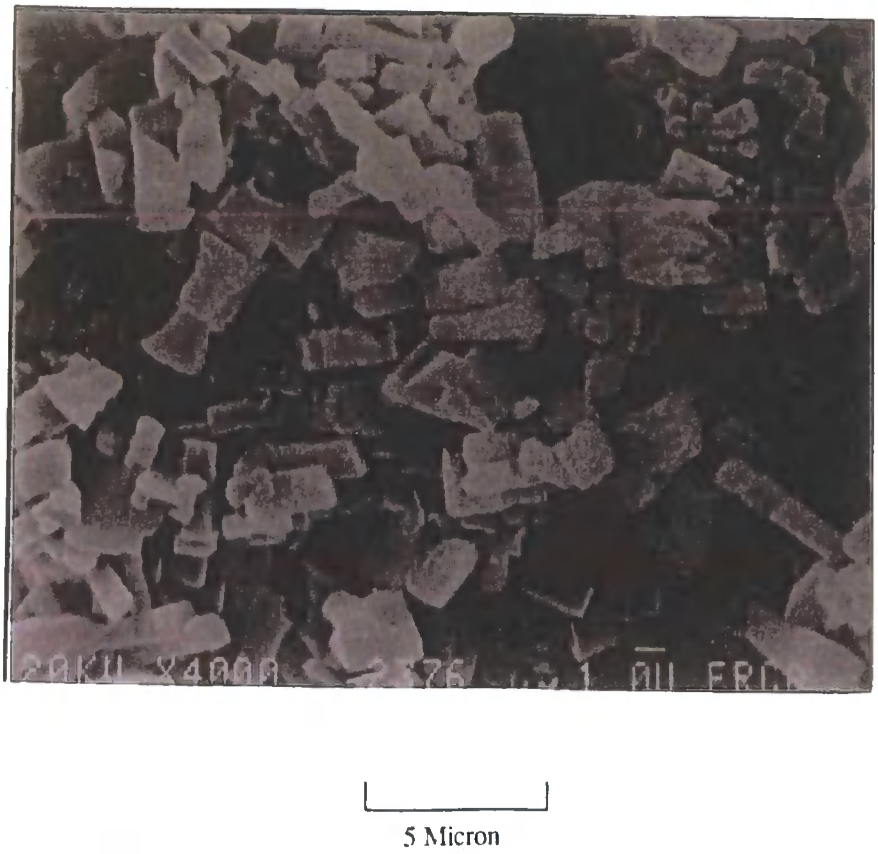


FIGURE 1.2.4 Cubic wax crystals confined to the micron range

1.3 WAX CRYSTALS

Normal alkanes and isoalkanes, on cooling, form the most highly organised type of organic matter, crystals; that is an orderly array of alkane molecules as shown schematically in Figure 1.3.1.[1]

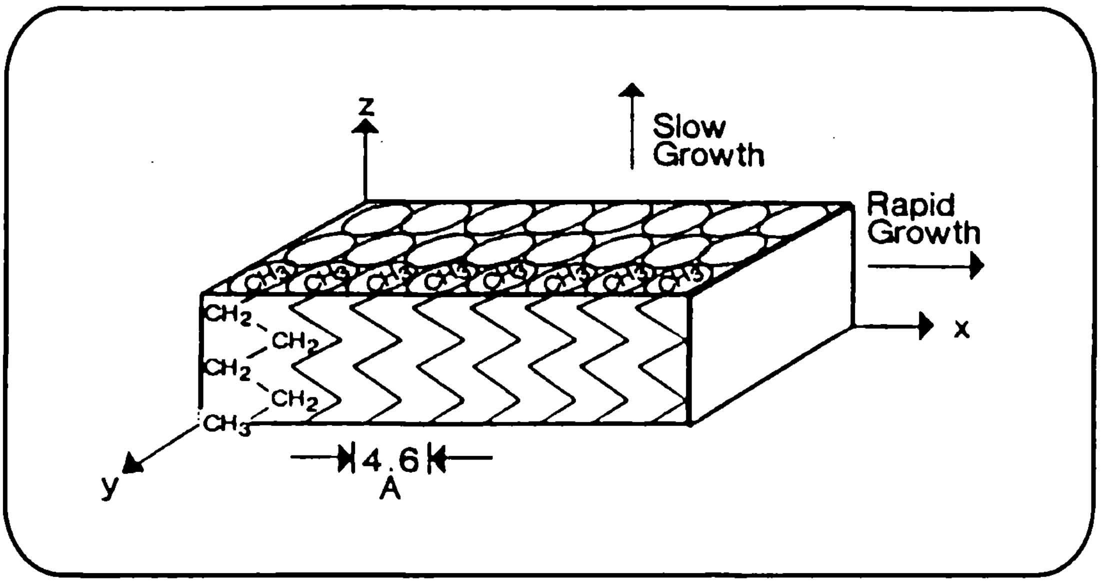


FIGURE 1.3.1 Idealised wax crystal

It is these newly formed crystals that impede the movement of other molecules, increase viscosity of the fuel and eventually grow to form an interlocking wax crystal gel.

The crystallisation of alkanes in petroleum products is governed by three phenomena, nucleation, crystal growth and agglomeration or gelling, these are discussed in more detail below.

1.3.1 Nucleation

A fuel may be described as a solution of alkanes in a mixed solvent, that is an isotropic medium with interactions between the alkanes and various solvent molecules. The heavier n-alkanes are solubilised by the lighter hydrocarbons. However as the temperature decreases the interactions between alkane molecules increase to a point where the intermolecular forces of attraction are greater than those of the solvent alkane interactions and thermal motions. At this stage the alkane molecules associate to form a crystal nucleus.

1.3.2 Crystal growth

Crystal growth occurs on the faces of the crystal where the free energy of cohesion between the crystal and the incoming molecule is most favourable. In practice these are the surfaces perpendicular to the x and y directions in Figure 1.3.1 and this process yields large flat plate-like structures as illustrated.

1.3.3 Agglomeration

On further cooling, below the cloud point, the crystal size increases strongly modifying the rheological properties of the solution. The crystals finally agglomerate into particles that precipitate and become entangled in rigid lattices at the pour point (PP), that is the temperature at which the fuel will no longer pour.

WCM can influence the course of wax crystallisation in one or other of the above mentioned steps.

1.4 EFFECTS OF WAX CRYSTAL MODIFIERS ON WAX CRYSTALS

In general there are two ways in which WCM influence the course of formation of wax crystals.

1.4.1 Nucleation

Nucleators promote nucleation by crystallising just prior to the wax, this increases the number of nuclei present in the fuel compared to the untreated fuel leading to more but smaller wax crystals.

1.4.2 Crystal growth modification

Crystal growth modifiers generally produce one of two effects:-

i) The creation of morphologies with poorly defined shapes instead of a lamellar morphology and

ii) the hindrance of crystal growth in order to restrict crystal size to the micron range.

The former is mainly used in oils, whereas the latter is used mainly for diesel fuel applications to prevent filter plugging.

The restriction of crystal size is achieved by the use of growth inhibitors which bind to the fastest growing face of the wax crystal forcing any further growth to occur along the slow growth plane.

As yet there is no universal additive and generally combinations of additives are used in order to achieve the desired performance at low temperatures.

1.5 GENERAL CONSIDERATIONS FOR WAX CRYSTAL MODIFIERS

In order to make their use economical WCM must operate at low concentrations (0.01-0.1%) consequently their structures must be optimised with respect to:-

(i) the ability to associate strongly with the wax,

(ii) an appropriate solubility in the fuel,

(iii) appropriate groups to block crystal growth or promote nucleation and

(iv) ease and cost of production.

Each of these is discussed in more detail overleaf.

1.5.1 Association with the wax

In order to associate with the wax crystal part of the additive must be n-alkane like. Thus the molecule may have n-alkyl substituents or a polyethylene like segment in the polymer backbone.

1.5.2 Solubility

If too soluble a growth inhibitor will not adsorb onto the wax, except at high concentrations, or a nucleator will not separate before the wax and therefore they will be either ineffective or unacceptably expensive. If too insoluble the additive is likely to separate before the wax associating with itself and not with the wax. The solubility therefore has to be carefully controlled by the ratio of polar to non-polar groups, of branched alkyl or aromatics to linear alkyl groups and by molecular weight. For maximum effectiveness WCM must begin to precipitate at the same temperature or just above the temperature at which the wax crystallises.

1.5.3 Blocking groups

These need to be large enough and suitably situated on the adsorbed molecule to inhibit further growth on the face of the wax crystal where the inhibitor is adsorbed. However the blocking groups must not inhibit adsorption of the additive onto the wax crystal.

1.5.4 Ease and cost of production

In the past production costs have limited polymers to those produced by free-radical methodologies using low cost monomers; for example, α-olefins and derivatives such as dialkyl fumarates, alkyl methacrylates or alkyl acrylates. For the future and the more difficult to treat fuels the use of more complex syntheses and/or more expensive raw materials has not been ruled out.

1.6 WAX CRYSTAL MODIFIERS

WCM all contain polyethylene-like segments and most can be classified within four main groups.

1.6.1 Random co-polymers

These are ethylene vinyl ester co-polymers, the most notable example being ethylene vinyl acetate (EVA). EVA is one of the most effective wax crystal growth inhibitors modifying the PP and the cold filter plugging point (CFPP), that is the temperature at which a 45μm filter becomes plugged under standard conditions,[3] but not the CP. These co-polymers adsorb onto the growing face of the crystal via the polyethylene backbone with the acetate and short alkyl groups extending into the fuel, as illustrated in Figure 1.6.1.

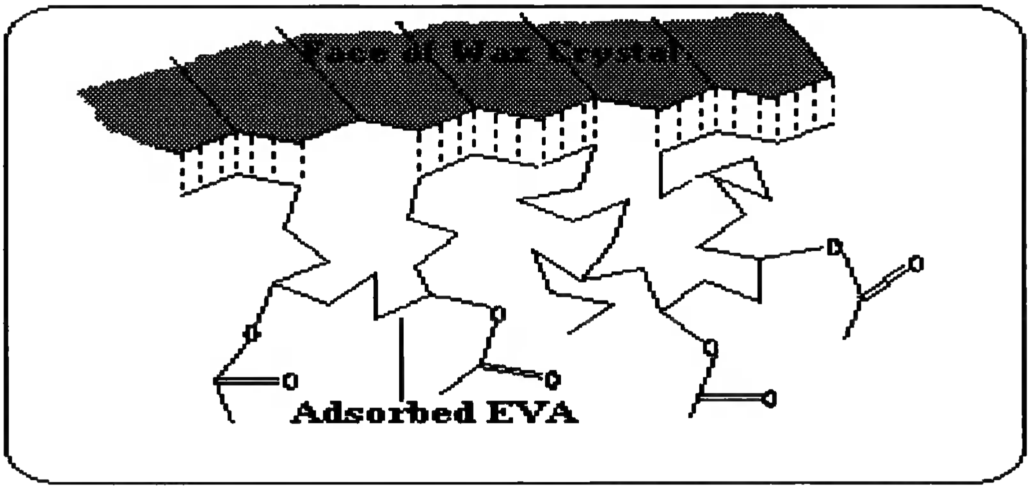


FIGURE 1.6.1 Adsorption of EVA onto a wax crystal

This adsorption and mode of action of the additive is not very selective but is efficient because of the polymer's multipoint contact, thus one or more segments may desorb but it is improbable that all the segments will desorb at the same time.

EVA is essentially a linear polymer although there are long side branches which affect its properties. Poly(vinylacetate) has predominately the repeat unit W with low concentrations of branch points through structures X and Y as illustrated in Figure 1.6.2. Hydrolysis followed by re-acetylation eliminates branch points of type Y giving a simpler structure which has been found to be more effective as a wax crystal modifier.

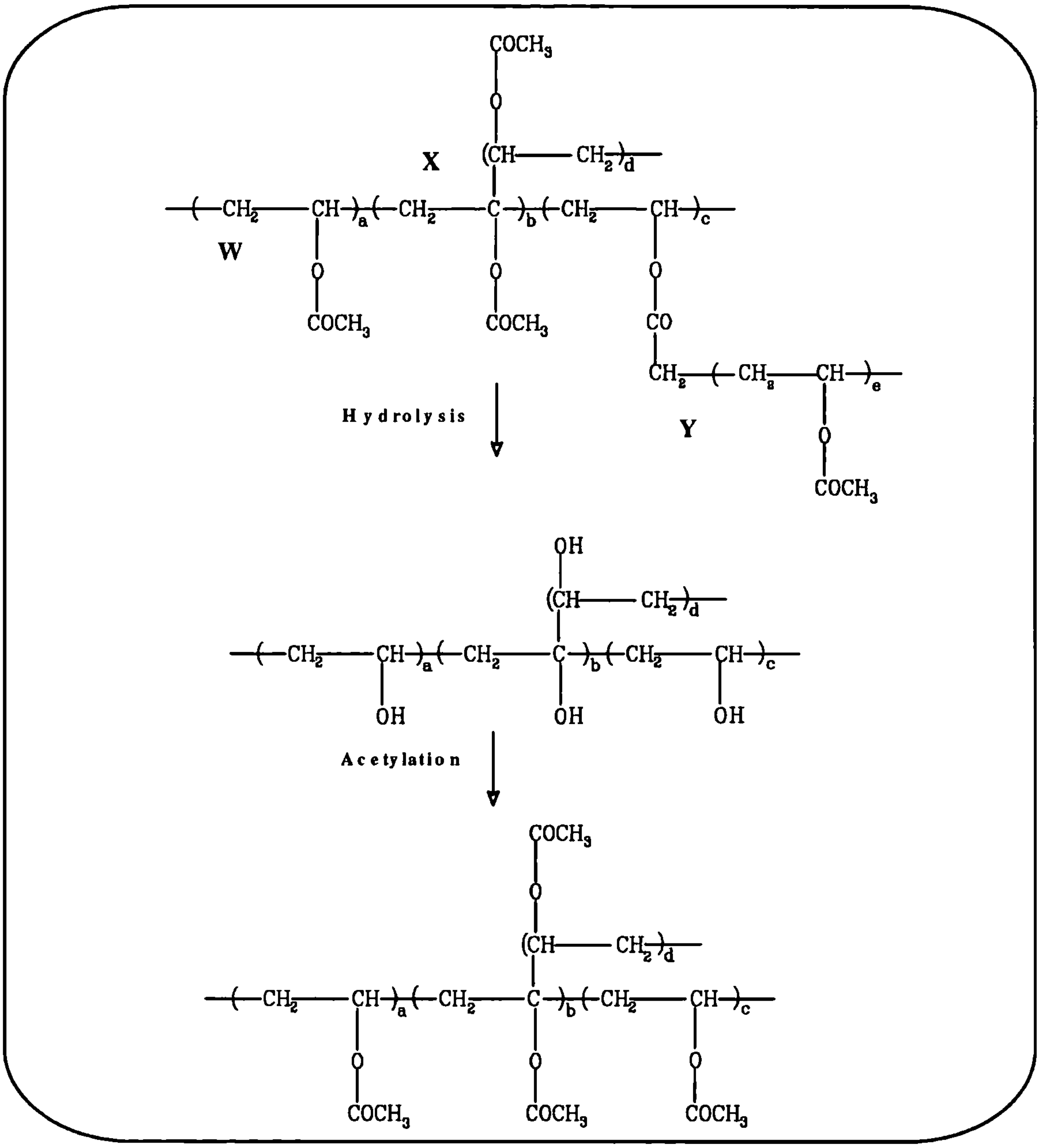


FIGURE 1.6.2 Hydrolysis and re-acetylation of EVA.

1.6.2 Comb type polymers

There are several variations of this type of WCM. They are characterised by the long n-alkyl side groups that protrude from the backbone, which can co-crystallise with the n-alkanes. Examples of this type of polymer include esters of fumaric acid co-polymerised with vinyl acetate (FVA) illustrated in Figure 1.6.3.

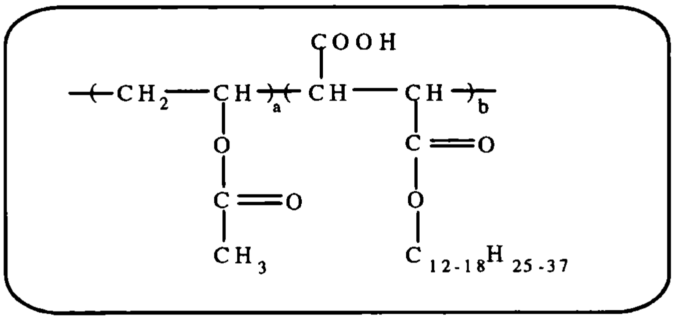


FIGURE 1.6.3 Esters of fumaric acid vinyl acetate

Different chain lengths can be used for the comb branches and those with between twelve and eighteen carbon atoms are generally favoured. These additives affect the cloud point and also provide antisettling effects for the crystallised n-alkanes.

1.6.3 Nucleators

These additives are low molecular weight polymers. Typical examples are polyethylene glycol (PEG) esters which have been esterified with docosanoic acid. These additives do not modify the crystal habit of the wax but increase the number of wax crystals present in the fuel compared to untreated fuel.

1.6.4 Non polymeric

A typical example of these additives is illustrated in Figure 1.6.4. The n-alkane segments can co-crystallise with the wax crystal and the non n-alkane part of the molecule inhibits any further incorporation of n-alkane onto the crystal, via steric effects, therefore slowing growth.

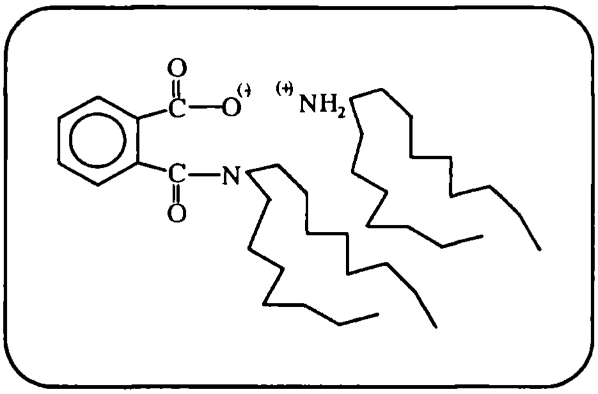


FIGURE 1.6.4 A non-polymeric wax crystal modifier

The chemistry of the wax crystal modifier is tailored to suit a specific purpose initially leading to the simple control of fuel gelation and ultimately to the total control of vehicle operability at low temperatures.

Unfortunately, some incompatibilities occasionally exist with regard to EVA type additives (which are used to improve CFPP and PP) and FVA type additives (which improve the CP). Ideally the aim is to find multifunctional additives that improve the CFPP, PP, CP and also give antisettling properties.

The subject of wax crystal modification in diesel and related hydrocarbon fuels has been the subject of many technical papers.[1-6]

1.7 PROPOSALS FOR SOME NEW POLYMERIC ADDITIVES

The proposals outlined overleaf for the synthesis of some new polymers as potential wax crystal modifiers may be divided into two main sections.

1.7.1 Hydrocarbon comb polymers and co-polymers

As stated previously, EVA and FVA type co-polymers are occasionally antagonistic when used in combination and consequently they do not produce the anticipated effects; that is only a limited beneficial effect on wax crystal modification is obtained. This interaction between the two polymers may be demonstrated by the depression in melting temperature that is obtained for FVA when blends of EVA and FVA are examined using DSC. Figure 1.7.1 (overleaf) illustrates an example of this depression in melting temperature, which increases as the % of EVA in the blend increases. This melting point depression is tentatively assigned to an unfavourable interaction between the EVA and the FVA co-polymers. It is has been suggested that this unfavourable interaction might be avoided if the co-polymers were covalently linked together. Under these circumstances such interactions may be prevented and beneficial effects on both the CP and CFPP might result.

Since the interaction with the wax is via the hydrocarbon elements of the co-polymers and the fuel is predominately hydrocarbon it could be argued that it would be logical to eliminate polar structures from the WCM and use polymers and co-polymers containing all hydrocarbon units. In this work it was proposed to prepare polymers and co-polymers of the type illustrated in Figure 1.7.2.

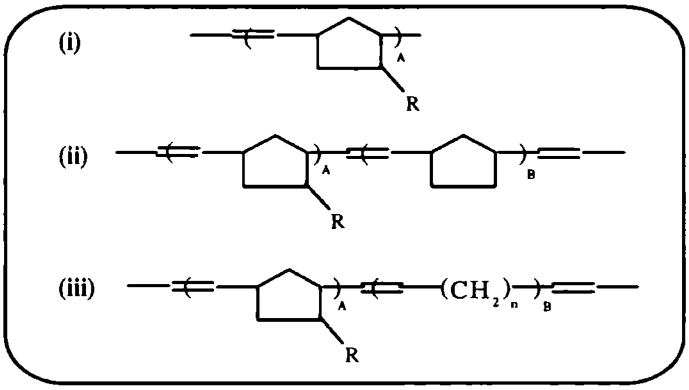


FIGURE 1.7.2 Proposed hydrocarbon polymers and block co-polymers

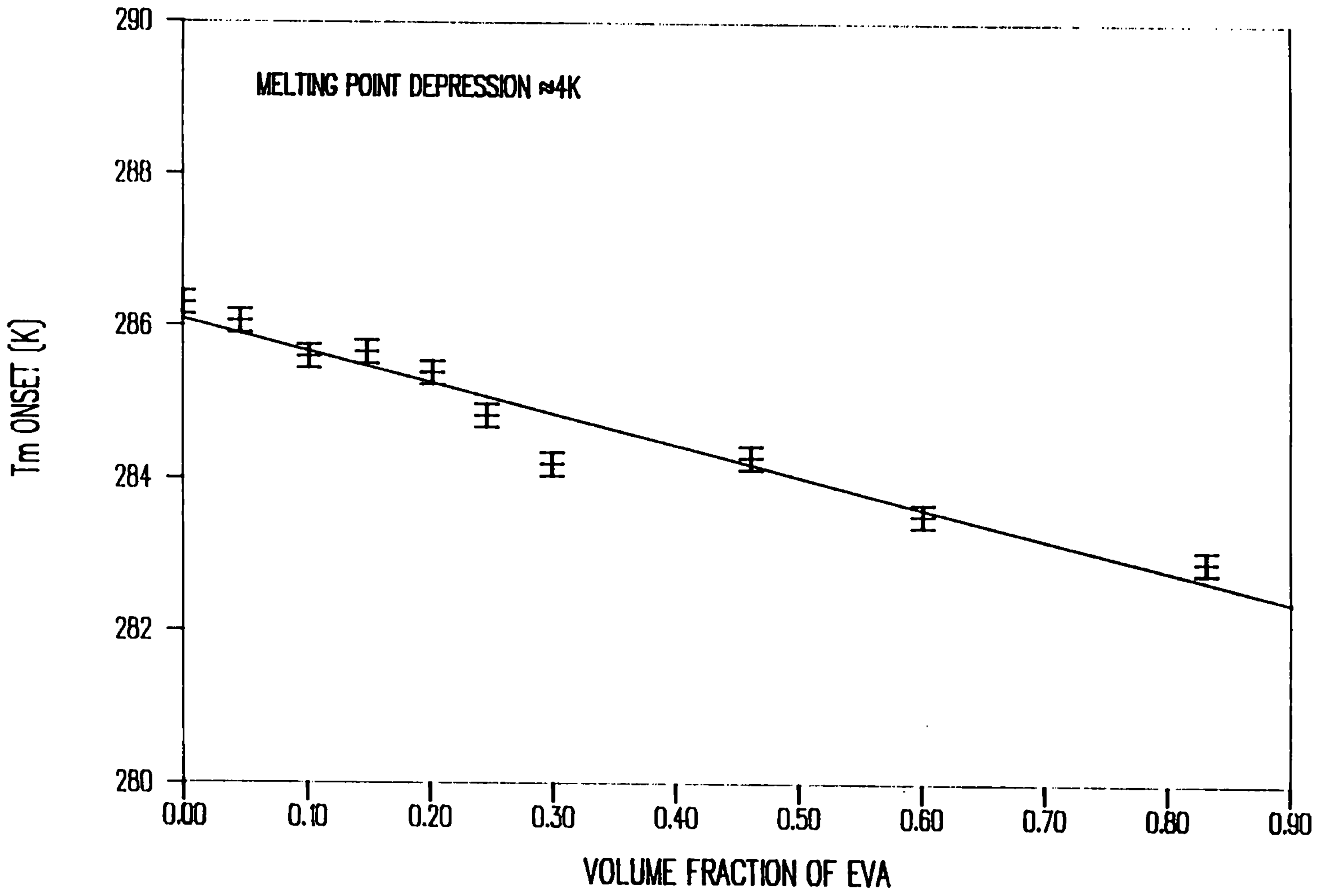


FIGURE 1.7.1 DSC Trace of EVA and FVA Blends

Polymer (i) could be prepared by the ring opening metathesis polymerisation of 5-substituted alkylnorbornenes and co-polymers (ii) and (iii) could be prepared from the ROM co-polymerisation of 5-substituted alkylnorbornenes with norbornene and monocyclic olefins respectively. The use of classical catalysts for these co-polymerisation reactions would yield random co-polymers. In order to prepare well-defined AB block co-polymers well-defined initiators, which allow living polymerisation, would be the initiating systems of choice.

The mechanism of ring opening metathesis polymerisation (ROMP) is discussed in Chapter 2, the details of the monomer syntheses are described in Chapter 3 and experimental details of the polymerisation reactions are given in Chapter 4.

1.7.2 EVA model

EVA is a random co-polymer and there is very little precise information on its detailed molecular structure, particularly regarding the distribution of co-monomer units. As already mentioned in section 1.6.1 a linear EVA structure is found to be more effective as a wax crystal modifier. It is thought that if a polymer could be prepared with a known vinyl acetate content and distribution, its behaviour with regard to wax crystal modification would provide insights into the mechanisms of the EVAs currently used in diesel fuels. It was proposed, again using ROMP, to polymerise monomers which possess an acetate group such as 1-acetoxy-4,8-cyclododecadiene; illustrated in Figure 1.7.3.

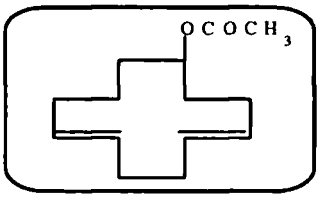
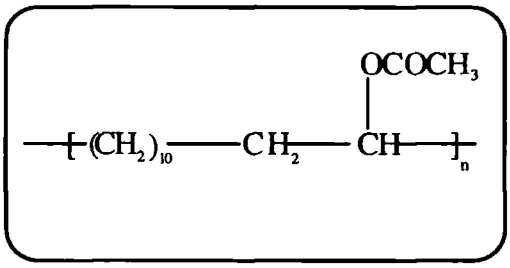


FIGURE 1.7.3 1-Acetoxy-4,8-cyclododecadiene

Ring opening polymerisation of this monomer followed by hydrogenation would yield an EVA type polymer with the structure as illustrated in Figure 1.7.4.



$$-\!\!\!\left[(CH_2)_{10} - CH_2 - \overset{OCOCH_3}{\overset{|}{CH}} - \right]_n$$

FIGURE 1.7.4 Hydrogenated poly(acetoxy cyclododecadiene)

The vinyl acetate content of this polymer could possibly be reduced by forming co-polymers with cycloalkenes. In the homo-polymer a fairly regular microstructure would be anticipated and for the co-polymer either block or random co-polymers could be prepared. The details of monomer synthesis is described in Chapter 3 and the experimental details of the polymerisation reactions are discussed in Chapter 4.

CHAPTER TWO

OLEFIN METATHESIS

2.1 DEFINITION AND HISTORICAL BACKGROUND

Olefin metathesis, also known as olefin disproportionation, is a catalytically induced bond re-organisation reaction involving the breaking and making of double bonds in which the total number and type of bonds remain unchanged. During the course of the reaction it is the alkylidene units which are interchanged as illustrated in Figure 2.1.1.

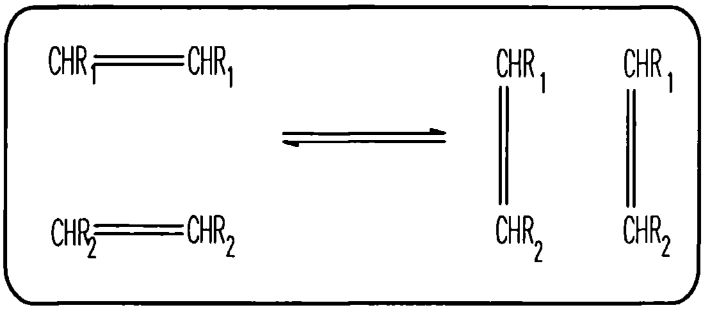


FIGURE 2.1.1 The olefin disproportionation reaction.

If the carbon carbon double bond is contained within a ring, that is a cyclic olefin, metathesis may yield a linear unsaturated polymer. Calderon[7] in 1967 recognized that the disproportionation of acyclic olefins and the metathesis of cyclic olefins were examples of the same chemical reaction. The ring opening metathesis of cyclic olefins is a special case of the more general olefin metathesis reaction and is termed ring opening metathesis polymerisation (ROMP). The first example, probably the first citation of the olefin metathesis reaction in general, was the ROMP of norbornene reported by Anderson and Merckling in 1955.[8]

There are several books and reviews on the subject of olefin metathesis which provide comprehensive coverage of its development and surveys of the early catalyst systems employed.[9-16]

In more recent years a new development in the ROMP reaction has been the synthesis of well-characterised initiators which allow living polymerisation with the consequent production of monodisperse polymers which are sometimes also highly stereoregular. These initiators are discussed in more detail in Section 2.2.2.

2.2 INITIATOR SYSTEMS

Initiators for metathesis may be heterogeneous or homogeneous systems, compounds of the transition metals; Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Re, Ru, Os, and Rh have been used. The most active initiators being based on Mo, W and Re.

Supported initiators are generally transition metal oxides, sulphides or carbonyls which are adsorbed on to a high surface area support such as alumina or silica. These systems can initiate metathesis of acyclic olefins but are rarely used for ROMP. Homogeneous catalysts are the preferred choice for ROMP and may be divided into two main groups, those known as classical catalysts and those based on well-characterised metallaolefins or metallacyclobutanes.

2.2.1 Classical catalyst systems

A large amount of work, most of which is empirical, has been carried out on these catalyst systems. This work has been extensively reviewed.[9-16] The three main groups of classical catalyst systems are discussed briefly below.

(i) Single component systems

In these systems the metallaolefin is already present within the molecule. The first catalysts of this type to be isolated were the Fischer[17] and Casey[18] types illustrated in Figure 2.2.1.

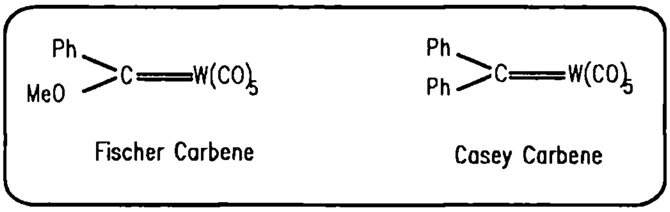


FIGURE 2.2.1 Metallaolefins

(ii) Multi-component systems

These were the first systems to be established and typically involve two or more components. They are transition metal compounds along with a co-catalyst. Co-catalysts normally consist of an organometallic compound of an element from groups I-IV with alkyl, aryl or allyl substituents and/or a Lewis acid. For example WCl_6 with $SnMe_4$, $SnPh_4$ or $EtAlCl_2$. It is proposed that the metallaolefin in these systems is generated by the reaction between the components, a mechanism illustrating the role of the alkyl groups in the generation of the metallaolefin is shown in Figure 2.3.2 for the $WCl_6/SnMe_4$ catalyst system.

(iii) Transition metal halides

Transition metal halides, for example WCl_6, $ReCl_5$ and $OsCl_3$, initiate metathesis without the addition of a co-catalyst. In such systems it is believed that the metallaolefin is generated by the reaction of the monomer with the transition metal, activators such as oxygen, water or ethanol are sometimes required in order for this reaction to occur.

The classical catalysts discussed above have several practical disadvantages which are listed below.

a) They are ill-defined and consequently there is uncertainty about how many active sites are present.

b) There is a lack of molecular weight control and polymers with broad molecular weight distributions are generally produced. This is due, in part, to back biting reactions. Back-biting reactions occur because the highly active metallaolefin can react intramolecularly, as illustrated in Figure 2.2.2, or intermolecularly with the carbon carbon double bonds in the polymer chain to yield cyclic or linear oligomers respectively.

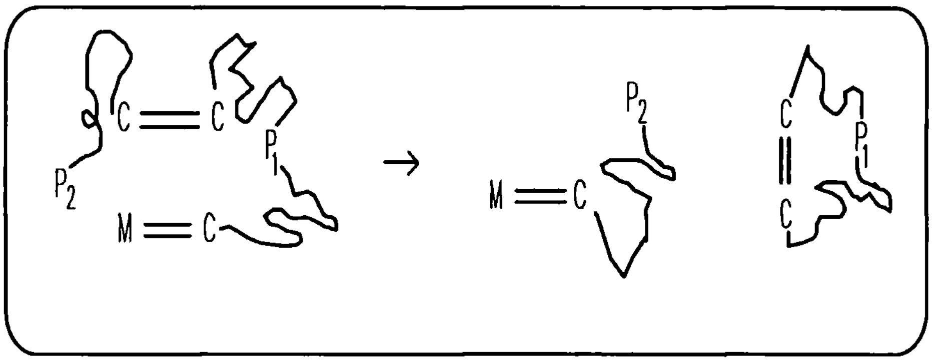


FIGURE 2.2.2 Formation of cyclic oligomers via backbiting

c) There is an element of irreproducibility regarding reactions with such systems as the production of the initiating metallaolefin tends to be dependant upon physical parameters such as temperature,[19] concentration and mixing rates.[20]

d) There is a limited tolerance of functional groups.

e) In these systems the metallaolefin complexes are generated in low yields and decompose during the course of the reaction.

f) Stereoregular polymers are rarely produced.

In order to prepare truly well-defined polymers and block co-polymers via living polymerisation well-defined initiators are required.

2.2.2 Well-defined initiator systems

Well-defined transition metal complexes in which each metallaolefin initiates the growth of a polymer chain give rise to living polymerisations. Such reactions are characterised by the absence of termination or chain transfer processes. The following experimental criteria for living polymerisation systems have been proposed.[15, 24]

a) Polymerisation proceeds until all the monomer is consumed and addition of more monomer results in further polymerisation.

b) The number average molecular weight of the resultant polymer is a linear function of conversion.

c) The number of polymer molecules and active centres in the living system is a constant.

d) Molecular weight of the polymer can be controlled by the stoichiometry of the reaction.

e) Sequential addition of different monomers yields, in favourable cases, block co-polymers.

f) Chain-end functionalised polymers can be prepared.

Such living systems have been demonstrated using titanacyclobutanes derived from strained cyclic olefins for the metatheticial polymerisation of norbornene.[25] A related tantalum complex[26] has also been used for the living polymerisation of norbornene. Well-defined ROM initiators derived from tungsten[27] and molybdenum[28,29] are more active than the titanium initiators already mentioned and have shown a greater tolerance for polar functional groups.

Schrock[30-32] and Grubbs[25,33] have reported the preparation of well-characterised high oxidation state metallaolefin complexes and their use to generate homo polymers and block co-polymers. For molybdenum and tungsten a suitable combination of ligands around the metallaolefin is two alkoxides and one imido.[34] A schematic outline of the Schrock type initiator is shown in Figure 2.2.3 illustrating the variation of alkoxide ligands which is possible.

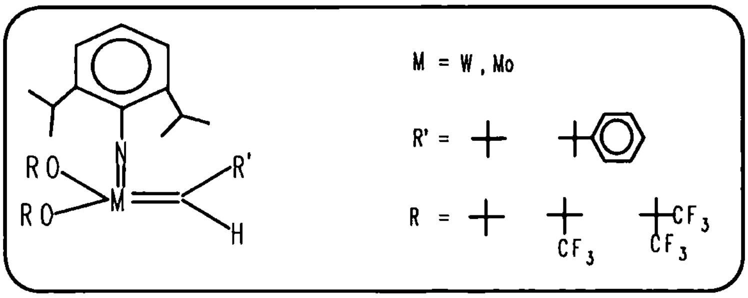


FIGURE 2.2.3 Schematic diagram of Schrock's initiator

The reactivity of the metallaolefin is increased when the methyl groups on the t-butoxide ligand are replaced with the more electronegative trifluoromethyl groups.[35,36] This increased reactivity is believed to be due to the trifluoromethyl groups drawing electron density away from the metal center making it more electrophilic and a better acceptor for the incoming π-donor olefin. This increased reactivity can be demonstrated for the tungsten initiator; when OR = $OCMe(CF_3)_2$ the initiator will readily metathesise acyclic olefins but when OR = O-t-Bu it will not react readily with acyclic olefins. Thus there is a degree of control in the reactivity of these well-defined initiators, in contrast to classical catalyst systems whose reactivity cannot be systematically controlled. This control of reactivity at the metal centre can be utilised for the ROMP of olefins which possess donor functional groups. These functionalities may interact with the metal centre in preference to the carbon-carbon double bond; with well-defined systems the possibility exists to alter the reactivity around the metal centre so it will react only with the double bond and not with the donor functionality. Norbornenes with ester, cyano and acetate functionalities have been polymerised in a living manner using well-defined molybdenum initiators.[37] Such reactions will be discussed in Chapter 4 section 4.3.1 with regard to the ROMP of 1-acetoxy-4,8-cyclododecadiene.

2.3 THE MECHANISM OF OLEFIN METATHESIS

Numerous schemes have been postulated in attempts to provide a mechanistic rationalisation for the metathesis reaction. The proposal by Hérrison and Chauvin[38] that the reaction was a chain process with the chain carrying species being a metallaolefin is now generally accepted. Polymerisation of a cyclic olefin under this scheme is a non-pairwise, non-concerted process where the metallaolefin reacts with the cyclic olefin to yield a metallacyclobutane which cleaves to generate the original reactants (non-productive or degenerate metathesis) or a new metallaolefin (ROMP).

2.3.1 The kinetic chain reaction

The non-pairwise mechanism of polymerisation is summarised in Figure 2.3.1 for ring opening metathesis polymerisation. The propagation reaction involves a metallaolefin which, in the earliest versions of this rationalisation, is assumed to possess a vacant co-ordination site. The carbon-carbon double bond of the cyclic olefin first co-ordinates to the metal centre to give a metal π complex followed by the formation of a metallacyclobutane intermediate via [2+2] cycloaddition. The metallacyclobutane then cleaves either degeneratively to yield the original reactants or productively resulting in the formation of a new metallaolefin and a new π complexed carbon-carbon double bond which can then leave the co-ordination shell of the metal to regenerate the active species. Several of these steps can be reversible and the outcome for both acyclic and cyclic olefins depends on reaction conditions, temperature and concentration, the structure of the olefin and the nature of the chain carrier.

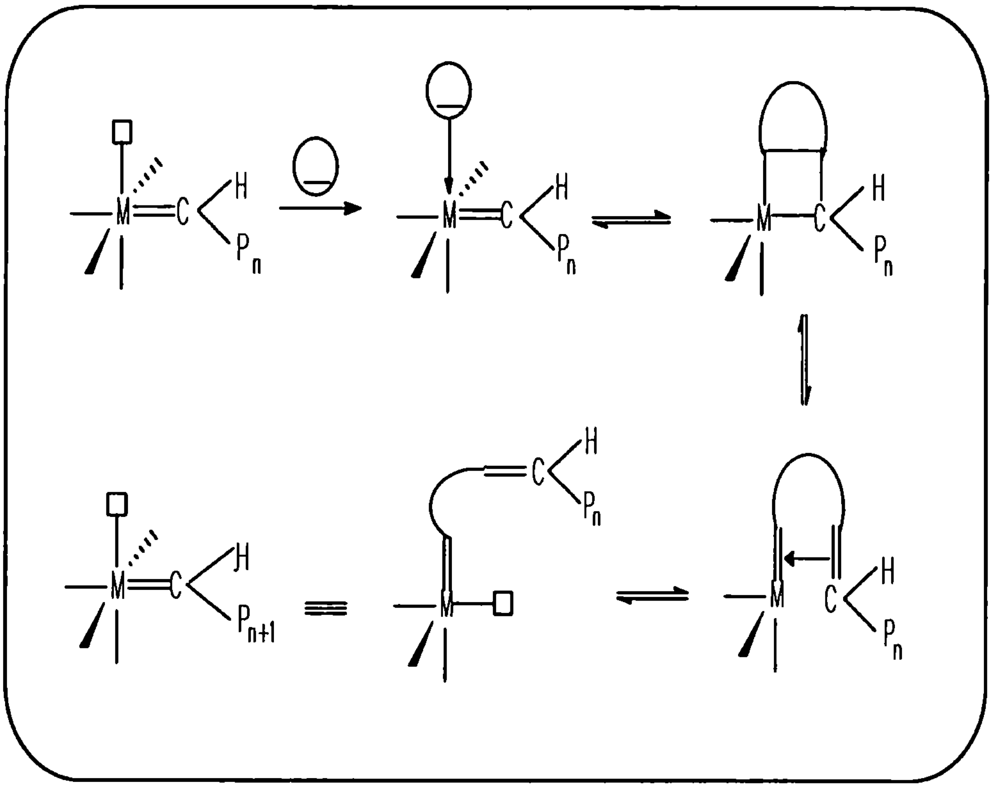


FIGURE 2.3.1 Propagation mechanism for ROMP

As for other chain processes the olefin metathesis reaction has three distinct steps, namely initiation, propagation and termination; scheme 2.3.1 outlines the propagation process.

2.3.2 Initiation

Stable metallaolefins such as those prepared by Casey[18,39] and Fischer[17,40-42] initiate metathesis and therefore provide good circumstantial evidence that metallaolefins are involved in the initiation step. Other stable metallaolefins,[43-46] although inactive or with low activity in metathesis reactions, give highly active initiator systems in the presence of Lewis Acids. For example the tungsten (VI) system, $W[\overline{C(CH_2)_3CH_2}](OCH_2\text{-t-Bu})_2Br_2$, synthesised by Kress and Osborn[46] has high activity as a metathesis catalyst in the presence of gallium tribromide.

Multi component systems which consist of transition metal halides and a co-catalyst are believed to form the metallaolefins required for initiation by the reaction between the two components. Muetterties[47] and Grubbs[48] demonstrated the production of methane from the catalyst systems WCl_6/Me_2Zn and WCl_6/Me_4Sn respectively. A proposed mechanism being the interaction of the alkyl groups with the metal centre, followed by elimination reactions, to yield methane and metallaolefins. A detailed scheme for metallaolefin generation has been proposed by Thorn-Csyani *et al*[49], using UV spectroscopy to study the $WCl_6/SnMe_4$ system, and is illustrated in Figure 2.3.2.

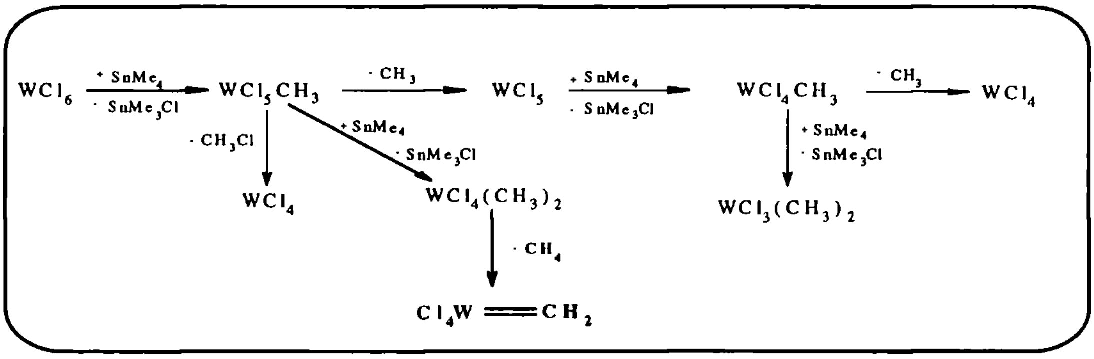


FIGURE 2.3.2 Proposed mechanism for metallaolefin generation

The above scheme illustrates, the complex nature of the reaction which is required to generate the metallaolefin, possible side reactions which are likely to be taking place and that alkyl groups play an important role in the generation of metallaolefins. Initiation in those systems which do not contain any alkyl groups i.e. the transition metal halides must proceed via a different mechanism. Amass[50] has reported that oxygen can activate some catalyst systems and proposed the formation of a W=O site which could then react with the olefin to initiate metathesis. Another possibility is the formation of the metallaolefin by the interaction of the olefin itself with the transition metal centre.

2.3.3 Propagation

The mechanism for propagation is illustrated in Figure 2.3.1. Support for the formation of a stable metallaolefin was provided by Green's[51] observation that the thermolysis or photolysis of a stable metallacyclobutane gave a metallaolefin and an olefin. Other evidence to support this mechanism was provided by Osborn[52] who observed the simultaneous occurrence and interconversion of a tungsten metallaolefin and a tungsten metallacyclobutane during ROMP of norbornene. More recently Schrock *et al*[30,34] have isolated metallacyclobutanes from a molybdenum metallaolefin and substituted norbornenes.

2.3.4 Termination

Termination reactions in ROMP, that is those reactions in which the propagating metallaolefin is destroyed, may be divided into three main groups.

(i) Wittig-type reactions

These termination reactions involve oxygen containing species, the most common being benzaldehyde and acetone.[53] These are often used for controlled termination in both classical and living metathesis reactions. An example of such a termination reaction is shown below in Figure 2.3.3 using acetone.

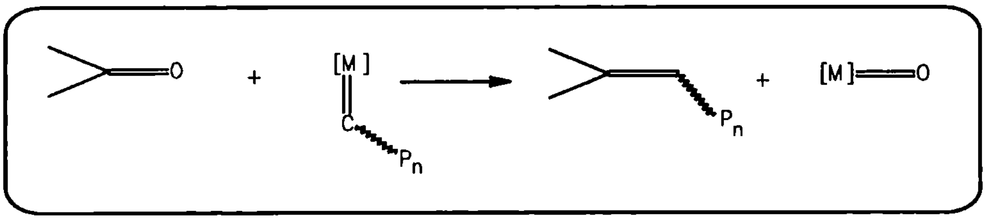


FIGURE 2.3.3 Termination reaction using acetone

(ii) β-Hydrogen abstraction

This termination reaction results in the destruction of the metallaolefin by β-hydrogen abstraction by the metal and is illustrated in Figure 2.3.4.

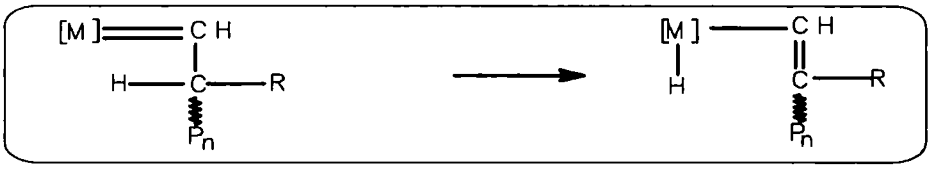


FIGURE 2.3.4 β-Hydrogen abstraction

(iii) Formation of cyclopropanes

Another termination reaction in ROMP is the formation of cyclopropanes as shown in Figure 2.3.5 below.

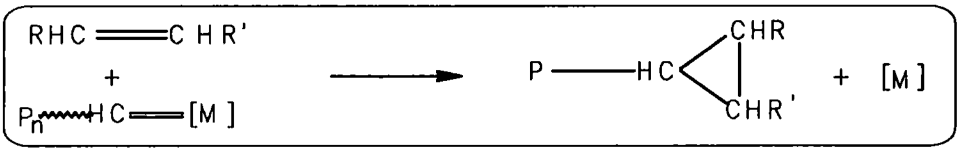


FIGURE 2.3.5 Cyclopropane formation

2.4. CHAIN TRANSFER

Chain transfer reactions may be divided into two main groups. These reactions do not destroy the active catalyst sites but result in a reduction in the molecular weight of the polymer and a broadening of the molecular weight distribution.

2.4.1 Chain transfer between polymer and propagating species

This is a non-productive intra or intermolecular metathesis reaction between a propagating metallaolefin and a carbon carbon double bond in a polymer chain. Figure 2.2.2 shows an intramolecular example of such a chain transfer reaction which yields cyclic oligomers, an intermolecular reaction would yield linear olefins.

2.4.2 Chain transfer between polymer and acyclic olefin

This reaction, known as cross metathesis, takes place between a polymer chain and an acyclic olefin and yields linear olefins, as illustrated in Figure 2.4.1.

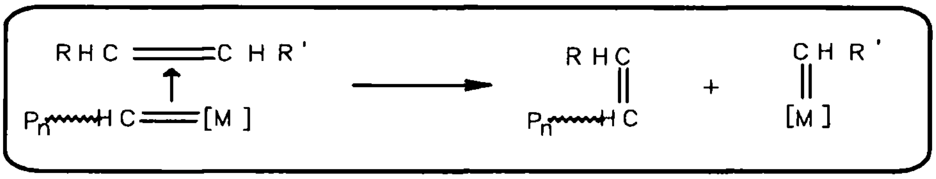


FIGURE 2.4.1 Chain transfer between polymer and acyclic olefin

This reaction can be used to control the molecular weight of the polymer, in such cases the acyclic olefin is known as a chain transfer agent (CTA).

2.4.3 Consequences of chain transfer

The main effect of chain transfer is a decrease in the molecular weight of the polymer but other effects may be detected if the rate of chain transfer is much greater than the rate of propagation and/or the ratio [CTA]/[M] is large enough. In such cases very small chains are produced, with 2-5 monomer units per chain; these are known as telomers.[9,54] Control of molecular weight is of importance in commercial environments and many studies have been carried out looking at the effects that acyclic olefins have on the ring opening polymerisation of cyclic olefins especially those systems involving cyclopentene and norbornene. In general an increase in the ratio [CTA]/[M] results in a reduction in the molecular weight of the polymer. However the effectiveness of acyclic olefins in reducing the molecular weight depends on their structure, the catalyst system and in particular the *cis* content of the polymer.[9] For polymerisation reaction systems which yield a high degree of *trans* double bonds in the polymer backbone α-olefins have been shown to be more effective in reducing the molecular weight of the polymer compared to internal olefins.[55] For high *cis* polymers it has been noted that a higher concentration of terminal olefins is necessary to reduce the molecular weight to a particular level compared to the same polymer with a lower *cis* content.[56] Ofstead *et al*[57] have interpreted this observation by suggesting that chain transfer is more difficult for *cis* selective systems, than for *trans* selective systems because the stereochemistry around the catalyst site is more restricted when the previously formed double bond is *cis*.

The slope of a plot of 1/Mn against [CTA]/[M] gives the chain transfer constant for a particular acyclic olefin. The chain transfer constant is defined as the ratio of the chain transfer rate constant to the propagation rate constant. These constants give an indication of the effectiveness of a particular CTA in a particular polymerisation system. However experimental uncertainties remain; for example the formation of cyclic oligomers during the polymerisation reaction and the effect that they have on the molecular weight distribution of the polymer.

2.5 ROMP - GENERAL CONSIDERATIONS FOR CYCLIC OLEFINS

For a reaction to occur the overall Gibbs free energy change (ΔG) must be negative in accordance with the equation below, where ΔH is the change in enthalpy, ΔS the change in entropy and T the temperature.

$$\Delta G = \Delta H - T\Delta S$$

Polymerisation reactions involving ring systems which contain 3,4,8 or more carbon atoms are thermodynamically favourable, that is the ΔG is negative, and polymerisation will proceed if a suitable mechanism is available. For 5,6 and 7 membered rings ΔG may be more sensitive to physical factors such as concentration, temperature and pressure along with chemical factors such as the nature and position of substituents on the ring.[9] The change in entropy on polymerisation will always be negative, because the freedom of the monomers will be reduced when they are fastened within a polymer chain. Therefore the -TΔS term will be positive and for a negative ΔG to be achieved, the change in enthalpy must be larger than TΔS. It follows that as the temperature is increased the TΔS term will also increase to a point where ΔG becomes positive and polymerisation will not occur, at a given monomer concentration. This point is known as the *ceiling temperature.*[58]

Substituents on the ring may also effect the polymerisability of the ring system. In general they are found to have an unfavourable effect on ΔG, i.e the overall Gibbs free energy change will become more positive. For ring opening to proceed substituents usually need to be well removed from the carbon carbon double bond.[59] In highly strained compounds however, such as methylcyclobutene and some bicyclic ring systems the relief of ring strain which is obtained on ring opening can, in some cases, overcome the unfavourable effects of the substituents.[60-66] A bulky substituent although removed from the carbon carbon double bond may in some instances hinder ring opening. There may be a possibility of orbital interaction between the substituent and the double bond which may have the effect of reducing the electron density at the double bond thus co-ordination to the metal centre will be less favourable.[67-67]

2.6 MICROSTRUCTURE OF RING OPENED POLYMERS.

A monomer unit may be incorporated in several different ways into a polymer chain, altering the microstructure and consequently the physical properties of the resultant polymer. In certain cases, altering the catalyst systems and/or the reaction conditions, it is possible to synthesise polymers which possess a specific microstructure.

The different microstructural possibilities are discussed below, one or all may apply to the ROMP of a monomer depending on its structure.

2.6.1 *Cis/Trans* effects

Monomers such as cyclopentene yield on ring opening, polymers in which only *cis/trans* isomerism is possible along the polymer backbone, denoted *c* or *t*. Thus each methylene group in the polymer chain will be situated between a *cc, ct, tc* or a *tt* pair of double bonds where the first letter always denotes the configuration of the nearest double bond. The proportion of *cis* double bonds is denoted by σ_c where a polymer with all *cis* double bonds has a $\sigma_c = 1.0$ and an all *trans* polymer has a $\sigma_c = 0$. Ivin[62] has proposed a model for the formation of *cis/trans* double bonds on the hypothesis of a chain propagating species which is an octahedrally substituted metallaolefin with one vacant site.

2.6.2. Meso/Racemic dyads

Monomers such as norbornene, which are achiral compounds, on ring-opening yield polymers which contain chiral centres at the tertiary carbon atoms. These polymers have, as well as *cis/trans* isomerism, meso (m) and racemic (r) dyad structures. Therefore it is possible to have chiral centres on either side of the double bond with the same or opposite chiralities. Sequences of racemic dyads, that is the same chirality on either side of the double bond, result in syndiotactic polymers and sequences of meso dyads, that is different chiralities on either side of the double bond, result in isotactic polymers. Atactic polymers are generated from a statistical distribution of dyads. Figure 2.6.1 illustrates syndiotactic and isotactic polymers for the *cis/trans* forms of poly(norbornene).

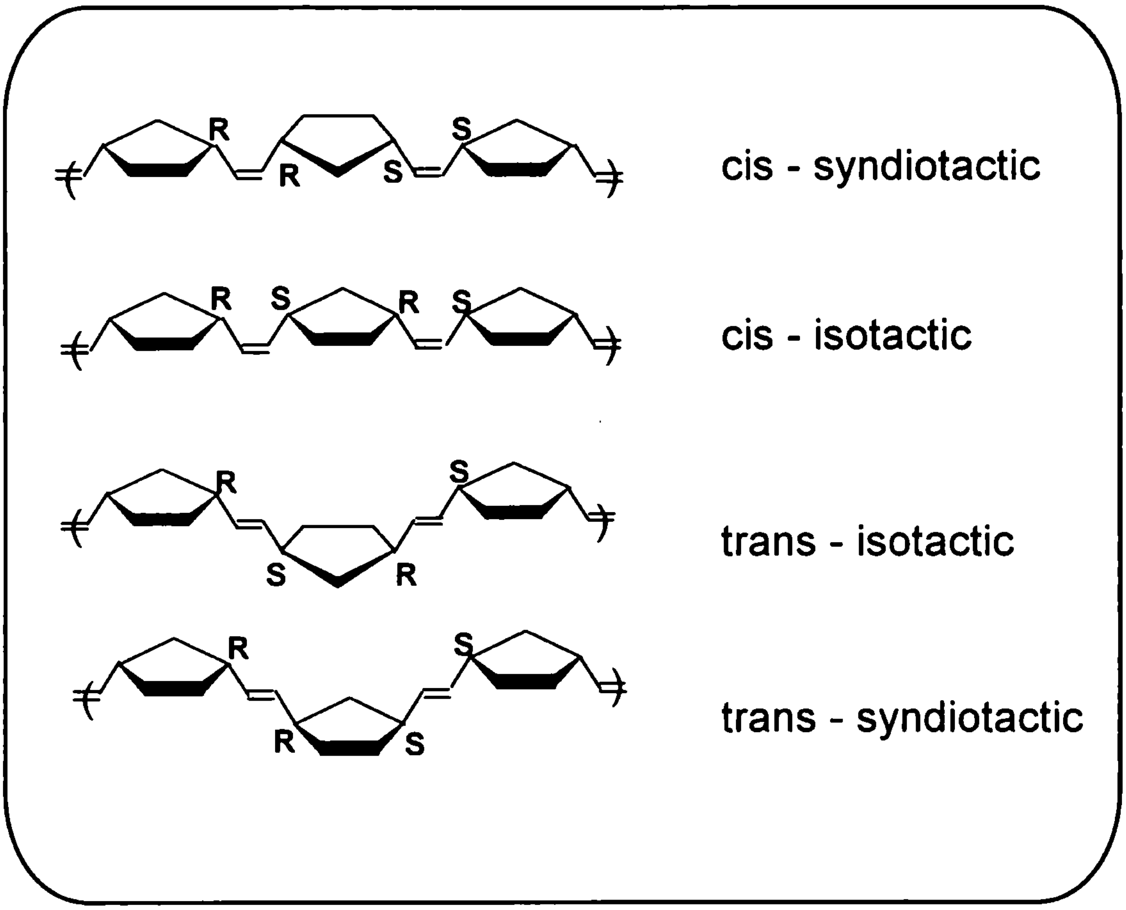


FIGURE 2.6.1 Some tacticities for ring opened norbornene

2.6.3. Head/Tail Effects

For unsymmetrically substituted monomers head/tail (H/T) effects can also occur along the polymer chain. Figure 2.6.2 illustrates an all *cis* polymer obtained from the ROMP of 5,5-dimethylnorbornene, where carbon atoms 3,4 and 5 are assigned head (H) and carbon atoms 1,2 and 6 are assigned as the tail (T). The head portion can be in two possible environments HH or HT depending on the orientation of the adjacent repeat unit, similarly the tail fragment can be TT or HT. These possible orientations are illustrated in Figure 2.6.2.[9]

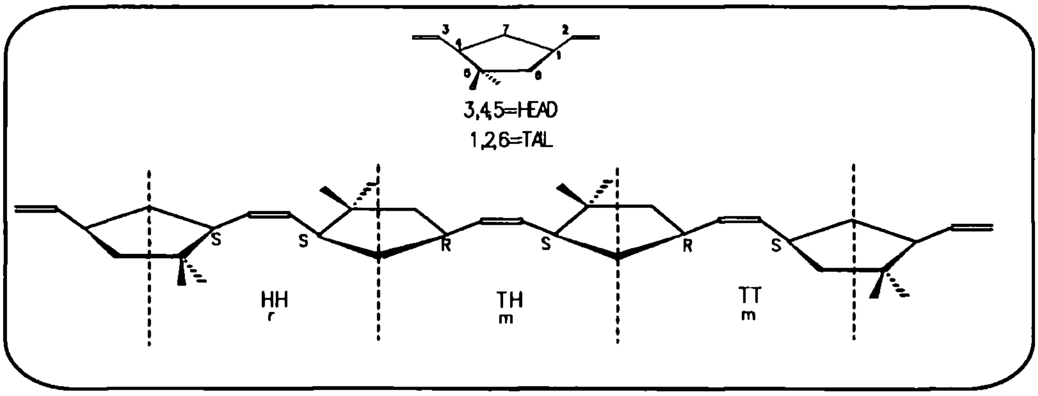


FIGURE 2.6.2 Head and tail effects in *cis* poly(5,5-dimethylnorbornene).

Classical ROMP catalysts only rarely produce stereoregular polymers.[62] Highly stereoregular polymers have been prepared using well-defined Schrock type initiators.[28,70,71] It has been found in some instances the microstructure of the resultant polymer is sensitive to the nature of the alkoxide ligands.[70] The Schrock type initiator with t-butoxide alkoxide ligands produces polymers of 5,6-bis(trifluoromethyl)norbornadiene with >98% *trans* double bonds, in contrast, when the alkoxide ligands are replaced with hexafluoro-t-butoxide ligands the polymer has >98% *cis* double bonds.

2.7 CONCLUDING REMARKS

Developments over the past few years have produced a new generation of ROMP initiators which provide, in favourable cases, the means to control the molecular weight and distribution as well as the microstructure of the polymer. More recent developments have used rhenium[15,72] and ruthenium[69,73] based initiators in order to polymerise a variety of functionalised monomers in protic and non-protic solvents. These new initiators have the potential to provide new approaches for the well-defined metathesis of a greater range of functionalised olefins than has been possible in the past.

CHAPTER THREE

SYNTHESIS AND CHARACTERISATION OF MONOMERS

3.1 GENERAL PROCEDURES

3.1.1 Reagents

All reagents (Aldrich Chemical Co. Ltd./Exxon Chemical Ltd/TCI Chemicals) and solvents (Aldrich Chemical Co. Ltd./BDH/Fisons, general purpose reagents) were used as supplied unless otherwise stated.

3.1.2 Apparatus

A HMS 500C Fischer Spaltror concentric tube column, fitted with a distillation control system DC10 operating with ninety theoretical plates (at maximum efficiency) with a hold up between 1 and 4mls, dependant upon throughput, was used for the final purification stages of the monomers. The Kugelrohr used was a Büchi GKR-51 with electric ball tube driver unit, an ice-cooler and used with four individual ground-joint ball tubes.

3.1.3 Characterisation

All NMR spectra were recorded on a Varian VXR 400 NMR spectrometer, operating at 399.952 MHz for ^{1}H NMR and 100.577 for ^{13}C NMR. Mass spectra were recorded on a VG Analytical model 7070E mass spectrometer or on a Fisons TR1000 mass spectrometer. Infrared spectra were recorded on a Perkin Elmer 1600 series Fourier Transform Infrared spectrometer or a Perkin Elmer 1720X series FTIR spectrometer. Gas liquid chromatographic analyses (gc) were carried out on a Hewlett Packard 5890A gas chromatograph fitted with a 25M cross linked methyl silicone column. Preparative gc was attempted using a Varian Aerograph

Model 920 gas chromatograph using columns packed with 10% silicone elastomer 30 on a chromosorb P column (10% SE30). HPLC was attempted using a Varian 9010 HPLC with a ODS 2 Hypersil reverse phase column, a pump rate of 1.4mls/min and solvent systems THF/water, dichloromethane/water and methanol/water.

3.2 ALKYL SUBSTITUTED NORBORNENES

3.2.1 The Diels-Alder reaction

The Diels-Alder reaction is probably the most useful way of making six membered rings available to the organic chemist. In its most general form it is the reaction of a conjugated diene and a dienophile (usually an olefin or acetylene derivative) to give a six membered ring as illustrated in Figure 3.2.1.

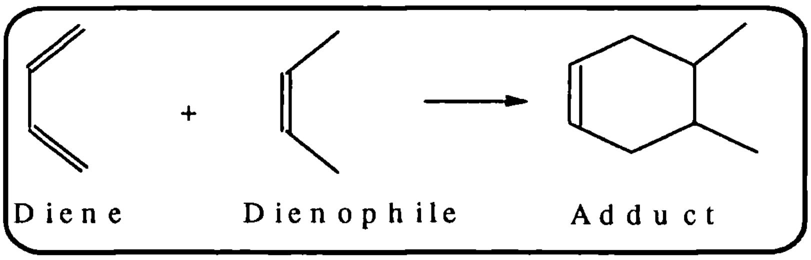


FIGURE 3.2.1 An example of the Diels-Alder reaction

The diene must be conjugated with the double bonds *cis* oriented at the time of reaction and is often substituted with electron donating groups, the dienophile can be practically any unsaturated compound and is normally substituted with electron withdrawing groups. The reaction is also successful when the diene carries electron withdrawing groups and the dienophile has donating groups, the reaction is least effective when both diene and dienophile carry the same kind of substituents or no substituents. Thus reactions between cyclopentadiene and ethene or unsubstituted α-olefins, as the dienophilic reagent, occur under conditions of elevated temperature and pressure. Competing reactions in Diels-Alder systems are polymerisation of either the diene or dienophile or both.[75]

When the diene is cyclic, for example cyclopentadiene, and the dieneophile is unsymmetric there are two possible ways in which addition can occur, *endo* or *exo*, as illustrated in Figure 3.2.2.

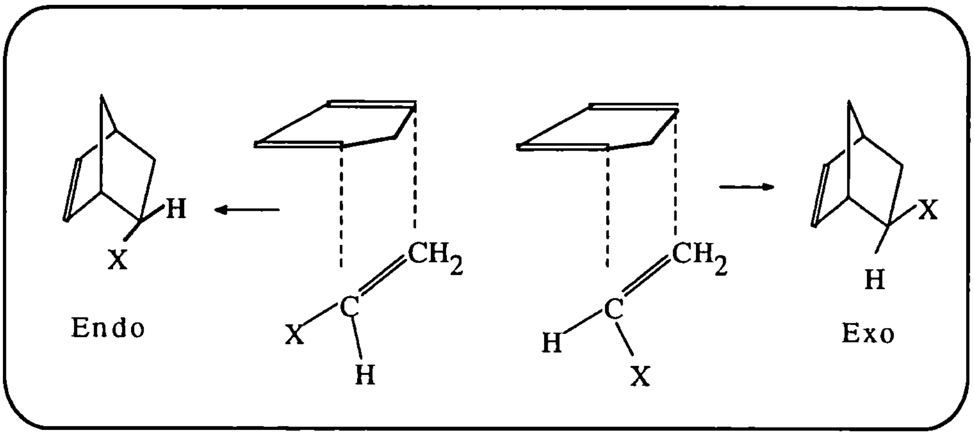


FIGURE 3.2.2 Stereochemistry of the Diels-Alder reaction

The *exo* isomer is the thermodynamically favoured product and the *endo* isomer is the kinetically favoured product. Diels-Alder reactions often show a preference for *endo* approach but *endo/exo* ratios depend on reaction conditions such as temperature, pressure, solvent polarity and on the exact structures of the diene and dienophile. Control of these factors can often favour the formation of one adduct over the other.[78]

Alkyl norbornenes may be synthesised by the reaction of an olefin with cyclopentadiene at elevated temperatures and pressures. Alkyl norbornenes substituted at carbon 5 are prepared when the reacting olefin is an α-olefin as illustrated in Figure 3.2.2, where X=alkyl. The stereochemistry of this reaction, as well as giving *exo/endo* isomers, yields optical isomers; that is a racemic mixture of both *endo* and *exo* adducts will be produced.

This process however often results in the formation of resinous polymeric materials. In order to combat this polymer build up the reaction has been carried out using an excess of the olefin[79] or in the presence of a hydrocarbon solvent.[80] Although hydrocarbon solvents are helpful in reducing polymer build up when norbornene or monoalkylnorbornenes are prepared there is, never the less, a considerable polymer build up which is sufficient to make the process impractical commercially.[78] The 5-substituted alkyl norbornenes synthesised during this project were prepared by reaction of dicyclopentadiene, as a source of cyclopentadiene, with α-olefins at elevated temperatures and pressures in the presence of a chlorinated solvent. Chlorinated and brominated solvents have been found to be effective in minimising the build up of undesirable polymeric materials in such reactions.[81]

3.2.2 Experimental

(i) Synthesis of 5-hexadecyl, 5-tetradecyl, 5-decyl and 5-hexylnorbornene

A 500ml stainless steel autoclave fitted with a thermocouple well was charged with dicyclopentadiene (93%, 35.5g, 0.25moles), α-olefins; 1-octadecene (160g, 0.635moles); or 1-hexadecene (140g, 0.625moles); or 1-dodecene (168g, 1.0moles); or 1-octene (135g, 1.2 moles) and 1,2 dichlorobenzene (100mls). The autoclave was sealed using a copper gasket and rocked for 4 hours at 240°C for 1-octadecene and 1-hexadecene and 200°C for 1-dodecene and 1-octene. After cooling to room temperature volatile gases were vented and the crude liquid product from the autoclave was poured into a round bottomed flask for storage.

(ii) Synthesis of 5-heptylnorbornene

A 160ml stainless steel autoclave fitted with a thermocouple well was charged with dicyclopentadiene (93%, 10g 0.07moles), 1-nonene (25g, 0.216moles) and 1,2-dichlorobenzene (25mls). The autoclave was sealed using a copper gasket, pressurised with nitrogen (6.9×10^6Pa) and rocked at 200°C for 4 hours. The crude liquid product was recovered as described in section 3.2.2(i).

(iii) Synthesis of 5-eicosylnorbornene

A 160ml stainless steel autoclave fitted with a thermocouple well was charged with dicyclopentadiene (93%, 22.5g, 0.162moles), 1-docosene (25g, 0.081moles) and 1,2-dichlorobenzene (25mls). The autoclave was sealed using a copper gasket, pressurised with nitrogen (13.8×10^6Pa) and rocked at 240°C for 4 hours. The crude liquid product was recovered as described in section 3.2.2(i).

The crude products from the above reactions were purified as follows; solvent and excess olefin were removed via a series of distillations at various reduced pressures so as to recover solvent and unreacted α-olefins. The crude residual product was then fractionally distilled using a Spaltrohr concentric tube column except for 5-eicosylnorbornene. This is a waxy solid and purification by recrystallisation, hplc and preparative gas chromatography was attempted without success. Initially hydroquinone was used as an additive, in order to suppress potential polymerisation reactions, however it was found that purification of the final product was easier if hydroquinone was not used as the crude materials were less likely to solidify whilst undergoing repeated distillations. The crude products prepared in the absence of hydroquinone were lighter in colour and yields were unaffected.

1-Octene, 1-nonene and 1-dodecene were used in a greater excess than the larger α-olefins to suppress the formation of a 2:1 cyclopentadiene adduct, shown for the 1-octene case in Figure 3.2.3.

When the amount of 1-octene used in the reaction was reduced this 2:1 adduct was the major product. This effect may also occur in the 1-nonene and 1-dodecene reactions but a large excess of olefin was always used and the 2:1 adduct was not detected. In the case of the larger α-olefins this reaction seems unimportant. The explanation of this observation is uncertain but may be a function of steric inhibition of the second cycloaddition in the case of the larger substituents.

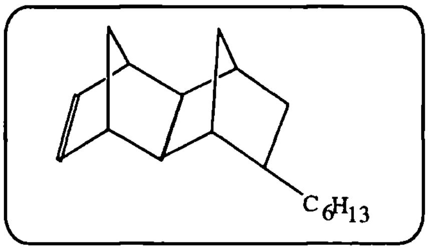


FIGURE 3.2.3 (2:1) Adduct cyclopentadiene:1-octene

Changes in reaction time seemed to have little effect on overall yields, which in general, are low due to the repeated distillations necessary to yield the products in greater than 97% purity (by gc) as required for polymerisation. Yields and distillation conditions are recorded in Table 3.2.1.

MONOMER	VACUUM (MBar)	TEMP. (°C)	YIELD (%)
(±)5-Tetradecylnorbornene	$2x10^{-1}$	118	15-26
(±)5-Hexadecylnorbornene	$2x10^{-1}$	133	15-28
(±)5-Decylnorbornene	$1x10^{-1}$	72-73	55
(±)5-Heptylnorbornene	$6x10^{-2}$	25-26	17
(±)5-Hexylnorbornene	$1x10^{-1}$	37	18-45

TABLE 3.2.1 Yields and distillation temperatures of some (±)-*exo/endo* 5-substituted norbornenes

3.2.3 Analysis of data

(i) (±)-*Exo/endo*-5-tetradecylnorbornene

The MS (Appendix A1) shows a molecular ion at 290 (1.3%) and a base peak at m/e 66 ($C_6H_5^+$-cyclopentadiene). It is evident from the ^{13}C NMR spectrum (Appendix B1) that there is a major and a minor component, presumably *endo* and *exo* isomers. In order to assign the shifts it is necessary to compare the ^{13}C NMR spectrum of (±)-*exo/endo*-5-tetradecylnorbornene with a suitable model compound. It has been established that ^{13}C NMR shifts are sensitive to molecular geometry and therefore ^{13}C NMR spectra can be valuable aids for stereochemical assignments. The relatively rigid and well-defined norbornene skeleton makes it possible to extrapolate shift data from similarly substituted norbornene compounds whose ^{13}C NMR spectra have been fully assigned. *Endo* and *exo*-5-methyl substituted norbornenes have been prepared from the carboxylic acids; formed by Diels-Alder addition of cyclopentadiene with acrylonitrile followed by hydrolysis. The *exo/endo* acids were separated by the iodolactonization procedure and their signals in the ^{13}C NMR spectrum assigned.[82] The shifts for *exo/endo*-5-methylnorbornene are tabulated below.

	C-1	C-2	C-3	C-4	C-5	C-6	C-7
***exo*-5-Me**	42.3	135.9	137	48.3	32.5	34.6	44.8
***endo*-5-Me**	43.1	136.7	132.1	47.1	32.5	33.7	50.1

TABLE 3.2.2 Literature ^{13}C NMR assignments for *exo/endo*-5-methylnorbornene

It has been found that *endo* substitution at C-5 gives a relatively large upfield shift at C-3 and a similar upfield shift at C-7 is obtained from *exo* substitution at C-5.

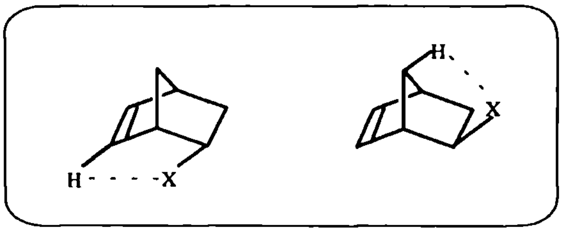
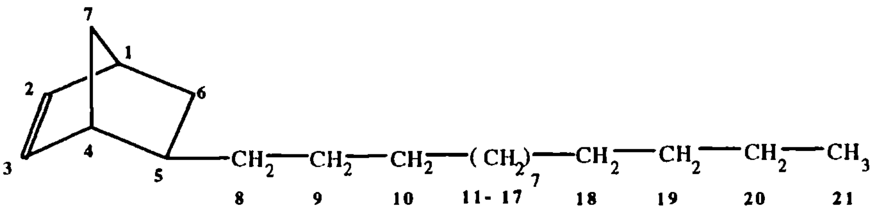


FIGURE 3.2.4 Steric effects in *exo/endo* 5-substituted norbornenes

These shift changes at C-3 and C-7 are mainly attributed to the steric effects experienced when the methyl group is *endo* or *exo* substituted as illustrated in Figure 3.2.4, where X = methyl.

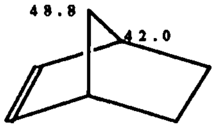
Now considering 5-tetradecylnorbornene,



the olefinic carbons C-2 and C-3 of the major component have shifts of 136.8 and 132.5ppm which correspond to the *endo* shifts of C-2 and C-3, in Table 3.2.2, whereas the olefinic carbons of the minor component have shifts of 136.9 and 136.1ppm which correspond to the *exo* shifts for C-3 and C-2, in Table 3.2.2. Hence the major component is assigned as (±)-*endo*-5-tetradecylnorbornene and the minor as (±)-*exo*-5-tetradecylnorbornene. This assignment is reinforced by the C-7 signals at 49.6ppm (*endo*) and 45.0ppm (*exo*).

On examination of the DEPT spectrum (Appendix D1, expanded spectrum Appendix D2) it is again evident that there is a major component assigned *endo* and a minor component assigned *exo*. Considering the major component we can identify the following; one methyl group; eight individual methylene groups plus a large peak at ~ 30ppm and five CH groups. (±)-5-Tetradecylnorbornene illustrated on page 42 has; one methyl group; fifteen methylene groups and five CH groups. Hence we are able to assign the large peak at ~ 30ppm to coincident signals from seven of the methylene groups in the middle of the aliphatic side chain.

Using DEPT and the literature values[83] for shifts in norbornene:-



we can assign all the major peaks in the ^{13}C NMR spectrum (Appendix B1)

SHIFT (ppm)	CARBON ASSIGNMENT	SHIFT (ppm)	CARBON ASSIGNMENT
14.14	CH_3 **21**	38.72	CH **5**
22.73	CH_2 **20**	42.53	CH **1**
28.71	CH_2 **19**	45.42	CH **4**
29.41-29.97	$9xCH_2$ **10-18**	49.56	CH_2 **7**
31.97	CH_2 **9**	132.45	CH **3**
32.45	CH_2 **6**	136.81	CH **2**
34.85	CH_2 **8**		

TABLE 3.2.3 Carbon assignments for (±)-*endo*-5-tetradecylnorbornene.

The methylene carbon at C-6 is separately assigned using the 2D spectrum (Appendix D3). In the proton spectrum this methylene group is split into two peaks at 0.5ppm and 1.8ppm. This is not unexpected as the two protons attached to this carbon will be locked stereochemically into two different environments within the norbornene ring system. The CH carbons 1,4 are separately assigned by comparison with shift values for C1 and C4 in *endo*-5-methylnorbornene (see Table 3.2.2).

The ring carbons for (±)-*exo*-5-tetradecylnorbornene are assigned in an identical manner to that used in order to assign the shifts for (±)-*endo*-5-tetradecylnorbornene.

C-1	C-2	C-3	C-4	C-5	C-6	C-7
42.0	136.1	136.8	46.2	38.7	33.2	45.0

TABLE 3.2.4 Ring carbon assignments for (±)-*exo* 5-tetradecylnorbornene

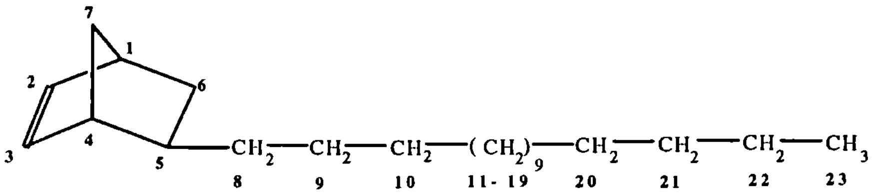
The shift for C-5 *exo* is identical to that for C-5 *endo* a trend which is also seen for the *endo*/*exo*-5-methylnorbornenes in Table 3.2.2. The shift at 32.5ppm for C-5 *exo*/*endo*-5-methylnorbornene is upfield from the shift at 38.7ppm which is observed for C-5 (±)-*exo*/*endo*-5-tetradecylnorbornene This phenomenon is explained by substituent effects using incremental systems developed by Grant and Paul and Lindeman and Adams.[84] An unsubstituted norbornene ring would show a signal at 24.8ppm[83] for the C-5 carbon. An α substituent, e.g. methyl, would cause this signal to be shifted downfield by approximately 9ppm to a value of 33.8ppm; comparable to the shift at 32.5ppm observed for *exo*/*endo*-5-methylnorbornene in Table 3.2.2. A β substituent, e.g. ethyl, would result in a further downfield shift of 9.4ppm to approximately 42.4ppm. A γ substituent, e.g. propyl, results in an upfield shift of approximately 2.5ppm to 40ppm. These substituent shifts correlate well with the shifts at 38.7ppm obtained for (±)-*exo*/*endo*-5-tetradecylnorbornene. These steric factors are negligible after γ substituents.

It is not possible to assign the ^{13}C NMR shifts for all the carbons in (±)-*exo*-5-tetradecylnorbornene from the information available here as the spectra are dominated by (±)-*endo*-5-tetradecylnorbornene, particularly the CH_2 peaks and there is a large degree of overlap in these areas.

Now considering the ^{1}H NMR spectrum (Appendix C1). As already mentioned the peaks at 0.5ppm and 1.8ppm are assigned to the protons attached to C-6. On examination of the remainder of the ^{1}H spectrum, in conjunction with the two-dimensional spectrum, (Appendix D3) the rest of the peaks may be assigned. A set of complex multiplets at 6ppm assigned to the olefinic protons (**2,3**-2H); two peaks between 2.5 and 2.8ppm assigned to the bridgehead protons (**1,4**-2H), on closer examination of this area four distinct regions are visible; two major components and two minor components. The two major components and one of the minor components are associated with the peak at 2.8ppm in the proton spectrum, with the other minor component associated with the peak at 2.5ppm. As the major component has been previously assigned as (±)-*endo*-5-tetradecylnorbornene and the minor component as (±)-*exo*-5-tetradecylnorbornene then the shift at 2.5ppm in the proton spectrum with a corresponding shift at 46.42ppm in the carbon spectrum may be assigned to the proton at C-4 in (±)-*exo*-5-tetradecylnorbornene and thus the shift at 2.8ppm can be assigned to the protons at C-1 in (±)-*exo*-5-tetradecylnorbornene and at C-1 and C-4 in (±)-*endo*-5-tetradecylnorbornene. Continuing the assignment of the remainder of the spectrum a set of peaks at 1.95ppm is assigned to the methine proton α to the aliphatic chain (**5**-1H); a large peak at 1.4ppm which is assigned to twelve methylene groups in the aliphatic chain plus the bridging methylene group of the norbornene ring (**7,8-19**-26H), a set of peaks at 1.05ppm assigned to methylene group adjacent to the methyl group (**20**-2H) and finally a triplet at 0.9ppm assigned to the methyl group (**21**-3H).

Assigning the proton at C-4 in (±)-*exo*-5-tetradecylnorbornene to the shift at 2.5ppm and the shift at 2.8ppm to the protons at C-1 in (±)-*exo*-5-tetradecylnorbornene and C-1 and C-4 in (±)-*endo*-5-tetradecylnorbornene, the ratio of *endo:exo* from the integration of these peaks was 78:22.

(ii) (±)-*Exo*/*endo*-5-hexadecylnorbornene



The MS (Appendix A2) shows the parent molecule at 318(1%) and a base peak at m/e 66 ($C_6H_5^+$-cyclopentadiene). Using the information previously derived from the analysis of (±)-*exo*/*endo*-5-tetradecylnorbornene we can assign the ^1H and ^{13}C NMR spectra for (±)-*endo*-5-hexadecylnorbornene. Initially considering the ^{13}C NMR spectrum (Appendix B2) we can assign the chemical shifts as follows:-

SHIFT (ppm)	CARBON ASSIGNMENT	SHIFT (ppm)	CARBON ASSIGNMENT
14.14	CH_3 **23**	38.78	CH **5**
22.73	CH_2 **22**	42.54	CH **1**
28.72	CH_2 **21**	45.42	CH **4**
29.41-29.98	11xCH_2 **10-20**	49.57	CH_2 **7**
31.97	CH_2 **9**	132.45	CH **3**
32.46	CH_2 **6**	136.81	CH **2**
34.86	CH_2 **8**		

TABLE 3.2.5 Carbon assignments for (±)-*endo*-5-hexadecylnorbornene

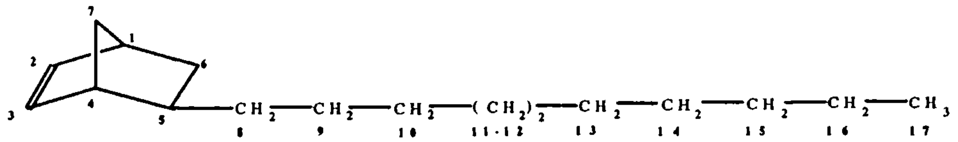
The chemical shifts in the ^1H NMR spectrum (Appendix C2) are assigned below :-

SHIFT (ppm)	PROTON ASSIGNMENT	SHIFT (ppm)	PROTON ASSIGNMENT
0.5 1.8	**6**	1.95	**5**
		2.5	**4**
0.9	**23**	2.8	**1**
1.05	**22**	6.0	**2,3**
1.4	**7,8-21**		

TABLE 3.2.6 Proton assignments for (±)-*endo*-5-hexadecylnorbornene

The *endo*/*exo* ratio can be calculated in the same way used to calculate the *endo*/*exo* ratio for (±)-*exo*/*endo*-5-tetradecylnorbornene and in this case is found to be 83:17.

(iii) (±)-*Exo*/*endo*-5-decylnorbornene



The GC/MS (Appendix A3) shows the molecular ion at 234(3.2%) and a base peak at m/e 66 ($C_6H_5^+$-cyclopentadiene). Using information already gained in the analysis of (±)-5-*exo*/*endo*-tetradecylnorbornene the ^{13}C NMR spectrum (Appendix B3) and the ^1H NMR spectrum (Appendix C3) for (±)-*endo*-5-decylnorbornene can be assigned.

SHIFT (ppm)	CARBON ASSIGNMENT	SHIFT (ppm)	CARBON ASSIGNMENT
14.14	CH_3 **17**	38.83	CH **5**
22.75	CH_2 **16**	42.56	CH **1**
28.76	CH_2 **15**	45.44	CH **4**
29.46-30.03	5xCH_2 **10-14**	49.59	CH_2 **7**
32.0	CH_2 **9**	132.4	CH **3**
32.48	CH_2 **6**	136.8	CH **2**
34.89	CH_2 **8**		

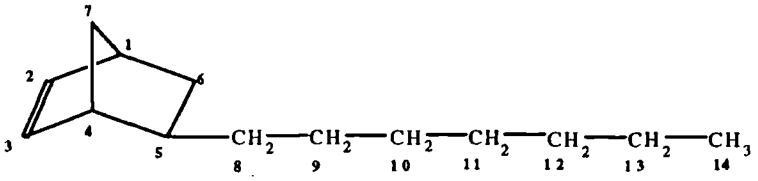
TABLE 3.2.7 Carbon assignments for (±)-*endo*-5-decylnorbornene

SHIFT (ppm)	PROTON ASSIGNMENT	SHIFT (ppm)	PROTON ASSIGNMENT
0.5 1.85	**6**	2.0	**5**
		2.5	**4**
0.9	**17**	2.8	**1**
1.05	**16**	6.0	**2,3**
1.3	**7, 8-15**		

TABLE 3.2.8 Proton assignments for (±)-*endo*-5-decylnorbornene

The ratio *endo*/*exo* for (±)-*exo*/*endo*-5-decylnorbornene is calculated to be 85:15.

(iv) (±)-*Exo*/*endo*-5-heptylnorbornene



The GC/MS (Appendix A4) shows the molecular ion at 192(3.5%) and a base peak at m/e 66 ($C_6H_5^+$-cyclopentadiene).

The ^{13}C NMR (Appendix B4) and the ^1H NMR spectra (Appendix C4) of (±)-*endo*-5-heptylnorbornene may be assigned as follows.

SHIFT (ppm)	CARBON ASSIGNMENT	SHIFT (ppm)	CARBON ASSIGNMENT
14.13	CH_3 **14**	38.78	CH **5**
22.72	CH_2 **13**	42.53	CH **1**
28.71	CH_2 **12**	45.4	CH **4**
29.92	2xCH_2 **10,11**	49.56	CH_2 **7**
31.95	CH_2 **9**	132.44	CH **3**
32.45	CH_2 **6**	136.8	CH **2**
34.84	CH_2 **8**		

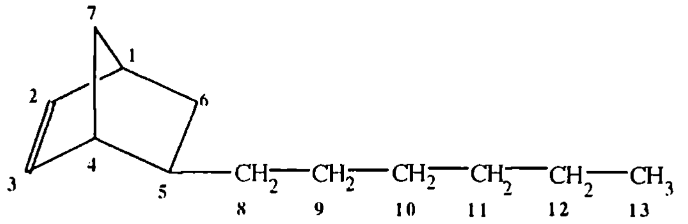
TABLE 3.2.9 Carbon assignments for (±)-*endo*-5-heptylnorbornene

SHIFT (ppm)	PROTON ASSIGNMENT	SHIFT (ppm)	PROTON ASSIGNMENT
0.45	**6**	1.95	**5**
1.8		2.5	**4**
0.85	**14**	2.75	**1**
1.05	**13**	6.0	**2,3**
1.3	**7,8-12**		

TABLE 3.2.10 Proton assignments for (±)-*endo*-5-heptylnorbornene

Ratio *endo*/*exo* for (±)-*exo*/*endo*-5-heptylnorbornene, calculated as before, is found to be 86:14.

(v) (±)-*Exo*/*endo*-5-hexylnorbornene



The MS (Appendix A5) shows the molecular ion at 178(1.2%) and a base peak at m/e 66 ($C_6H_5^+$ cyclopentadiene). Again using the information previously derived the ^{13}C NMR spectrum (Appendix B5) and the ^{1}H NMR spectrum (Appendix C5) for (±)-*endo*-5-hexylnorbornene can be fully assigned:-

SHIFT (ppm)	CARBON ASSIGNMENT	SHIFT (ppm)	CARBON ASSIGNMENT
14.2	CH_3 **13**	38.9	CH_2 **5**
22.8	CH_2 **12**	42.6	CH **1**
28.8	CH_2 **11**	45.5	CH **4**
29.8	CH_2 **10**	49.6	CH_2 **7**
32.1	CH_2 **9**	132.4	CH **3**
32.5	CH_2 **6**	136.8	CH **2**
35.0	CH_2 **8**		

TABLE 3.2.11 Carbon assignments for (±)-*endo*-5-hexylnorbornene

SHIFT (ppm)	PROTON ASSIGNMENT	SHIFT (ppm)	PROTON ASSIGNMENT
0.5 1.8	**6**	1.96	**5**
		2.5	**4**
0.88	**13**	2.8	**1**
1.07	**12**	6.0	**2,3**
1.3	**7, 8-11**		

TABLE 3.2.12 Proton assignments for (±)-*endo*-5-hexylnorbornene

Ratio *endo/exo* for (±)-*exo/endo*-5-hexylnorbornene, calculated as before, is found to 85:15.

(vi) (±)-*Exo/endo*-5-eicosyl norbornene

The GC/MS of the impure product (Appendix A6) shows the molecular ion at 374(0.3%) and a base peak at m/e 66 ($C_6H_5^+$-cyclopentadiene). The major impurity being 1-docosene one of the starting materials used for the preparation of (±)-*exo/endo*-5-eicosylnorbornene.

3.3 ACETOXY SUBSTITUTED CYCLIC OLEFINS

3.3.1 Introduction

A suitable starting material for the preparation of an acetoxy substituted twelve membered cyclic olefin is 1,2-epoxycyclododecadiene. This material is commercially available and the reduction of epoxides is easily carried out, the most commonly used reagent being lithium aluminium hydride.[78,85,86] The resultant alcohol on acetylation would yield a monoacetoxy substituted cyclic olefin. The acetylation of alcohols may be carried out by reaction with acetyl chloride in the presence of N,N-dimethyl aniline.[87] Experimental details are give in sections 3.3.3 and 3.3.4.

The cleavage of ethers has also been carried using anhydrous ferric chloride and acetic anhydride[78,88] which would in the case of cyclic ethers, such as epoxides, yield a diacetoxy substituted product. However, attempts to cleave the epoxide ring in the presence of ferric chloride and acetic anhydride proved unsuccessful, in this case, yielding a complex mixture of products which was abandoned. Using acetic anhydride alone was also unsuccessful even at reflux the epoxide ring remained intact. Acetic acid was therefore selected as the reagent of choice to cleave the epoxide ring, in order to yield a diacetoxy substituted product. Experimental details are given in section 3.3.2.

Figure 3.3.1 below illustrates the reaction schemes employed for the synthesis of an acetoxy substituted cyclic olefin.

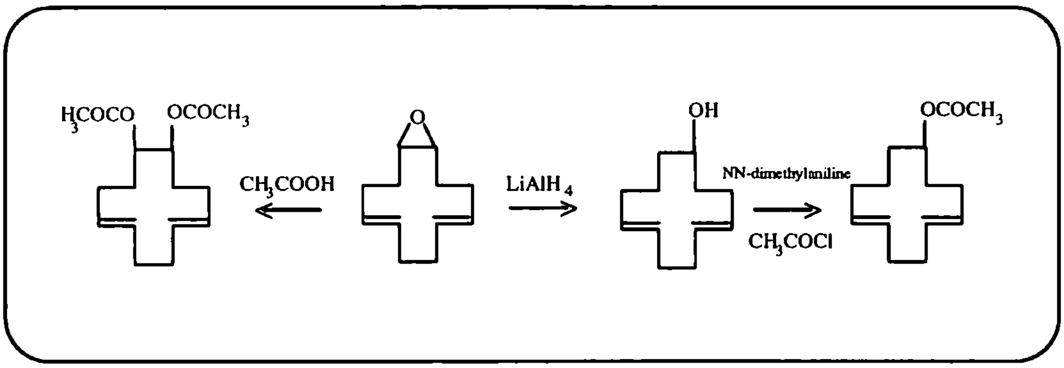


FIGURE 3.3 1 Proposed methods for synthesis of an acetoxy cyclic olefin

3.3.2 Preparation of 1,2-diacetoxy-5,9-cyclododecadiene

1,2-Epoxy-5,9-cyclododecadiene (99%, 10g, 0.056moles) and glacial acetic acid (10g, 0.25moles) were heated at 120°C for 18 hours and then allowed to cool. The resulting dark orange solution was diluted with water and extracted with hexane. The water layer was extracted twice more with hexane. The hexane extracts were combined, washed with water (x2), saturated sodium hydrogen carbonate solution and dried over magnesium sulphate. The mixture was filtered and the solvent evaporated. The resulting dark orange oil was further purified by Kugelrohr distillation.

Infrared analysis of the main fraction showed a strong OH stretch at υ=3450cm^{-1} i.e.the reaction was incomplete (Appendix E1).

The main fraction (1.5g), recovered from the earlier reaction, was boiled with acetic anhydride (99%, 2.75mls, 3.15g, 0.031moles) for 3-4hrs. The resulting oil was purified as above to yield as a colourless oil; 1,2-diacetoxy-5,9-cyclododecadiene (1g, 3.5mmoles 6.4% overall).

Infrared analysis showed the absence of OH stretching absorptions (Appendix E2). GC/MS data (Appendix A7) shows the expected molecular ion at 280 followed by a complex fragmentation pattern with the loss of $OCOCH_3$ at 221. The spectrum displayed relatively intense M+1 and M-1 peaks. The ^1H NMR spectrum (Appendix C6) is consistent with the product being a mixture of the isomers of 1,2-diacetoxy 5,9-cyclododecadiene. Two sharp singlets at 2.038 and 2.046 ppm assigned to the methyls of the acetoxy group (6H); a set of complex of overlapping multiplets between 1.4 and 2.4 ppm assigned to the methylene hydrogens at **C3,4,7,8,11** and **12** (12H); a set of complex overlapping multiplets between 5.35 and 5.6ppm assigned to the vinylic hydrogens **C5,6,9** and **10** (4H). The tertiary hydrogens α to the acetoxy groups are associated with the absorptions between 5.0 and 5.2ppm (2H). The general complexity of the spectrum together with the presence of two resolved methyl signals suggests that the product is a mixture of the isomers of 1,2-diacetoxy-5,9-cyclododecadiene.

This method was not optimised and work has concentrated on the easier synthesis and purification of the mono-acetoxy cyclododecadiene, as a monomer to be used to yield an EVA type polymer.

3.3.3 Preparation of 1-hydroxy-4,8-cyclododecadiene

Lithium aluminium hydride (4g, 0.12moles) was slurried in tetrahydrofuran (150mls, distilled from potassium) under nitrogen. 1,2-Epoxy-5,9-cyclododecadiene (99%, 5g, 0.03moles) was added dropwise over 5mins. The reaction mixture was refluxed under nitrogen for ten days. The mixture was cooled to 0°C and water (15mls) was added dropwise with vigorous stirring. Stirring was continued for 2hrs at room temperature. After filtering, solvent was removed to yield an opaque oil which crystallised on standing. The off white solid was dissolved in diethyl ether, dried over magnesium sulphate and the solvent removed to yield as a white crystalline solid, 1-hydroxy-4,8-cyclododecadiene (Mpt 64.5-65°C, 4.5g, 0.025moles, 83%). The MS (Appendix A8) showed a molecular ion at 180 which is consistent with the product being 1-hydroxy-4,8-cyclododecadiene and a major fragment at 162 ($M-H_2O$) which is also consistent with the expected product. To partially analyse the ^1H NMR spectrum it is necessary to compare the spectra of the starting material and the final product (Appendix C7). It is clear from a simple inspection, of the spectra of both the starting material (i) and the final product(ii), that they are a mixture of isomers. The overall appearance of the spectra are similar apart from the loss of the sets of multiplets between 2.4 and 2.8ppm, associated with the epoxide protons (**1,2** 2H),[81] in the starting material and the appearence of signals at 3.65ppm and 1.4ppm in the product which are associated with the protons α to the hydroxy group (**1** 1H) and the methylene protons β to the hydroxy group respectively. The remainder of the spectra consist of complex over lapping multiplets between 1 and 2.35ppm, associated with saturated aliphatic protons, and complex overlapping multiplets between 5.0 and 5.5ppm associated with the vinylic protons. The ^{13}C NMR spectra of the starting material and the product also indicates that we have a complex mixture of isomers, (Appendix B6). Both spectra display peaks between 20 and 40ppm associated with saturated aliphatic carbons and peaks between 128 and 134ppm associated with vinylic carbons. In the spectrum of the starting material (i) there is a set of peaks at 59ppm which are absent from the product (ii) and the product has a set of peaks at 68ppm which are absent in the starting material. This would be expected if the epoxy group had been removed and replaced with a hydroxy group. Further evidence for the removal of the epoxy group and its replacement with a hydroxy group comes from a comparison of the

FTIR spectra of the starting material and the product. The wide scan spectra of these material are compared in Appendix E3 and enlarged scans of the regions 1600-600cm^{-1} are compared in Appendix E4. The complexity of the spectra are consistent with the earlier assumption that both starting material and product are mixtures of isomers. The main feature in Appendix E3 is that the absorption at υ = 873cm^{-1} (associated with epoxy),[81] in the starting material, has disappeared in the product spectrum and a broad band centred at υ = 3233cm^{-1} (associated with OH stretch) is visible. A detailed examination of the fingerprint region in (Appendix E4) indicates substantial differences between starting material and product. However due to the multiplicity of the bands it is hazardous to assign particular bands to particular structural features. The main feature of interest is the disappearance of the υ = 873cm^{-1} absorption associated with the epoxide ring.

3.3.4 Preparation of 1-acetoxy-4,8-cyclododecadiene

1-Hydroxy-4,8-cyclododecadiene (7.55g 0.042moles) was dissolved in ether (10mls, distilled from lithium aluminium hydride). Distilled N,N-dimethylaniline (99%, 5.6g 0.046moles) added, the flask immersed in a water bath at 25°C and whilst stirring distilled acetyl chloride (99%, 3.3g, 0.042moles) added dropwise over ten minutes. Ten minutes after complete addition a white precipitate of N,N-dimethyl-anilinehydrochloride was observed. The reaction was left to stir over night, then water (5mls) was added in order to dissolve the precipitate. The ether layer was separated, extracted with 10% sulphuric acid until the acid did not turn cloudy when rendered alkaline with sodium hydroxide solution; and then dried over sodium sulphate. The mixture was filtered, solvent evaporated and the residual viscous liquid was distilled under vacuum (4×10^{-4}mbar 85-86°C) to yield, as a colourless oil, 1-acetoxy-4,8-cyclododecadiene (4.6g, 0.021moles, 50%).

MS (Appendix A9) shows a peak at 240 (molecular ion + NH_4) and the loss of $HOCOCH_3$ and NH_3 at 163. FTIR (Appendix E5) shows the loss of the OH peak at υ = 3233cm^{-1}, that is present in the FTIR spectrum of the starting material (Appendix E3(ii)), together with the appearance of peaks at υ = 1735cm^{-1} (-OCO-), υ = 1374.2cm^{-1} (-$COCH_3$) and υ = 1239cm^{-1} (-COC-). The ^{1}H NMR spectrum (Appendix C8) may be compared with the ^{1}H NMR spectrum of 1-hydroxy-4,8-cyclododecadiene (Appendix C7(ii)). The complexity of the spectrum indicates that the product is a mixture of isomers. The signal at 3.65ppm in Appendix C7(ii), associated with the proton α to the hydroxy group, has been shifted down field to 4.83ppm; now associated with a proton α to an acetoxy group. The remainder of the spectrum consists of complex overlapping multiplets between 1.2 and 2.2ppm associated with saturated aliphatic protons and a set of complex overlapping multiplets between 5.1 and 5.5ppm associated with the vinylic protons. The ^{13}C NMR (Appendix B7) is consistent with the presence of a complex mixture of isomers. As for the ^{13}C NMR spectra of both 1,2-epoxy-5,9-cyclododecadiene and 1-hydroxy-4,8-cyclododecadiene (Appendices B6(i) and (ii)) there are peaks between 20 and 40ppm associated with saturated aliphatic carbons and peaks between 128 and 134ppm associated with the vinylic carbons. The set of peaks at 68ppm associated with the carbon attached to the OH group (Appendix B6(ii)) have been shifted downfield to 71ppm consistent with the OH group being replaced by $OCOCH_3$.

CHAPTER FOUR

POLYMERISATION

4.1 GENERAL PROCEDURES

4.1.1 Reagents

Transition metal chlorides; tungsten hexachloride, molybdenum pentachloride, metalalkyls; tetramethyltin, diethylaluminiumiodide, diethylaluminiumchloride, hydrogenating agent; p-toluenesulphonyl hydrazide (Aldrich) and solvents (Aldrich/BDH laboratory grade) were used as supplied. Toluene (analytical reagent) was distilled from sodium benzophenone ketyl, chlorobenzene was distilled twice from diphosphorus pentoxide and ethyl acetate, 1-octene and monomers were distilled from calcium hydride. Trifluorotoluene, and deuterated solvents benzene, dichloromethane and chloroform were distilled from diphosphorus pentoxide and deuterated tetrahyrdrofuran was distilled from potassium. Well defined initiators were prepared according to the literature methods[31,34] (supplied by J.P.Mitchell/E.Khosravi).

4.1.2 Characterisation

Polymer characterisation using NMR and FTIR spectroscopy was carried out using the equipment already described in Chapter 3 section 3.1.3. ^{13}C NMR Analysis of the poly(5-alkylnorbornenes) was carried out using a Brucker AMX 500 operating at 125.759MHz.

Molecular weights of the ring opened polymers were measured by gel permeation chromatography (GPC) using tetrahydrofuran as the eluent. The equipment comprised of a Knauer 64 HPLC pump, a Viscotek differential refractometer/viscometer detector and a two 10μm column set of mixed gel (Polymer Laboratories). The calculation of molecular weights was performed using a Unical 4.03 software package from the Viscotek Corporation and the equipment was calibrated using narrow polystyrene standards (Polymer Laboratories).

Melting points (Tm) and glass transition temperatures (Tg) were determined by differential scanning calorimetry (DSC) using a Perkin Elmer DSC7 calibrated with indium and zinc standards. Calculations were performed using a thermal analysis software package, 3.1 series, from Perkin Elmer. Thermogravimetric analysis (TGA) was carried out using a Shimadzu TGA-50 or a Thermal Sciences TGA 760 series.

4.1.3 Polymerisation

Manipulations of the classical catalyst systems were carried out under dry nitrogen conditions on a dual nitrogen/vacuum line. The front manifold being connected to a vacuum pump and the back manifold to a dry oxygen free nitrogen supply. The nitrogen supply, BOC white spot grade, was passed through diphosphorus pentoxide and molecular sieve stacks into the line and out through a mercury bubbler. Teflon taps and greaseless joints were used throughout. Glassware was dried for at least 12hrs before use, evacuated whilst hot and let down to nitrogen, cannula and syringes were dried in the oven and allowed to cool under a flow of nitrogen. The catalyst was added to an ampoule in a dry box. The ampoule was then connected to the vacuum/nitrogen line, let down to nitrogen and with a positive pressure of nitrogen in the ampoule, the tap was removed and replaced by a septum seal; then the required amount of solvent was added using a syringe or via cannula transfer.

The reaction vessel used for polymerisation is illustrated in Appendix F1(i), to which the required amount of monomer, solvent, catalyst solution and chain transfer agent were added, via the septum seal, using airtight syringes. In cases where the catalyst required activation prior to its addition to the reaction pot, the vessel illustrated in Appendix F1(ii) was required. A magnetic follower was added to this vessel against a flow of nitrogen followed by the addition, via the septum seal using air tight syringes, of the required volume of catalyst, co-catalyst and solvent (if required). This mixture was stirred for the appropriate time then transferred, via a syringe, to the reaction vessel. Terminations of the polymerisation reactions were achieved, when required, by the addition of acetone.

Manipulations of the well-defined initiator systems were carried out in a dry box. Glassware was dried for at least 12hrs before being transferred into the dry box. In the dry box the required amounts of initiator and monomer were weighed out and the appropriate solvent added to each. A deuterated solvent was used for the NMR scale experiments. When both monomer and initiator had dissolved the monomer solution was added to the catalyst solution with stirring. This addition was carried out rapidly for the NMR scale experiments. For larger scale experiments one third of the monomer solution was added first with the remainder of the solution added dropwise. For NMR scale experiments the polymerisation reaction was followed using ^{1}H NMR spectroscopy. This allowed the consumption of the initiating alkylidene and the growth of the propagating alkylidenes, which in this instance were initially the major points of interest in the spectrum, to be observed. Both the NMR and larger scale polymerisation reactions were terminated by the addition of benzaldehyde. The details of catalyst, monomer, solvent and chain transfer concentrations used in the polymerisation reactions are given in the text.

After termination of the polymerisation reaction the mixture was added dropwise, to a large excess of stirred methanol, in order to precipitate the polymer. The polymer was then recovered, dissolved in toluene and reprecipitated, this process was repeated, to yield a clean polymer which was then dried under vacuum for at least 24hrs. The manipulations on the recovered polymer were carried out under a nitrogen atmosphere, as far as was possible.

4.1.4 Hydrogenation

The polymers were homogeneously hydrogenated following standard literature methods.[90,91] The polymer was dissolved in *p*-xylene, to form a 0.01 mole % solution, and heated to reflux whilst stirring under nitrogen. p-Toluenesulphonylhydrazide (5% molar excess) was then added and the heating was continued, under nitrogen, for an additional 2hrs. The contents of the flask were then allowed to cool and the polymer recovered by precipitation into stirred methanol. The recovered polymer was then treated as already described in section 4.1.3 to yield a clean dry polymer.

Heterogeneous hydrogenation has been found to be more difficult for polynorbornenes than for other unsaturated polymers.[9] Attempted catalytic hydrogenations using catalysts such as PtO_2, $Rh(C_6H_5)_3Cl$ and palladium on carbon have been unsuccessful.[92,93] Successful catalytic hydrogenation of poly(norbornene) has recently been reported; using catalysts based on ruthenium[94] and Pd/Pt supported on metal oxides.[95]

4.1.5 Codes

The following codes are used throughout this chapter.

a C- chlorobenzene, T- toluene

b Approximate temperature some polymerisation reactions were notably exothermic-no monitor of temperature was placed in the vessel.

c After reprecipitation and drying under vacuum for at least 24hrs.

d DSC measurements and optical microscopy carried out by N.E.Clough at the IRC in Polymer Science and Technology at Durham University.

e Polymer sample sent to Exxon Chemical Ltd for fuel testing.

r Polymer sample recovered from the reaction and dried.

h Hydrogenated poymer.

4.2 ALKYL SUBSTITUTED NORBORNENES

4.2.1 Polymerisation using $MoCl_5/Et_2AlI$

Molybdenum based catalysts tend to be less reactive than tungsten based catalysts for the metathesis of cyclic olefins, in spite of this molybdenum catalyst systems can be effective for ROMP.[9] The ring opening polymerisation of alkylnorbornenes with molybdenum pentachloride and diethylaluminiumiodide has been reported,[96] with the molybdenum pentachloride component being dissolved in toluene and ethyl acetate. The use of an ester in the solvent system was found to produce a brief induction period after the addition of the molybdenum salt to the reaction mixture. This effect is sometimes described as moderation and patent reports suggest addition of esters produces a more uniform polymerisation process. Thus the polymerisation of the alkylnorbornenes, prepared in Chapter 3, was carried out using this catalyst system. The reactant solutions used for the polymerisation were 0.25 molar diethylaluminiumiodide in dry toluene and 0.05 molar molybdenum pentachloride and 3.0 molar ethyl acetate in dry toluene. The ratio of catalyst:co-catalyst was 1:4.

(i) (±)-*Exo*/*endo*-5-tetradecylnorbornene

The polymerisation of (±)-*exo*/*endo*-5-tetradecylnorbornene was attempted using $MoCl_5/Et_2AlI$ and following the techniques outlined in section 4.1.3 for classical catalyst systems. These initial experiments resulted in gel formation or a very low recovery of soluble polymer as illustrated in table 4.2.1 below.

Expt. No.	**Monomer (mmol)**	**Catalyst (mmol)**	**Co-catalyst (mmol)**	**Solvent[a] (cm^3)**	**Temp.[b] (°C)**	**Time (mins)**	**Yield[c] (%)**
1	10.3	0.0225	0.09	T(20)	RT	5	GEL
2	10.3	0.0225	0.09	T(20)	RT	5	GEL
3	10.3	0.0225	0.09	T(20)	RT	2	3
4	10.3	0.0225	0.09	T(20)	5	2	GEL

TABLE 4.2.1.

Following these polymerisation reactions a chain transfer agent (CTA) was used in an attempt to prevent gel formation and control the molecular weight of the polymer. As discussed, in Chapter 2 section 2.4.3, the effectiveness of acyclic olefins in reducing molecular weight depends on their structure, the catalyst system and in particular the *cis* content of the polymer.[9] It has been found that for high *cis* polymers a higher concentration of terminal olefins is necessary in order to reduce the molecular weight to a particular level compared to polymers which have a lower *cis* content.[56] Some molybdenum catalyst systems are known to proceed with high *cis* selectivity.[9] For example the ring opening polymerisation of cyclopentene, initiated by $MoCl_5/Et_3Al$, yields a polyalkenemer with 99% *cis* double bonds.[97] Molybdenum based catalysts which demonstrate a bias towards *trans* selectivity also exist, for example the polymerisation of norbornene using $MoCl_5/EtAlCl_2$ yields a polymer with 35% *cis* double bonds.[98] In the absence of an unambiguous guide from the literature it was decided to test the effectiveness of the readily available 1-octene as a CTA using $MoCl_5/Et_2AlI$ as the catalyst system.

(ii) Chain transfer studies

(a) (±)-*Exo*/*endo*-5-tetradecylnorbornene

A series of small scale reactions were carried out to examine the effects of the catalyst:monomer ratio, % CTA, and time upon the molecular weight of poly(5-tetradecylnorbornene). The apparatus which was used for these small scale experiments is illustrated in Appendix F1(ii). The reactions were carried out at room temperature with toluene as the solvent (10% solution w/v).

Preliminary results were as follows :-

With a CTA concentration of 0%, catalyst:monomer ratios of 1:200, 1:100 and 1:50 and reaction times of 15 minutes, all the resulting polymers were insoluble gels. At CTA concentrations of 5%, 10%, and 20%, a catalyst:monomer ratio of 1:200 and reaction times of 15 minutes, 240 minutes and 18hrs the resulting polymers were all insoluble gels. With a catalyst:monomer ratio of 1:50, chain transfer concentrations and reaction times as above the resulting polymers were all soluble with the exception of the reaction with a 5% concentration of CTA and a reaction time of 18hrs; the polymer in this experiment was recovered as a gel.

A few simple conclusions can be drawn from these experiments. In these systems, in order to yield soluble polymer the percentage of 1-octene needs to be >10 and the catalyst:monomer ratio needs to be less than 1:200. Reaction time seemed to have little effect on the molecular weight of the recovered polymer in this instance.

Similar chain transfer experiments were repeated in order to provide a more detailed picture of the effects that 1-octene and the catalyst:monomer ratio have on the molecular weight of poly(5-tetradecylnorbornene). The solvent used was toluene (10%-solution w/v) and reaction times were 240mins. Table 4.2.2 overleaf gives the catalyst:monomer ratio, %CTA, the molecular weight and the molecular weight distribution of the recovered polymer. Yields of recovered polymer were between 77 and 89%.

Expt. No.	Mn ($x10^4$)	PDI (M_w/M_n)	Cat:Mon	CTA (%)
5	11	3.6	1:100	15
6	8.6	3.7	1:100	20
7	22	1.8	1:100	30
8	5.8	2.5	1:100	40
9	3.9	3.4	1:100	50
10	9.2	3.5	1:50	15
11	15	3.0	1:50	20
12	5.5	3.1	1:50	30
13	5.6	2.5	1:50	40
14	3.9	3.3	1:50	50

TABLE 4.2.2.

The GPC traces for the above series of reactions are illustrated in Appendix G1(5-9) and G2(10-14), showing the reduction in molecular weight which is obtained as the % of CTA is increased. Polymer No 7 gives a molecular weight higher than expected, when calculated using the Unical software, but if the GPC traces in Appendix G1 are examined it is apparent that the molecular weight of this polymer is in between the molecular weights for polymers Nos.6 and 8 as expected. In these small scale systems changing the catalyst:monomer ratio from 1:100 to 1:50 seemed to have little effect on the molecular weight of the recovered polymers.

(b) (±)-*Exo/endo*-5-hexylnorbornene

The above chain transfer studies were repeated using (±)-*exo/endo*-5-hexylnorbornene as the monomer. The solvent used was toluene (10%-solution w/v) and reaction times were 240mins. Table 4.2.3 overleaf gives the catalyst:monomer ratio, %CTA, the molecular weight and molecular weight distribution of the recovered polymer. Yields of recovered polymer were between 84 and 92%.

Expt. No.	Mn ($x10^4$)	PDI (M_w/M_n)	Cat:Mon	CTA (%)
15	2.9	3.7	1:100	15
16	1.1	4.6	1:100	20
17	2.0	4.7	1:100	30
18	0.93	7.1	1:100	40
19	0.97	4.7	1:100	50
20	2.7	7.7	1:50	15
21	3.5	5.2	1:50	20
22	2.9	4.0	1:50	30
23	1.7	5.7	1:50	40
24	1.7	3.5	1:50	50

TABLE 4.2.3.

The GPC traces for the above series of reactions are illustrated in Appendix G3(15-19) and G4(20-24) showing the gradual reduction in molecular weight that is achieved as the percentage of CTA used is increased.

(iii) (±)-*Exo/endo*-5-tetradecylnorbornene with 1-octene as CTA

Using the results obtained from the chain transfer studies described in sections 4.2.1(ii)a) and b) as a guide and following the general techniques outlined in section 4.1.3, for classical catalyst systems, the polymerisation reaction of (±)-*exo/endo*-5-tetradecylnorbornene was scaled up. The reaction conditions and yields are illustrated in table 4.2.4 below.

Expt. No.	Monomer (mmol)	Catalyst (mmol)	Co-catalyst (mmol)	C.T.A. %	Solvent[a] (cm^3)	Temp.[b] (°C)	Time (min)	Yield[c] (%)
25	14	0.03	0.12	30	T(45)	RT	5	74
26	10.3	0.1	0.4	15	T(40)	RT	15	71
27	14	0.28	1.05	15	T(45)	RT	o/n	73.5
27B	14	0.28	1.12	15	T(50)	RT	30	90

TABLE 4.2.4.

Recovered polymer

The results obtained from GPC and DSC analyses on the recovered polymers are tabulated below.

Expt. No.	**Mn ($x10^4$)**	**PDI (M_w/M_n)**	**Mpt. (°C)**
25^r	7.9	3.0	16
26^r	5.1	2.7	15
27^r	3.7	4.0	15
$27B^r$	4.9	4.1	15

TABLE 4.2.5.

It can be seen that polymer 25^r with a catalyst:monomer ratio of 1:450 and a CTA concentration of 30% yields a polymer with a molecular weight that is greater than the molecular weight observed for polymers 26^r, 27^r and $27B^r$ which had a catalyst:monomer ratio 1:50 and a CTA concentration of 15%. The ^{13}C NMR spectrum of poly(5-tetradecylnorbornene) shows similar splitting patterns and chemical shifts to those described in section 4.2.1(vi) for poly(5-hexylnorbornene). DSC analysis of poly(5-tetradecylnorbornene) gives a large melting peak, this suggests that the polymer has a large proportion of crystalline or well-ordered regions,[99] no glass transition was observed.

Hydrogenation

The polymers were hydrogenated following the general procedure outlined in section 4.1.4. The results from GPC and DSC analyses on the recovered hydrogenated polymer are shown in table 4.2.6 overleaf. The ^{13}C NMR spectrum of a sample of hydrogenated poly(5-tetradecylnorborene) is shown in Appendix B8 with no signals in the 130-135ppm region indicating; an absence of double bonds. FTIR spectra of the non-hydrogenated and hydrogenated polymer are compared in Appendix E6 (i) and (ii). The hydrogenated polymer (ii) shows a loss of the absorption band at υ = 967cm^{-1} which is associated with the *trans* vinylene C-H out of plane deformation, a loss of the absorption band at υ = 661cm^{-1} and a loss of the shoulder on the high frequency edge of the absorption band at υ = 735cm^{-1} which are associated with the *cis* vinylene C-H out of plane deformation. These bands are both present in the non-hydrogenated polymer (i). Thermogravimetric analysis (TGA) on the hydrogenated polymer ($27^{h/e}$), illustrated in Appendix H1, as a plot of % weight of polymer remaining verses temperature, shows a slow weight loss up to 400°C with a 10% weight loss at 430°C, a similar weight loss pattern is observed for polymer 25^{h}.

Expt. No.	**Mn ($\times 10^4$)**	**PDI (M_w/M_n)**	**Mpt (°C)**
$25^{h/d}$	6.7	2.4	14
26^{h}	2.6	3.7	11
$27^{h/e}$	2.7	2.0	11
$27B^{h/e}$	4.5	2.1	15

TABLE 4.2.6.

Hydrogenation under the conditions described above results in a reduction in the molecular weight of the polymer. Molecular weight degradation under these conditions is known in the literature,[100,101] and it is established that the use of a mixture of p-toluenesulfonylhydrazide and tri-n-propyl amine minimises the effect.[101] In this work the degradation of the molecular weight was not an unfavourable reaction and the alternative method of hydrogenation was not attempted.

(iv) (±)-*Exo/endo*-5-hexadecylnorbornene

Similar polymerisation reactions to those already described for (±)-*exo/endo*-5-tetradecylnorbornene in section 4.2.1(iii) were carried out using (±)-*exo/endo*-5-hexadecylnorbornene as the monomer. Reaction conditions, yields and results from GPC and DSC analyses are given in tables 4.2.7 and 4.2.8 overleaf.

Expt. No.	Monomer (mmol)	Catalyst (mmol)	Co-catalyst (mmol)	Solvent[a] (cm^3)	CTA %	Temp.[b] (°C)	Time (min)	Yield[c] (%)
28	12.6	0.125	0.5	T(45)	10	RT	120	72.5
29	12.6	0.25	1.0	T(45)	15	RT	120	85
30	12.6	0.25	1.0	T(45)	15	RT	120	80

TABLE 4.2.7.

Recovered polymer

Expt. No.	Mn ($x10^4$)	PDI (M_w/M_n)	Mpt (°C)
28^r	7.1	2.8	29
29^r	6.1	2.4	31
30^r	4.0	2.2	31

TABLE 4.2.8.

DSC analysis showed, as for (±)-*exo/endo*-5-tetradecylnorbornene, a large Tm. A Tg was not observed. This suggests that poly(5-hexadecylnorbornene) has a large proportion of well-ordered or crystalline regions.

The peak melting temperatures for polymers 28^r, 29^r and 30^r do not follow their molecular weights as might be expected. If the temperature at the onset of melting (T_{onset}) is considered a trend can be seen more clearly. T_{onset} for the polymers 28^r, 29^r and 30^r are 4°C, -9°C and -13.5°C respectively. This decrease in T_{onset} temperature follows the decrease in the molecular weight of the polymers, as expected. The ^{13}C NMR spectrum of poly(5-hexadecylnorbornene) shows similar chemical shifts and splitting patterns to those described in section 4.2.1(vi) for poly(5-hexylnorbornene).

Hydrogenation

Expt. No.	Mn ($x10^4$)	PDI M_w/M_n	Mpt (°C)
28^h	4.1	2.0	30
$29^{h/e}$	5.1	2.4	30
$30^{h/e}$	1.4	2.7	30

TABLE 4.2.9.

The ^{13}C NMR spectrum of hydrogenated poly(5-hexadecylnorbornene) showed no signals in the olefinic region (130-135ppm) and FTIR on the hydrogenated sample gave similar results to those described for poly(5-tetradecylnorbornene) in section 4.2.1(iii); indicating an absence of double bonds. The melting temperatures of all the polymers are identical and in order to establish a trend it is necessary to consider T_{onset}. For polymers 28^h, 29^h and 30^h the T_{onset} temperatures are 1°C, 10°C and -2.7°C respectively. These results follow the decrease in the molecular weight of the polymers as would be expected. When examined by TGA polymer $30^{h/e}$ shows a slow weight loss up to 400°C with a 10% weight loss at 425°C, polymer $29^{h/e}$ shows a similar weight loss pattern.

(v) (±)-*Exo/endo*-5-decylnorbornene

Reaction conditions, yields for the polymerisation of (±)-*exo/endo*-5-decylnorbornene as well as the results from GPC and DSC analyses on the recovered polymer are given in tables 4.2.10 and 4.2.11 below.

Expt. No.	**Monomer (mmol)**	**Catalyst (mmol)**	**Co-catalyst (mmol)**	**Solvent[a] (cm^3)**	**CTA (%)**	**Temp[b] (°C)**	**Time (min)**	**Yield[c] (%)**
31	17	0.34	1.36	T(50)	15	RT	240	92

TABLE 4.2.10

Recovered polymer

Expt. No.	**Mn ($x10^4$)**	**PDI (M_w/M_n)**	**Tg (°C)**
31[r]	2.4	4.2	/

TABLE 4.2.11

^{13}C NMR Spectrum of the recovered polymer shows similar shifts and splitting patterns as described in 4.2.1(vi) for (±)-*exo/endo*-5-hexylnorbornene.

Hydrogenation

Expt. No,	Mn ($x10^4$)	PDI (M_w/M_n)	Tg (°C)
31[h/e]	2.4	2.6	-30

TABLE 4.2.12

Hydrogenation, in this instance, did not reduce the molecular weight of the polymer; as previously described for poly(5-hexacdecylnorbornene) and poly(5-tetradecylnorbornene). The ^{13}C NMR and FTIR spectra of the hydrogenated polymer gave results, which indicated an absence of double bonds, as already described in 4.2.1(iii) for poly(5-tetradecylnorbornene). Poly(5-decylnorbornene) shows a Tg not a melting point as previously seen for poly(5-tetradecylnorbornene) and poly(5-hexadecylnorbornene) this suggests, that in contrast to the latter polymers, poly(5-decylnorbornene) has of a large proportion of disordered or amorphous regions. When examined by TGA the polymer shows a slow loss of weight up to 325°C with a 10% weight loss at 420°C.

(vi) (±)-*Exo*/*endo*-5-hexylnorbornene

The ROMP of (±)-*exo*/*endo*-5-hexylnorbornene was carried out with the reaction conditions, as well as yields, DSC and GPC results obtained from the recovered polymer given in tables 4.2.13 and 4.2.14 below.

Expt. No.	Monomer (mmol)	Catalyst (mmol)	Co-catalyst (mmol)	Solvent[a] (cm^3)	CTA (%)	Temp[b] (°C)	Time (min)	Yield[c] (%)
32	22.5	0.45	1.8	T(50)	3.4	RT	360	93

TABLE 4.2.13

Recovered polymer

Expt. No.	Mn ($x10^4$)	PDI (M_w/M_n)	Tg (°C)
32[r]	3.2	3.0	-31

TABLE 4.2.14

^{13}C NMR Spectroscopy of the recovered polymer (Appendix B9) shows the presence of double bonds with multiple signals between 130-135ppm; the observed complexity of the splitting patterns is a result of *cis/trans, endo/exo* and HH, TT and HT sequence distribution effects on the signal from the double bond in the polymer backbone. The complexity of the system cannot be interpreted in detail from the available data. The signals with chemical shifts between 36-46ppm are associated with the carbons of the 5-membered ring and the splitting results from whether the nearest double bond is *cis* or *trans,* the unit is *endo* or *exo* and the location in a HH, TT or HT placement. The remainder of the spectrum can be assigned to the aliphatic chain with the chemical shift of the methyl group at 14ppm, the methylene group adjacent to the methyl at 23ppm, the methylene group adjacent to the five membered ring at 32ppm and the remaining methylene groups with chemical shifts between 28-30ppm. The spectrum is entirely consistent with the assigned structure but, apart from the recognition that the polymer does not have a simple uniform structure, no details of microstructure can be assigned.

Hydrogenation

The results obtained from the DSC and GPC analyses on the hydrogenated polymer are given in table4.2.15 below.

Expt. No.	**Mn ($x10^4$)**	**PDI (M_w/M_n)**	**Tg (°C)**
$32^{h/e}$	3.3	2.1	-20

TABLE 4.2.15

The ^{13}C NMR and FTIR spectra of the hydrogenated polymer gave results, which indicate an absence of double bonds, similar to those described in section 4.2.1(iii) for poly(5-tetradecylnorbornene). Again a Tg and not a Tm is observed for poly(5-hexylnorbornene) suggesting that, as for poly(5-decylnorbornene), this polymer has a large proportion of disordered or amorphous regions. TGA on the polymer shows a slow loss of weight up to 175°C and a 10% weight loss at 410°C.

(vii) Co-polymers

(a) (±)-*Exo*/*endo*-5-tetradecylnorbornene (A) and norbornene (NBE)

A co-polymerisation reaction between (±)-*exo*/*endo*-5-tetradecylnorbornene and norbornene was carried out using $MoCl_5/Et_2AlI$ as the catalyst system, at room temperature for 4hrs. The amounts of monomer, solvent, catalyst, co-catalyst and chain transfer agent used in the reaction along with the results from GPC and DSC analyses on the recovered polymer are given in table 4.2.16 below. The yield of recovered polymer was 90%.

Expt. No.	A (mmol)	NBE (mmol)	Solvent[a] (cm^3)	Catalyst (mmol)	Co-catalyst (mmol)	CTA (mmol)	Mn ($x10^4$)	PDI (M_w/M_n)	Mpt/Tg (°C)
33	15	15	T(60)	0.596	2.38	4.47	2.6	28	-13

TABLE 4.2.16.

When examined by DSC homopolymers of poly(5-tetradecylnorbornene) show a Tm; as discussed in section in 4.2.1(iii) and homopolymers of NBE show a Tg.[102] This polymer when examined by DSC shows only one broad transition which has characteristics of both a Tm and a Tg, see Appendix H2. It is possible that this represents two overlapping transitions with a Tm like peak resulting from the crystalline regions which are present in poly(5-tetradecylnorbornene) and a Tg resulting, in the main, from the amorphous regions which dominate in poly(norbornene); however this explanation is, at best, only provisional. A homopolymer of poly(5-tetradecylnorbornene) has a vinylic:methyl ratio of

1:1.5. For a 50:50 co-polymer of poly(5-tetradecylnorbornene) and norbornene the vinylic:methyl ratio is calculated to be 1:0.75. ^1H NMR on this polymer gives a spectrum from which a vinylic:methyl ratio can be calculated and in this example the ratio was found to be 1:0.9. The ratio 1:0.75 calculated for a 50:50 co-polymer did not take into consideration the incorporation of 1-octene which was present in the above reaction system. When recalculated to include the 1-octene which was present and assuming equal probabilities of incorporation of monomers, which were present in a 1:1 feed ratio, the ratio vinylic:methyl was computed to be 1:0.8. Thus, within experimental error, the experimental value of 1:0.9 and calculated value of 1:0.8 are in agreement and consistent with approximately equal probabilities of incorporation of the two monomers.

(b) (±)-*Exo*/*endo*-5-tetradecylnorbornene (A) and norbornene (NBE)

Following the co-polymerisation reaction, described above, five small scale experiments were carried out in order to study the incorporation of (±)-*exo*/*endo*-5-tetradecylnorbornene and norbornene in the co-polymerisation reaction. The apparatus illustrated in Appendix F(ii) was used for these reactions. The reagents used in fixed concentrations for the experiments were $MoCl_5$ (0.0382mmoles), Et_2AlI (0.153mmoles), 1-octene (0.382mmoles) and toluene (6mls). The reactions were carried out at room temperature for 240mins, yields of recovered polymer varied between 75-90%. Table 4.2.17 overleaf gives the amounts of monomer used in each reaction. A comparison between the vinylic:methyl ratio expected from the monomer feed ratio and the ratio calculated from the ^1H NMR spectra of the recovered polymers is also given. The expected values for these ratios agree, assuming random incorporation and within experimental error, with the observed values.

Expt. No.	A (mmol)	NBE (mmol)	VINYLIC:METHYL expected	 calculated	Mn (x10^4)	PDI (M_w/M_n)
34	1.72	0.19	1:1.27	1:1.3	2.4	2.5
35	1.43	0.48	1:1.09	1:1.03	0.95	3.8
36	0.95	0.95	1:0.81	1:0.8	1.0	3.7
37	0.48	1.43	1:0.52	1:0.6	1.0	4.4
38	0.19	1.72	1:0.35	1:0.4	3.2	3.4

TABLE 4.2.17.

As already discussed in 4.2.1(vii) when examined by DSC samples of poly(norbornene) and poly(5-tetradecylnorbornene) show a Tg and a Tm respectively. These co-polymers when examined by DSC show only one transition with a gradual change from a Tm dominated trace to a Tg dominated trace as the % of norbornene in the system is increased. Appendix H3 reproduces the experimental data showing only a Tm for polymer 34 and only a Tg for polymer 38 with polymers 35, 36 and 37 showing a gradual change involving the loss of crystallinity. TGA of these co-polymers shows a slow weight loss between 353-404°C with a 10% loss of weight being achieved between 420-430°C.

(c) (±)-*Exo/endo*-5-hexylnorbornene (B) and norbornene (NBE)

The series of experiments described above were repeated in order to examine the co-polymerisation of (±)-*exo/endo*-5-hexylnorbornene and norbornene. Reagents used in fixed concentration for the five experiments were $MoCl_5$ (0.0625mmoles), Et_2AlI (0.25mmoles), 1-octene (0.625mmoles) and toluene (6mls). The reactions were carried out at room temperature for 240mins and yields of recovered polymers were between 78-90%. Table 4.2.18 overleaf gives the amounts of monomer used in the reactions along with the expected and observed vinylic:methyl ratios. The expected and observed vinylic:methyl ratios agree, within experimental error for co-polymers 39-41. The measured vinylic:methyl ratio for polymers 42 and 43 show a larger deviation from the expected values. These polymers, according to the calculated vinylic:methyl ratio contain more methyl groups than expected, from the stoichiometry of the reaction, suggesting that monomer B is more reactive than norbornene. This co-polymerisation reaction was repeated and similar vinylic:methyl ratios were calculated.

Ref	B	NBE	VINYLIC:METHYL		Mn	PDI
	(mmol)	(mmol)	expected	calculated	(x10^4)	(M_w/M_n)
39	2.81	0.31	1:1.27	1:1.2	6.1	2.0
40	2.34	0.78	1:1.09	1:1.08	4.7	2.2
41	1.56	1.56	1:0.81	1:0.93	3.9	2.2
42	0.78	2.34	1:0.52	1:0.76	3.1	2.4
43	0.31	2.81	1:0.35	1:0.76	1.0	2.1

TABLE 4.2.18.

When examined by DSC homopolymers of both poly(norbornene) and poly(5-hexylnorbornene) show a Tg. DSC analysis of the above polymers showed a single Tg implying that a random co-polymer was formed or; to be more precise that there is insufficient tendency to blockiness to produce separate phases with separate Tgs. When examined by TGA these polymers showed a 10% loss of weight achieved between 253-365°C.

4.2.2 Polymerisation using $WCl_6/SnMe_4$

There exist many examples of tungsten based catalyst systems which are effective for ROMP.[9] Norbornene has been polymerised many times using $WCl_6/SnMe_4$ as the catalyst system with chlorobenzene as the solvent.[98] As the monomers to be polymerised in this work are alkyl derivatives of norbornene, $WCl_6/SnMe_4$ was the catalyst system of choice for these reactions. The initiator precursor solutions were either were 0.2M tungsten hexachloride in dry chlorobenzene or 0.05M tungsten hexachloride in dry toluene; tetramethyltin was used neat. The ratio of catalyst:co-catalyst used was 1:2.

(i) (±)-*Exo/endo*-5-tetradecylnorbornene

Using 0.2M tungsten hexachloride in chlorobenzene (0.09mmoles), tetramethyltin (0.19mmoles) and (±)-*exo/endo*-5-tetradecylnorbornene (10.3mmoles) in dry chlorobenzene (3mls, 0.35% solution w/v) a rubbery polymer was recovered (60% yield) Mn=2.8x10^4 PDI=6.5. All other reactions using the same concentrations of catalyst, co-catalyst and monomer but increasing the amount of chlorobenzene (0.35% to 0.035% solutions w/v) either gelled or failed to polymerise even those in which trans-4-oct-1-ene (5%) was used as chain transfer agent. These results are anomalous; closely related reactions invariably gave soluble polymers (see below). A satisfactory explanation has not been established.

(ii) (±)-*Exo/endo*-5-hexadecylnorbornene

The polymerisation of (±)-*exo/endo*-5-hexadecylnorbornene using 0.2M tungsten hexachloride in dry chlorobenzene yielded white waxy soluble polymers. Reaction conditions and yields are illustrated in table 4.2.19 below.

Expt. No.	**Monomer (mmol)**	**Catalyst (mmol)**	**Co-Catalyst (mmol)**	**Solvent[a] (cm^3)**	**Temp[b] (°C)**	**Time (min)**	**Yield[c] (%)**
44	9.4	0.09	0.19	C(3)	RT	2	70
45	9.4	0.09	0.19	C(10)	RT	2	68
46	9.4	0.09	0.19	C(10)	RT	3	81
47	14	0.14	0.29	C(18)	RT	1.5	90

TABLE 4.2.19.

Recovered polymers

The results from DSC and GPC analyses on the recovered polymers are tabulated overleaf.

Expt. No.	**Mn ($x10^4$)**	**PDI (M_w/M_n)**	**Mpt. (°C)**
44^r	3.0	1.8	29
45^r	8.4	2.0	34
46^r	10	1.8	38
47^r	3.8	2.7	/

TABLE 4.2.20.

^{13}C NMR of the recovered polymer, illustrated in Appendix B10, shows similar chemical shifts to those already described in section 4.2.1(vi) for poly(5-hexylnorbornene).

Hydrogenation

Hydrogenation of these polymers was carried out as described in section 4.1.4 and the GPC and DSC results from analyses of the recovered polymers are tabulated below.

Expt. No.	**Mn ($x10^4$)**	**PDI (M_w/M_n)**	**Mpt. (°C)**
44^h	2.4	2.0	29
$(45^h+46^h)^{e/d}$	4.9	1.7	37
$47^{h/e}$	2.7	2.3	23

TABLE 4.2.21.

After hydrogenation a reduction in molecular weight of these polymers is observed this phenomenon has been described previously in section 4.2.1(iii); in relation to polymer prepared using $MoCl_5/Et_2/AlI$ initiation. ^{13}C NMR of the hydrogenated polymer gave results, indicating an absence of double bonds, similar to those already described in section 4.2.1(iii) for poly(5-tetradecylnorbornene). The FTIR spectra of non-hydrogenated and hydrogenated poly(5-hexadecylnorbornene) are compared in Appendix E7. The hydrogenated polymer (ii) shows a loss of the absorption band at $\upsilon = 967cm^{-1}$ associated with the *trans* vinylene out of plane deformation, a loss of the absorption band at $\upsilon = 680cm^{-1}$ (very weak) and a loss of the shoulder on the high frequency edge of the absorption band at $\upsilon = 736cm^{-1}$ which are associated with the *cis* vinylene C-H out of plane deformation.

When examined by TGA polymer $(45^h+46^h)^{e/d}$ showed a slow weight loss up to 395°C with a 10% loss of weight at 450°C, a similar weight loss pattern was observed from TGA on polymer $47.^{h/e}$

(iii) Chain transfer studies

These chain transfer studies were carried out using 1-octene as the CTA and the initiator precursor solution was 0.05M tungsten hexachloride in dry toluene; tetramethyltin was used neat. Using the same CTA and the same catalyst:monomer ratio the results may be compared to the chain transfer studies described in section 4.2.2(ii) which used $MoCl_5/Et_2/AlI$ initiation.

(a) (±)-*Exo/endo*-5-tetradecylnorbornene

A series of small scale chain transfer studies were carried out using (±)-*exo/endo*-5-tetradecylnorbornene. Table 4.2.22 below gives the catalyst:monomer ratio, %CTA, as well as the molecular weight and the molecular weight distribution of the recovered polymer. Yields of recovered polymer were between 84-87%.

Expt. No.	**Mn ($x10^3$)**	**CAT:MON**	**Solvent[a] (cm^3)**	**CTA (%)**	**Time (mins)**	**PDI (M_w/M_n)**
48	5.7	1:100	T(6)	10	240	2.5
49	5.1	1:100	T(6)	20	240	2.0
50	2.9	1:100	T(6)	30	240	1.9
51	2.2	1:100	T(6)	40	240	1.8
52	1.8	1:100	T(6)	50	240	1.7
53	11	1:50	T(6)	10	240	1.6
54	7.8	1:50	T(6)	20	240	1.5
55	6.9	1:50	T(6)	30	240	1.5
56	5.7	1:50	T(6)	40	240	1.5
57	5.6	1:50	T(6)	50	240	1.5

TABLE 4.2.22.

The GPC traces recorded for the products of the above reactions are illustrated in Appendices G5(48-52) and G6(53-57) showing the reduction in molecular weight of the recovered polymers. The molecular weights of the recovered polymers in these chain transfer reactions are smaller, by approximately a factor of ten, than the molecular weights of the polymers that were prepared using $MoCl_5/Et_2AlI$ as the catalyst; these reaction systems are discussed in section 4.2.1(ii)a). These results indicate that 1-octene is more effective as a CTA for polymers that are prepared using $WCl_6/SnMe_4$ initiation compared to those polymers prepared using $MoCl_5/Et_2AlI$ initiation.

(b) (±)-*Exo/endo*-5-hexylnorbornene

The above chain transfer studies were repeated using (±)-*exo/endo*-5-hexylnorbornene. Table 4.2.23 below gives the catalyst:monomer ratio %CTA, as well as the molecular weight and molecular weight distribution of the recovered polymer. Yields of recovered polymer were between 78-90%.

Expt. No.	**Mn ($x10^3$)**	**CAT:MON**	**Solvent[a] (cm^3)**	**CTA (%)**	**Time (mins)**	**PDI (M_w/M_n)**
58	5.9	1:100	T(6)	10	240	1.6
59	5.1	1:100	T(6)	20	240	1.6
60	3.9	1:100	T(6)	30	240	1.6
61	3.5	1:100	T(6)	40	240	1.4
62	3.4	1:100	T(6)	50	240	1.5
63	0.9	1:50	T(6)	10	240	1.7
64	1.0	1:50	T(6)	20	240	1.7
65	0.79	1:50	T(6)	30	240	1.5
66	0.68	1:50	T(6)	40	240	1.6
67	0.56	1:50	T(6)	50	240	1.5

TABLE 4.2.23.

The GPC traces of the above polymers are illustrated in Appendices G7(58-62) and G8(63-67) showing the reduction in molecular weight which is obtained as the % of 1-octene in the reaction system is increased. The Mn values are again smaller by a factor of ten when compared with those obtained in section 4.2.1(ii)b) for the polymerisation of (±)-*exo/endo*-5-hexylnorbornene using 1-octene as the CTA but with $MoCl_5/Et_2AlI$ as the initiator.

(iv) Co-polymers

Co-polymerisation reactions identical to those discussed in sections 4.2.1(vii)b) & c) for (±)-*exo/endo*-5-tetradecylnorbornene and (±)-*exo/endo*-5-hexylnorbornene with norbornene, which used $MoCl_5/Et_2AlI$ initiation, were carried out using the same monomers but using $WCl_6/SnMe_4$ initiation. 0.05M tungsten hexachloride in dry toluene and neat tetramethyltin were used for the co-polymerisation reactions.

(a) (±)-*Exo/endo*-5-tetradecylnorbornene (A) and norbornene (NBE).

Reagents used in constant concentration for these reactions were, WCl_6 (0.0382mmoles), $SnMe_4$ (0.0764mmoles), 1-octene (0.382mmoles) and toluene (6mls). Monomer concentrations used in the reactions, the molecular weight and molecular weight distribution of the recovered polymers and the expected and observed vinylic:methyl ratios are given in table 4.2.24 below. The reactions were carried out for 240mins at room temperature with yields of recovered polymers between 80-95%.

Expt. No.	**A (mmol)**	**NBE (mmol)**	**VINYLIC:METHYL**		**Mn ($x10^2$)**	**PDI (M_w/M_n)**
			expected	**observed**		
68	1.7	0.19	1:1.35	1:1.2	8.9	1.3
69	1.4	0.48	1:1.13	1:0.94	10	1.4
70	0.96	0.96	1:0.5	1:0.86	12	1.4
71	0.48	1.4	1:0.4	1:0.72	9.2	1.3
72	0.19	1.7	1:0.15	1:0.6	8.3	1.3

TABLE 4.2.24.

As discussed in section 4.2.1(vii)a) homopolymers of poly(5-tetradecylnorbornene) and poly(norbornene) show a Tm and a Tg respectively. DSC analyses of polymers 68-72 (Appendix H4) illustrates the gradual reduction in crystallinity which is observed as the proportion of NBE in the co-polymer increases. TGA on these co-polymers show a slow loss of weight upto 310-340°C with a 10% loss of weight between 360-390°C.

(b) (±)-*Exo/endo*-5-hexylnorbornene (B) and norbornene (NBE)

The above series of reactions were repeated in order to study the co-polymerisation of (±)-*exo/endo*-5-hexylnorbornene and norbornene using WCl$_6$/SnMe$_4$ initiation. Reagents used in constant concentrations were WCl$_6$ (0.0625mmoles), SnMe$_4$ (0.1248mmoles), 1-octene (0.627mmoles) and toluene (6mls). Monomer concentrations used in the reactions and the expected and observed vinylic:methyl ratios, for the co-polymers, are given in table 4.2.25 below. The reactions were carried out for 240mins at room temperature and yields of recovered polymers were between 78-93%.

Expt.	B	NBE	VINYLIC:METHYL		Mn	
No.	(mmol)	(mmol)	expected	calculated	Major(x10^5)	Minor(x10^3)
73	2.81	0.31	1:1.27	1:1.4	1.8	3.4
74	2.34	0.78	1:1.09	1:1.25	1.7	2.5
75	1.56	1.56	1:0.81	1:0.9	1.0	2.5
76	0.78	2.34	1:0.52	1:0.7	1.1	2.2
77	0.31	2.81	1:0.35	1:0.6	0.8	1.9

TABLE 4.2.25.

The GPC traces for these reactions show a bimodal distribution with the minor, lower molecular weight component being approximately 10% of the main component. Such a bimodal distribution has not been observed for any of the previous co-polymerisation reactions. This observation suggests that there is some process which generates low molecular weight by-product. This process maybe a consequence of the high activity of the $WCl_6/SnMe_4$ initiator system used in this co-polymerisation. The DSC traces of these polymers show only one, Tg dominated, transition as illustrated in Appendix H5. TGA of these co-polymers show a slow weight loss upto 355-385°C with a 10% loss of weight at 405-420°C.

4.2.3 Polymerisation using well-defined initiators

(i) Introduction

In order to prepare AB block co-polymers where A is the comb like segment and B is a polyethylene like segment (as discussed in Chapter 1 section 1.7.1) the well characterised initiators, which allow well-defined living polymerisation, are the initiator systems of choice. In favourable cases the addition and polymerisation of a second monomer can be achieved after the first monomer has been consumed. Such a reaction would yield an AB type block co-polymer. Living AB block co-polymers of norbornenes with benzonorbornadiene, 1-methyl norbornene and *endo/exo* dicyclopentadiene have been prepared with titanium based catalyst systems[103] and block co-polymers of norbornene and 5,6-dicarbomethoxy norbornene have been prepared using the well-characterised Schrock molybdenum initiators.[104]

Attempts to prepare co-polymers of the 5-substituted alkylnorbornenes, prepared in Chapter 3, with monocyclic olefins using well-defined initiators will be discussed in this section.

(ii) Polymerisation of (±)-*exo/endo*-5-hexyl and 5-decylnorbornene

Polymerisation of (±)-*exo/endo*-5-hexyl and 5-decylnorbornene was attempted using $Mo(NAr)(O\text{-}t\text{-}Bu)_2(CHC(CH_3)_2Ph)$ as the initiator. The ultimate objective of these reactions was the synthesis of AB block co-polymers. In order to prepare well-defined block co-polymers it is necessary to consume all the initiating alkylidene before the addition of the second monomer. In these polymerisation reactions the A portion of the co-polymer would be either poly(5-hexylnorbornene) or poly(5-decylnorbornene) and the B portion a poly(alkenemer). ^{1}H NMR Spectroscopy was used to examine the consumption of the initiating alkylidene during these reactions. Earlier studies of co-polymerisations[103,104] report reaction procedures which vary the amount of solvent used to prepare block co-polymers. The reactions discussed below use deuterated solvents, in varying dilutions, so the consumption of the initiating alkylidene can be observed by ^{1}H NMR spectroscopy. (±)-*Exo/endo*-5-hexylnorbornene (0.364mmoles) dissolved in C_6D_6 (500μl) was added to a stirred solution of $Mo(NAr)(O\text{-}t\text{-}Bu)_2(CHC(CH_3)_2Ph)$ (0.0182mmoles) in C_6D_6 (500μl). ^{1}H NMR spectrum showed broad peaks consistent with the monomer being converted to polymer. The initiating alkylidene was still present at 11.23ppm, indicating that propagation was faster than initiation. Two new sets of doublets were observed at 11.63ppm and 11.56ppm associated with the living chain end presumably arising from the *exo/endo* and/or HT/TH isomers of the propagating chain end. The septet of the initiator was present at 4.05ppm with a new septet at 3.85ppm. After 60hrs no peaks associated with the propagating species were present, but the initiating alkylidene and associated septet were still visible. This reaction was repeated with identical results.

Increasing the amount of solvent used from 1ml total to 3mls total and using $CDCl_3$ as the solvent gave similar results; that is the initiating alkylidene was not all consumed although the monomer had polymerised.

Similar dilute polymerisations were carried out using (±)-*exo/endo*-5-decylnorbornene. Again these reactions did not consume all the initiating alkylidene although polymerisation of the monomer was complete.

As these trial reactions did not result in complete consumption of the initiating alkylidene it was not possible to add a second monomer, such as a monocyclic olefin, in order to prepare well-defined AB block co-polymers. Addition of a second monomer in reactions where the initiating alkylidene is still present would result in a mixture of homo and co-polymers. In order to prepare well-defined block co-polymers using these alkyl substituted norbornenes it will be necessary perhaps to move to a more dilute solvent system[104] or use an initiator which is less reactive with respect to these monomers. These alternative systems could perhaps provide polymerisation reactions for these alkyl norbornenes which would allow complete consumption of the initiating alkylidene. This would allow, in favourable cases, the synthesis of well-defined AB block co-polymers by the addition and polymerisation of a second monomer after the first monomer had been consumed. Time did not allow for a thorough examination of all the variables which might influence the successful generation of a well-defined living system from this class of monomer.

4.3 ACETOXY SUBSTITUTED CYCLIC OLEFINS

4.3.1 Introduction

As discussed in Chapter 1 section 1.7.2, one of the author's objectives was the polymerisation of 1-acetoxy-4,8-cyclododecadiene in order to yield, after hydrogenation, a model EVA type polymer.

Metathesis catalysts that will tolerate functionalities have long been sought.[9,10] In the well defined Schrock type initiators, which have been most successful in tolerating functional substituents, the metal centre shows electrophilic character and therefore there may be some interaction with a potential donor other than the π-electrons of the carbon carbon double bond. Norbornenes with acetate functionalities have been polymerised using well-defined molybdenum initiators[37] and classical tungsten based systems.[105] Tungsten based systems have also been used for the polymerisation of 1,3-acetoxycarbonylbicyclo[1,10]trideca-trans-4-trans-8-diene[106] and 1,5,9-cyclododecatriene.[107] Generally it has been found that the inhibitory effects of polar groups are not as pronounced when the groups are attached to a strained cyclic olefin; that is the release of ring strain provides a driving force for metathesis which outweighs the inhibiting effect of the substituent.[108] The reactivities of classical catalyst systems cannot be systematically controlled, it is possible however that a well-defined initiator could be tailored so that it will react only with the double bond and not with a functionality.[37] The polymerisation of 1-acetoxy-4,8-cyclododecadiene using classical catalysts and well-characterised initiators is examined in this section, following general procedures outlined in section 4.1.3.

4.3.2 Polymerisation using classical initiator systems.

Attempts to polymerise 1-acetoxy-4,8-cyclododecadiene and/or 1,2-epoxy-5,9-cyclododecadiene using classical catalysts are discussed below. The reactant solutions were 0.25M diethylaluminiumiodide and diethylaluminiumchloride both in dry toluene; 0.05M tungsten hexachloride and 0.05M molybdenum pentachloride/3.0M ethylacetate both in dry toluene, tetramethyltin was used neat. Amounts of catalyst, co-catalyst, monomer and solvent used are given in table 4.3.1 below.

Expt. No.	**Monomer (mmol)**	**Catalyst (mmol)**	**Co-catalyst (mmol)**	**Solvent[a] (cm^3)**
78	1-acetoxy-4,8-cyclododecadiene (4.5)	WCl_6 (0.045)	$SnMe_4$ (0.09)	T(10)
79	1-acetoxy-4,8-cyclododecadiene (2.25)	$MoCl_5$ (0.0225)	Et_2AlI (0.09)	T(10)
80	1,2-epoxycyclododecad-1,5-diene (2.8)	$MoCl_5$ (0.028)	Et_2AlCl (0.112)	T(10)

TABLE 4.3.1.

The attempted polymerisation of 1-acetoxy-4,8-cyclododecadiene with tungsten hexachloride resulted in deactivation of the catalyst solution when it was added to the monomer solution. This was indicated by a colour change of the solution, brown to green/blue on stirring, and the addition of (±)-*exo*/*endo*-5-hexylnorbornene (0.5mls) to this solution gave no polymer. Polymerisation of 1-acetoxy-4,8-cyclododecadiene with molybdenum pentachloride and diethylaluminiumiodide showed no colour change when the catalyst solution was added to the monomer solution. No polymer was present in the system after stirring for 24hrs. The reaction mixture was then split into two portions, (±)-*exo*/*endo*-5-hexylnorbornene (0.5mls) was added to one portion and the second portion was warmed to 40°C for 12hrs. The warmed solution gave a colour change from brown to light red with dark red/brown solids precipitated, again no polymer was recovered. A polymer was recovered from the first portion but the FTIR showed no acetoxy groups present; suggesting that although the catalyst was not deactivated by 1-acetoxy-4,8-cyclododecadiene only (±)-*exo*/*endo*-5-hexylnorbornene had polymerised.

The polymerisation of 1,2-epoxycyclododecadiene, the starting material for the preparation of 1-acetoxy-4,8-cyclododecadiene, was attempted using molybdenum pentachloride and the more active diethylaluminiumchloride as the co-catalyst. The results from this reaction were identical to those obtained for the attempted polymerisation of 1-acetoxy-4,8-cyclododecadiene with molybdenum pentachloride and diethylaluminiumiodide (see above).

Following these results, attempts to polymerise 1-acetoxy-4,8-cyclododecadiene were continued using well-defined molybdenum initiators of the Schrock type.

4.3.3 Polymerisation using Mo(NAr)(CHCMe$_2$Ph)(O-tBu)$_2$

1-Acetoxy-4,8-cyclododecadiene (121mg, 5.46x10^{-1}mmoles) in C_6D_6 (500μl) was added to Mo(NAr)(CHCMe$_2$Ph)(O-tBu)$_2$ (10mg, 1.82x10^{-2} mmoles) in C_6D_6 (500μl) with stirring. The initiating alkylidene is observed in the ^{1}H NMR spectrum at 11.26ppm (Appendix C9). After 1hr part of a possible triplet is observed on the low field side of the initiating alkylidene and a new set of complex multiplets is observed at 3.83ppm. The septet associated with the initiator is present at 3.9ppm (associated with the CH protons of the isopropyl group on the phenyl ring). A new set of complex overlapping multiplets is observed and not a simple septet as the monomer has two possible sites for ring opening thus the propagating species may possess a variety of different stereochemical arrangements giving rise to several slightly different chain ends. Considering the ^{1}H NMR spectrum of the monomer (Appendix C8) the shift associated with the protons α to the acetoxy group is present at 4.85ppm with the vinylic region between 5.1 and 5.5ppm consisting of three major absorptions. In the spectrum of the polymerising mixture (Appendix C9) these regions show changes with the peaks at 4.85ppm no longer visible and the vinylic region consisting of four major absorptions between 4.97 and 5.5ppm. These observations could correspond to the formation of a new propagating species from the insertion and ring opening of 1-acetoxy-4,8-cyclododecadiene. After 36hrs no further change was observed in the spectrum and no polymer was recovered; as a result of these observations a more active initiator was studied (see below).

4.3.4 Polymerisation using Mo(NAr)(CH-t-Bu)(O-CMe$_2$CF$_3$)$_2$

The conditions used for the attempted polymerisation of 1-acetoxy-4,8-cyclododecadiene with the more active initiator, Mo(NAr)(CH-t-Bu)(O-CMe$_2$CF$_3$)$_2$, are shown in table 4.3.2 overleaf. The results are discussed in more detail below.

Expt. No.	Solvent ($1cm^3$)	Temp (°C)	CAT ($mmolx10^{-2}$)	MONOMER ($mmolx10^{-1}$)
81	C_6D_6	RT	1.68	6.1
82	C_6D_6	RT	1.68	5
83	C_6D_6	RT	1.68	5
84	C_6D_6	RT	1.68	5
85	C_6D_6	40	1.68	5
86	$CDCl_3$	0	1.68	5
87	THF	RT	1.68	6.1
88	C_6D_6:THF 60:40	RT	1.68	5
89	C_6D_6:THF 80:20	RT	1.68	5
90	C_6D_6:$PhCF_3$ 50:50	RT	1.68	5

TABLE 4.3.2.

The ^{1}H NMR spectrum of reaction (81) in progress shows the initiating alkylidene at 11.58ppm and two new peaks at 11.39 and 11.36ppm (Appendix C10), possibly associated with the propagating chain ends. The septet of the initiator is present at 3.7ppm and a new set of complex multiplets is observed at 3.84ppm. A comparison of the ^{1}H NMR spectrum of the monomer (Appendix C8) with the ^{1}H NMR spectrum of the polymerising mixture (Appendix C10) shows changes which parallel those made in section 4.3.3; that is in the polymerising mixture the shift associated with the proton α to the acetoxy group is no longer visible and the vinylic region now consists of four major absorptions. These changes observed in the ^{1}H NMR spectrum could again be consistent with the insertion and ring opening of this monomer to yield several propagating species. After 4hrs there is no change in the ^{1}H NMR spectrum. After 24hrs the reaction solution was more viscous and a colour change was observed from pale yellow to dark brown. Also significant changes were observed in the ^{1}H NMR spectrum after 24hrs (Appendix C11). The peaks are broad, typical of a polymeric species, the vinylic protons being simplified into one main peak at 5.4ppm. The protons α to the acetoxy group appear at 5.0ppm with the aliphatic peaks appearing as a complex set of unresolvable broad peaks between 1 and 2.1ppm. The initiating alkylidene is still present at 11.57ppm with the initiating septet at 3.7ppm and a complex set of multiplets at 3.83ppm, possibly associated with the propagating species, no peaks are observed for the propagating alkylidenes at this stage.

The recovered polymer (yield 70%), with a $Mn=3.8x10^4$ and a PDI=1.6, has a molecular weight approximately five times larger than the 8000 expected, from the initiator:monomer ratio, and the polydispersity is greater than expected for a living system. The high molecular weight is not surprising as all the initiating alkylidene was not consumed during the course of the polymerisation reaction. When examined by DSC the polymer showed a Tg at -47°C and TGA of the polymer gave the degradation pattern illustrated in Appendix H6. The polymer shows a slow loss of weight upto 310°C. The weight loss then increases with 65% weight remaining at 395°C. The rate of weight loss then slows slightly before increasing again with 5% weight remaining at 555°C. The ^{1}H NMR spectrum illustrated in Appendix C12 shows broad peaks characteristic of a polymer. These peaks are difficult to resolve which is not surprising as the ring opening of 1-acetoxy-4,8-cyclododecadiene will produce a multitude of microstructutal and sequence possibilities. This monomer contains two carbon carbon double bonds which are available for ring opening. On ring opening each double bond will yield a slightly different polymer microstructure. 1-Acetoxy-4,8-cyclododecadiene is unsymmetrical and therefore there are possibilities for head/tail effects in the polymer.

Chiral centres and meso and racemic dyads are also possible in the ring opened polymer, finally the double bonds in the polymer backbone may be *cis* or *trans*. However the major features of the polymer spectra may be assigned. The vinylic carbons at 5.4ppm, the protons α to the acetoxy group at 4.85ppm with the remaining aliphatic peaks between 1.2 and 2.1ppm. The ^{13}C NMR spectrum illustrated in Appendix B11 also shows complex sets of peaks due to the wide variety of possible microstructures in the polymer. Main groups of peaks may be identified, the carbonyl carbon at 171ppm, the olefinic carbons around 130ppm, the protons α to the acetoxy group at 73.8ppm and the aliphatic carbons between 21-34ppm.

The ^{1}H NMR spectrum of the second polymerisation reaction (82) showed the same initial set of changes as already described for reaction 81. However this polymersiation reaction however did not show the broad peaks seen previously. The recovered polymer (yield 40%), with a $Mn=1.1x10^4$ and a PDI = 1.3, has a molecular weight approximately twice the expected molecular weight of 6600 expected from the initiator:monomer ratio. TGA shows a similar degradation pattern to that obtained for polymer 81. As this reaction did not appear to go to completion it is assumed that a mixture of monomer and polymer remain, in the reaction system, with some unestablished factor inhibiting the completion of the polymerisation reaction.

The polymerisation of 1-acetoxy-4,8-cyclododecadiene was repeated with the same conditions and also varying the type of solvent and the temperature, as shown in the table at the beginning of this section, in an attempt to reproduce the results that were obtained for Expt.No.81. The broad peaks seen in this polymerisation reaction were not obtained in any of the subsequent reactions. Small amounts of polymer may have been present in the polymerising mixture but as for Expt.No.82 no broad peaks, associated with a polymeric species, were visible in the ^{1}H NMR spectrum. Polymerisation with the more active $Mo(NAr)(CH\text{-}t\text{-}Bu)(OCMe(CF_3)_2)_2$ in deuterated benzene showed similar changes in the vinylic region to those already described but again no broad peaks associated with a polymeic species were detected.

A possible explanation for these results may be the interaction of the acetoxy residue with the metallaolefin. Such co-ordination of an in-chain acetoxy group with a living chain end might occur only for particular distances and stereochemistries of the chain between the living end and the substituent, if these circumstances occur relatively rarely, this could account for the changes that are observed during this reaction and such a co-ordination might prevent the polymerisation reaction going to completion. From these observations we can conclude that this polymerisation is experimentally feasible but that a more detailed analysis of the effects of catalyst, solvent and temperature is required before a reproducible polymerisation process can be established.

CHAPTER FIVE

POLYMER TESTING

5.1 GENERAL PROCEDURES

5.1.1 Apparatus

Optical microscopy was carried out using an Olympus BH2 microscope fitted with a phase contrast condenser and a CK10 objective. The temperature of the sample was varied using a Linkam THM 600 hot stage. The image from the microscope was monitored by a JVC KYF-30 video camera and relayed as a SVHS signal via a Linkam VTO 233 text overlayer, to a Sony VP-5000P mavigraph printer. Samples were prepared by placing a small amount of the polymer blend on a glass cover slide and compressing with another slide.[109]

Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer DSC7 which was calibrated using indium and zinc standards.

5.1.2 Fuel testing

The pour point is defined as the temperature at which the amount of wax which precipitates from the fuel is sufficient to cause the fuel to solidify, that is the temperature at which the fuel will no longer pour. In order to measure the pour point 50mls of fuel is cooled at 10°C per hour in a cold chamber. The fuel is regularly tipped over to see if it will still pour. The temperature at which it will no longer pour is recorded as the pour point. To determine the effect which a particular additive has on the pour point of the fuel a sample of the same fuel is treated with the additive at a known concentration. The treated fuel is then cooled as described above and the temperature at which it will no longer pour recorded.

Pour point tests are very straightforward, quick and easy as they do not involve any formulation studies with other cold flow additives. Pour point modifiers which are in use commercially are generally EVA type co-polymers although the FVA or comb type co-polymers are occasionally used. A pour point test is used to examine whether new additives, in this case comb type additives, will have any effect on modifying the cold flow properties of the fuel. If the results from these tests are favourable then a more detailed series of tests can be carried out in order to examine the effects these additives may have on different fuels and on different aspects of wax crystal modification. Such studies require considerable effort and the pour point test provides a useful preliminary screening test. The fuel testing was conducted in the sponsor's laboratory and here we shall only report the results of this preliminary screening procedure.[110]

5.2 POLYMER BLENDS

Two of the polymers, which were prepared as described in Chapter 4 (see below), were solution blended with an EVA co-polymer, supplied by the sponsor, in freshly distilled chloroform and solvent cast at room temperature.

Polymer Expt.No.	**M_n (10^4)**	**PDI M_n/M_w**
$25^{h/d}$	6.7	2.4
$(45^h+46^h)^{e/d}$	4.9	2.3

TABLE 5.2.1.

The resulting blends were examined using DSC and optical microscopy. DSC analysis of these polymer blends examined the effect that EVA has on the Tm of the comb type polymers and optical microscopy examined the miscibility of the blends as they were cooled, to room temperature, from the melt.

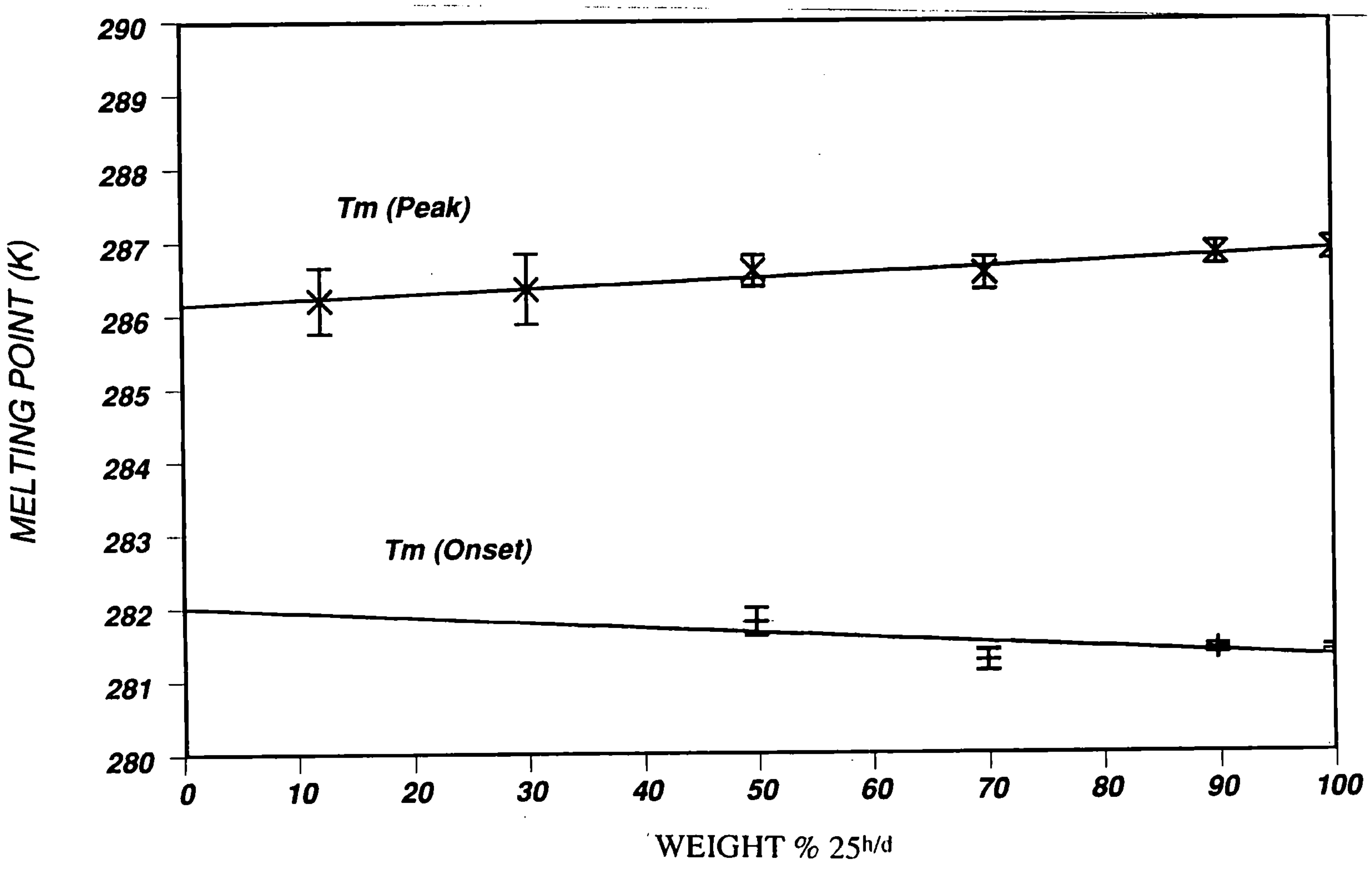


FIGURE 5.2.1 Melting point analysis in EVA:poly(5-tetradecylnorbornene)($25^{h/d}$)

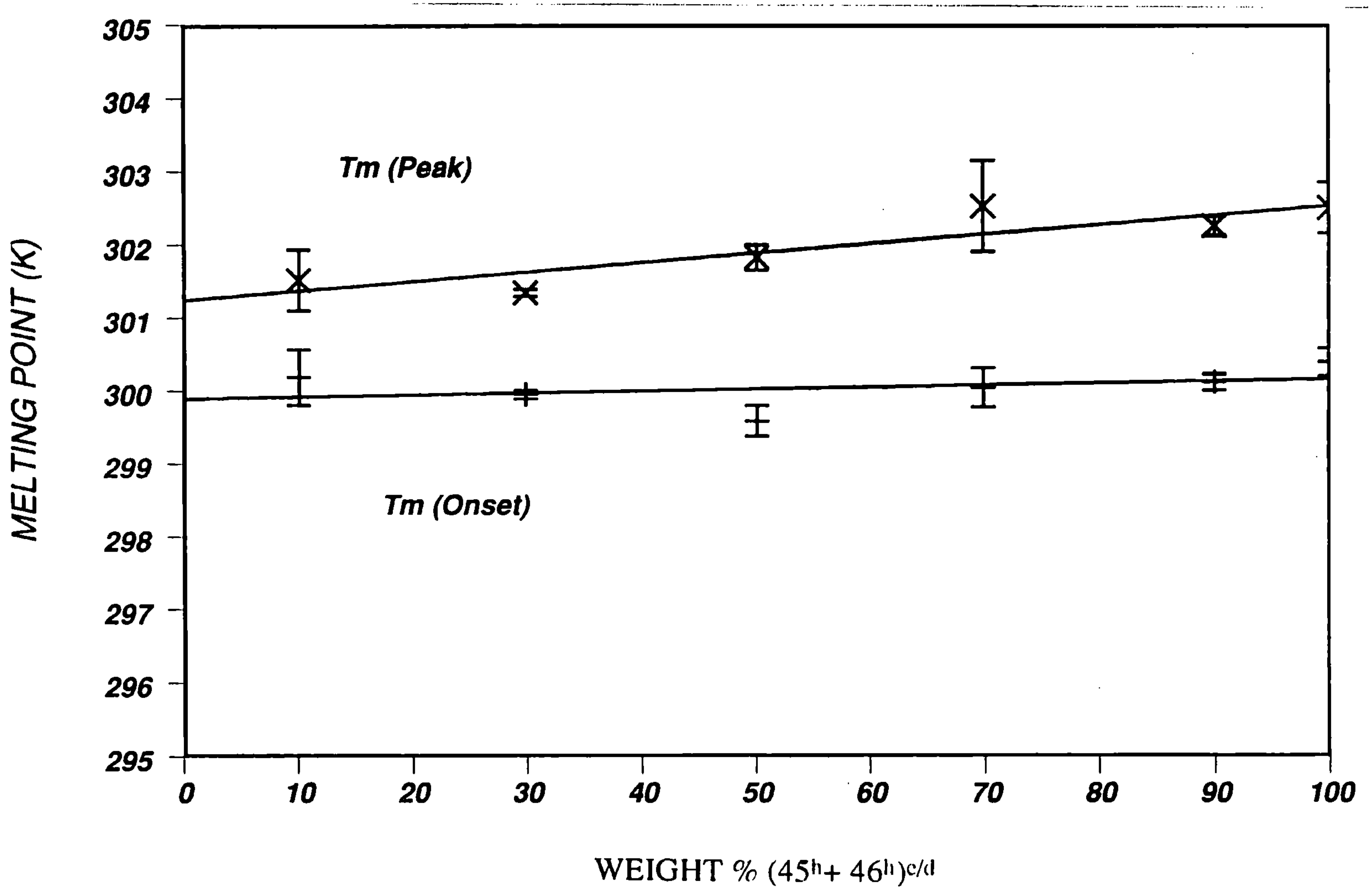


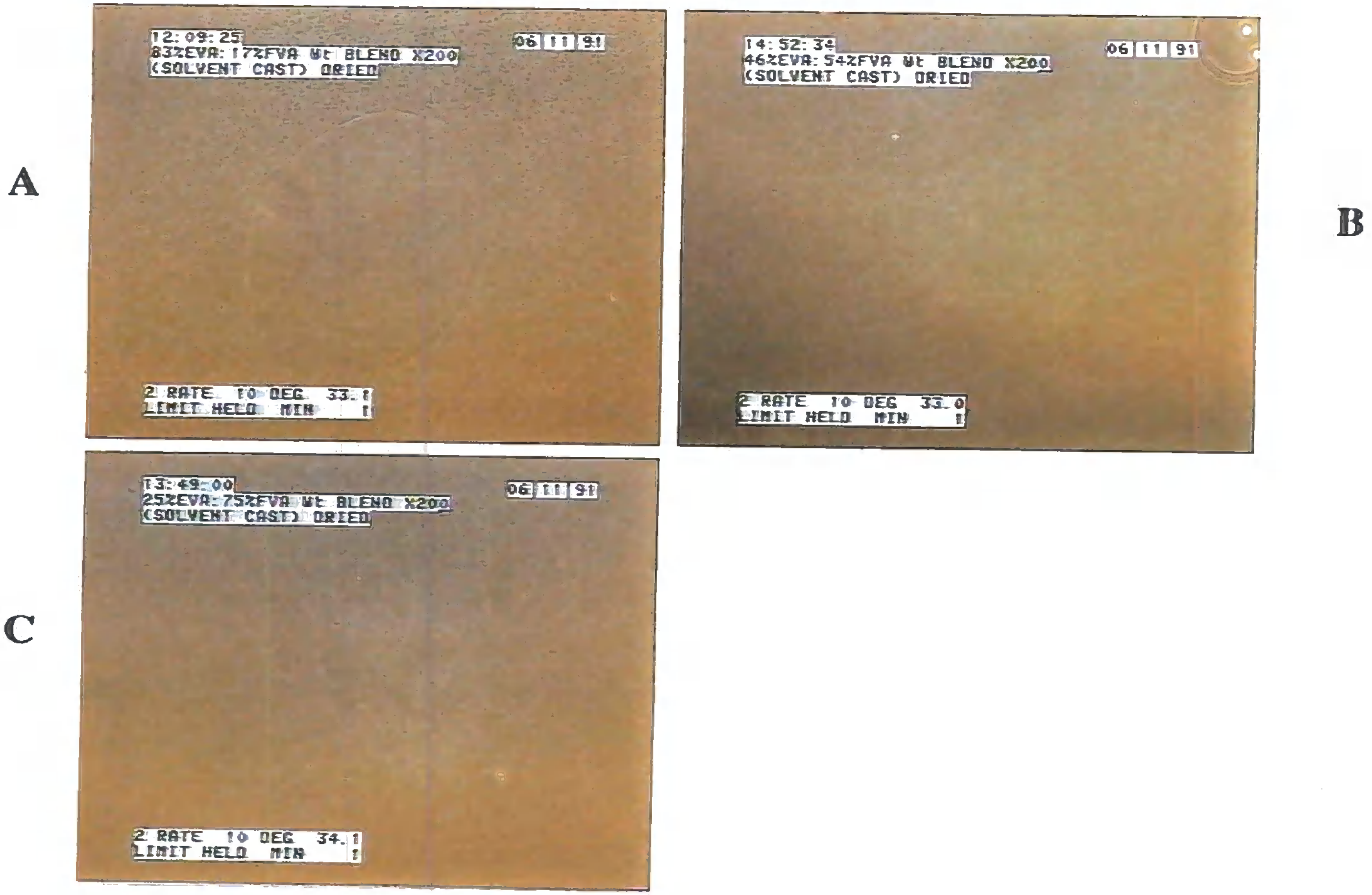
FIGURE 5.2.2 Melting point analysis in EVA:poly(5-hexadecylnorbornene)(45^h+46^h)$^{e/d}$

5.2.1 Melting point analysis

The melting point analyses for blends of poly(5-tetradecylnorbornene) ($25^{h/d}$) and EVA are recorded in Figure 5.2.1 as a plot of % weight poly(5-tetradecylnorbornene) against melting point. Figure 5.2.2 illustrates the melting point analysis for blends of poly(5-hexadecylnorbornene) ($(45^{h}+46^{h})^{e/d}$ and EVA. In these blends the melting temperatures, Tm_{peak} and Tm_{onset}, for both poly(5-tetradecylnorbornene) (Figure 5.2.1) and poly(5-hexadecylnorbornene) (Figure 5.2.2) show no depression as the % of EVA in the blend is increased. This is in contrast to the melting point analysis of blends of FVA and EVA, illustrated in Chapter 1 Figure 1.7.1, these blends show melting point depressions for FVA, Tm_{peak} and Tm_{onset}, which increase as the % of EVA in the blend is increased.

5.2.2 Optical microscopy

EVA and FVA are immiscible except at high temperatures or at high concentrations of EVA. Figure 5.2.3 illustrates optical micrographs of polymer blends of EVA and FVA, where A consists of 83% EVA, B of 46% EVA and C of 25% EVA. The small droplets and larger pools, that are visible in these micrographs, are assumed to be the EVA component finely dispersed in FVA.[109] All of these blends show a large degree of phase separation at room temperature the detailed form of which is a function of the temperature from which the blend is cooled, in this case 120°C. Figure 5.2.4 illustrates optical micrographs for blends of poly(5-tetradecylnorbornene) (25^{h}) and EVA where, A consists of 88% EVA, B of 70% EVA, C of 50% EVA and D of 10% EVA. Large phase separations were also observed for these blends at room temperature, they were cooled from a melt temperature of 70°C. This phase separation is similar to that already seen in Figure 5.2.3 for blends of EVA and FVA but there appears



5.2.3 Optical micrographs of EVA:FVA blends

FIGURE 5.2.4 Optical micrographs of EVA:poly(5-tetradecylnorbornene)($25^{h/d}$) blends

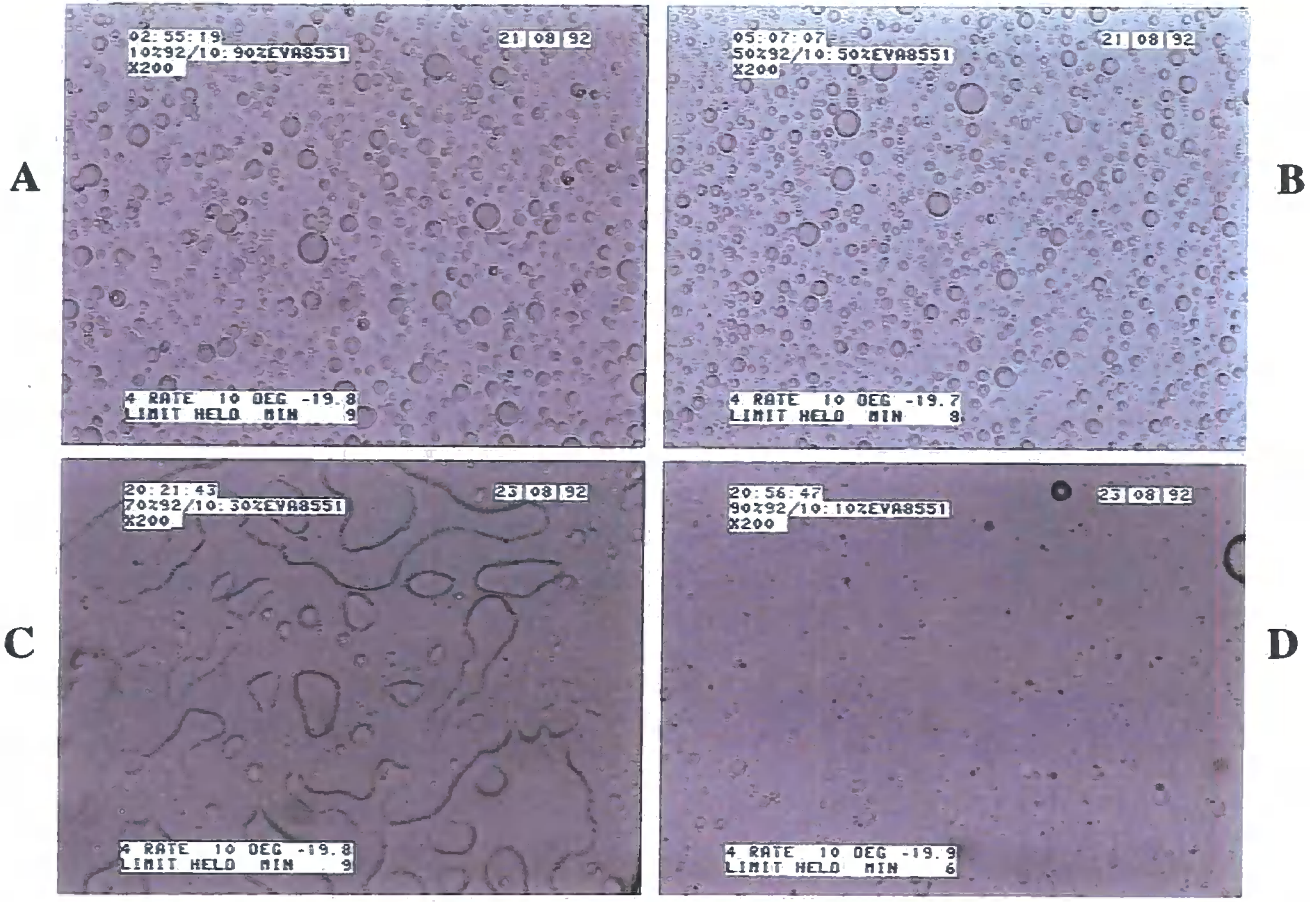


FIGURE 5.2.5 Optical micrographs of EVA:poly(5-hexadecylnorbornene)$(45^{h}+46^{h})e/d$ blends.

to be a preference to form a larger number of small immiscible droplets rather than the much larger pools noted in the EVA:FVA blends. A similar room temperature phase separation was observed for blends of EVA with poly(5-hexadecylnorbornene), cooled from a melt temperature of 70°C. The optical micrographs of these blends are illustrated in Figure 5.2.5 Where A consists of 90% EVA, B of 50% EVA, C of 30% EVA and D of 10% EVA.

5.3 POUR POINT

Some of the polymers prepared, as described in Chapter 4, and tabulated below have been tested in the sponsor's laboratory to examine the effect they may have on pour point. The results communicated are recorded here. Other samples await testing at the time of writing.

Polymer Expt.No.	**Mn ($\times10^4$)**	**PDI M_n/M_w**
C_{16} $29^{h/e}$	5.1	2.4
C_{16} $30^{h/e}$	1.4	2.7
C_{16} $47^{h/e}$	2.7	2.3
C_{14} $27^{h/e}$	2.7	2.0
C_6 $32^{h/e}$	3.3	2.1

TABLE 5.3.1.

C_{16} = poly(5-hexadecylnorbornene)
C_{14} = poly(5-tetradecylnorbornene)
C_6 = poly(5-hexylnorbornene)

These polymers were tested on two different types of fuel. Fuel① is classified as having a low wax content and a low final boiling point and fuel② is classified as having a high wax content and a low final boiling point. The results obtained from the pour point tests are shown in table 5.3.2 overleaf. Table 5.3.2 also shows the pour point for the untreated fuels and the pour points that were obtained for the fuels when they were treated with a) a conventional comb polymer with fourteen carbon atoms in the comb branches (CombC_{14}) and b) a conventional EVA additive (Pd25) which is used commercially to lower the pour point of diesel fuel.

		Fuel①	Fuel②
Additive	**Treat rate (ppm)**	**Pour point (°C)**	**Pour point (°C)**
None	N/A	-6	-6
CombC_{14}	300	-15	-19
	500	-15	-19
Pd25	300	-39	-27
	500	-39	-27
$C_{16}29^{h/e}$	300	-21	-9
	500	-21	-9
$C_{16}30^{h/e}$	300	-15	-9
	500	-15	-9
$C_{16}47^{h/e}$	300	-18	-9
	500	-15	-9
$C_{14}27^{h/e}$	300	-21	-15
	500	-21	-15
$C_{6}32^{h/e}$	300	-12	-9
	500	-12	-9

TABLE 5.3.2.

These new comb additives did not perform as well as the Pd25 (EVA) additive as a pour point depressant. This is not unexpected as comb type additives are not generally used as pour point depressants. If we compare the performance of these new polymers, as pour point depressants, with the conventional comb polymer (CombC_{14}) in fuel① these polymers performed well and in some instances better than the conventional comb polymer. In fuel② these new polymers did not perform as well as the conventional comb polymer, as a pour point depressant, they were not however totally ineffective and depressed the pour point of the fuel, which untreated was -6°C, by between 3-9°C.

The results obtained from these, admittedly qualitative, pour point tests indicate that these new comb type polymers have the effect of depressing the pour point of these fuels. It is hazardous, from such limited data, to draw conclusions with regard to the overall performance of these new comb type polymers as wax crystal modifiers. However the above results illustrate that these new comb polymers show a degree of wax crystal modification and merit more detailed testing. Such tests will examine their effects on improving the cold flow behaviour of other types of fuel along with their possible effects with regard to the different aspects of wax crystal modification. Their interactions with other cold flow improvers will also be examined. This detailed testing is currently underway in the sponsor's laboratory.

CHAPTER SIX

CONCLUSIONS AND PROPOSALS FOR FUTURE WORK

6.1 INITIAL OBJECTIVES

Chapter 1 Section 1.7 describes the author's proposals for the synthesis of some new polymeric materials as potential cold flow improvers for diesel fuel. These proposals may be divided into two main groups:-

a) The synthesis of a range of new comb polymers and co-polymers.

b) The synthesis of a model EVA polymer.

The objectives, described in detail in Chapter 1, are summarised below.

6.1.1 Hydrocarbon comb polymers and co-polymers

In order to prepare a range of new comb polymers with various comb lengths the ring opening metathesis polymerisation of a range of 5-substituted alkylnorbornenes was suggested. Co-polymerisation of these monomers with norbornene and monocyclic olefins using classical and well-defined initiators was also proposed. Using classical initiators co-polymerisation reactions would yield random co-polymers. AB Block co-polymers could be prepared, using well-defined initiators, by the sequential addition of monomers.

6.1.2 EVA Model

In order to prepare a model EVA type polymer it was proposed to synthesise an acetoxy substituted cyclic olefin. Ring opening of this monomer using well-defined initiators could, in favourable cases, yield a well-defined EVA type polymer where the vinyl acetate content and distribution would be accurately known. Such a polymer may provide insights into the mode of action of the EVA co-polymers which are currently in use as wax crystal modifiers.

6.2 MONOMERS

6.2.1 Alkyl substituted norbornenes

The synthesis, via a Diels-Alder reaction, of a range of 5-substituted alkylnorbornenes was achieved. Experimental details are described in Chapter 3. The characterisation of these monomers, using mass spectroscopy, ^{1}H NMR and ^{13}C NMR spectroscopy, is also discussed in Chapter 3.

6.2.2 Acetoxy substituted cyclic olefins

The syntheses and characterisation of 1,2-diacetoxy-5,9-cyclododecadiene and 1-acetoxy-4,8-cyclododecadiene are discussed in Chapter 3 section 3.3. The preparation of 1,2-diacetoxy-5,9-cyclododecadiene was not optimised and effort was concentrated on 1-acetoxy-4,8-cyclododecadiene, which is easier to purify, in order to yield an acetoxy substituted cyclic olefin for ring opening

6.3 POLYMERS

6.3.1 Hydrocarbon comb polymers and co-polymers

The 5-substituted alkylnorbornenes, prepared in Chapter 3, have been polymerised using classical molybdenum and tungsten based initiators to yield poly(5-alkylnorbornenes) with varying comb lengths. Details of the polymerisation reactions are given in Chapter 4 sections 4.2.1 and 4.2.2. The molecular weight of these poly(5-

alkylnorbornenes) may be controlled by the use of 1-octene as a chain transfer agent. Results from this work indicate that 1-octene is more effective in reducing the molecular weight of polymers which are prepared using $WCl_6/SnMe_4$ initiation, compared to those polymers prepared using $MoCl_5/Et_2AlI$ initiation. As discussed in Chapter 2, section 2.4.3, it has been noted that for high *cis* polymers a larger concentration of terminal olefins is necessary to reduce the molecular weight of a polymer to a particular level compared to the same polymer with a lower *cis* content.[56] The results obtained from the chain transfer studies carried out in this work suggest that the $WCl_6/SnMe_4$ initiator system produces polymers with a lower *cis* content compared to those polymers prepared using $MoCl_5/Et_2AlI$. FTIR analysis of non-hydrogenated poly(5-tetradecylnorbornene), prepared using $MoCl_5/Et_2AlI$, is illustrated in Appendix E6(i) and Appendix E7(i) illustrates FTIR analysis of poly(5-hexadecylnorbornene), prepared using $WCl_6/SnMe_4$ initiation. The spectra of both these materials are dominated by CH_2 absorptions. The absorption at $\upsilon = 661cm^{-1}$ (Appendix E6(i)) associated with the *cis* C-H out of plane deformation appears much stronger than the corresponding absorption at $\upsilon = 665cm^{-1}$ observed in Appendix E7(i). These absorptions are, admittedly qualitative, as both spectra are dominated by the CH_2 absorptions but they correlate well with the results obtained from the chain transfer studies; that is polymers prepared using $WCl_6/SnMe_4$ initiation posses a lower *cis* content compared to those polymers prepared using $MoCl_5/Et_2AlI$ initiation. These observations are not unexpected as many molybdenum based initiators produce polymers which show a greater bias for *cis* selectively compared to polymers prepared using tungsten based initiators.[9]

DSC analysis of these poly(5-alkylnorbornenes) show a Tm for poly(5-tetradecylnorbornene) and poly(5-hexadecylnorbornene). In contrast poly(5-decylnorbornene) and poly(5-hexylnorbornene) show only a Tg. These results suggest that the crystalline or ordered regions, which give rise to the Tm peak result, in the main, from side chain crystallisation.

Co-polymers of norbornene and the 5-substituted alkylnorbornenes have been prepared using classical tungsten and molybdenum based initiators. Experimental details and data analysis are given in Chapter 4 sections 4.2.1(vii) and 4.2.2(iv).

Attempts to synthesise well-defined comb/ethylene AB block co-polymers, using well defined molybdenum based Schrock type initiators, have been unsuccessful. Complete consumption of the initiating alkylidene was not achieved, following the addition of the first monomer, therefore addition of a second monomer would yield a mixture of homopolymers and co-polymers. Modification of experimental procedure and/or the use of an initiating system which gives a propagating chain end which is relatively less active, with respect to these 5-substituted alkylnorbornene monomers, may provide a means for the preparation of these well-defined AB block co-polymers. Experimental details of these attempted co-polymerisations are given in Chapter 4 section 4.2.3.

Initial test results, described in detail in Chapter 5, from the poly(5-alkylnorbornenes) gave promising results. When examined by DSC and optical microscopy blends of the poly(5-alkylnorbornenes) with EVA gave results similar to those obtained when blends of EVA and FVA are examined under similar conditions. When examined by optical microscopy both types of polymer blend show phase separation as they are cooled, to room temperature, from the melt. When examined by DSC polymer blends of EVA and the poly(5-alkylnorbornenes) show no depression in the melt temperature of the alkyl norbornene component. Blends of EVA and FVA show a depression in the melting point of the

FVA component when examined by DSC. This melting point depression is tentatively assigned to an unfavourable interaction between the EVA and FVA co-polymers. The fact that these new poly(5-alkylnorbornenes) show no melting point depression, when they are blended with EVA, suggests that there is no interaction between the polymers in the blend. This is encouraging in that it implies there would not be an antagonistic interaction between the two polymers if both were used in fuel treatment.

Pour point test results from the poly(5-alkylnorbornenes) illustrate that these polymers depress the pour point of the fuels which were tested in Chapter 5. These poly(5-alkylnorbornenes) were more effective as pour point depressants in fuel① than fuel②. The results from fuel① indicate that some of these polymers are more effective as pour point depressants when compared with the conventional comb polymers which was tested. Results from fuel② show that although these polymers are, in general, not as effective as pour point depressants when compared with the conventional comb they do however depress the pour point of the fuel. These preliminary test results indicate that the polymers synthesised in this work do effect the cold flow behaviour of diesel fuel and therefore warrant more detailed investigations. Such testing would examine the effects which these polymers may have in different fuels and on the different aspects of wax crystal modification. The results obtained from such studies would hopefully highlight which of the poly(5-alkylnorbornenes) are most effective as cold flow performance improvers for diesel fuel and also the optimum molecular weight necessary to yield the best performance in the fuel.

6.3.2 EVA Model polymer

Attempts to prepare a model EVA polymer concentrated on the ring opening polymerisation of 1-acetoxy-4,8-cyclododecadiene. Attempted polymerisation of this monomer using classical tungsten and molybdenum based initiators proved unsuccessful. The use of well-defined initiators to polymerise these monomers proved irreproducible with polymer recovered from some reactions and not from others. Changes are observed in the ^{1}H NMR which suggest, that although a proportion of this monomer undergoes ring opening, complete polymerisation is hindered and a mixture of monomer and polymer remain in the reaction system. It is possible that the polymerisation is prevented from going to completion by the interaction of an acetoxy residue in the growing chain with the propagating metallaolefin chain end. A detailed analysis of the effects of temperature, concentration and initiator on the polymerisation of this monomer may yield a reproducible method for its polymerisation.

An alternative approach to the synthesis of a model EVA type polymer could be the epoxidation and acetylation of a polyalkenemer; as illustrated in Figure 6.3.1.

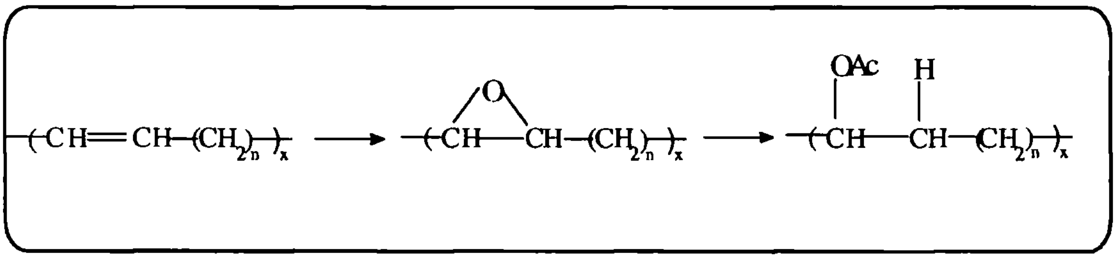


FIGURE 6.3.1 Possible route to an EVA model polymer

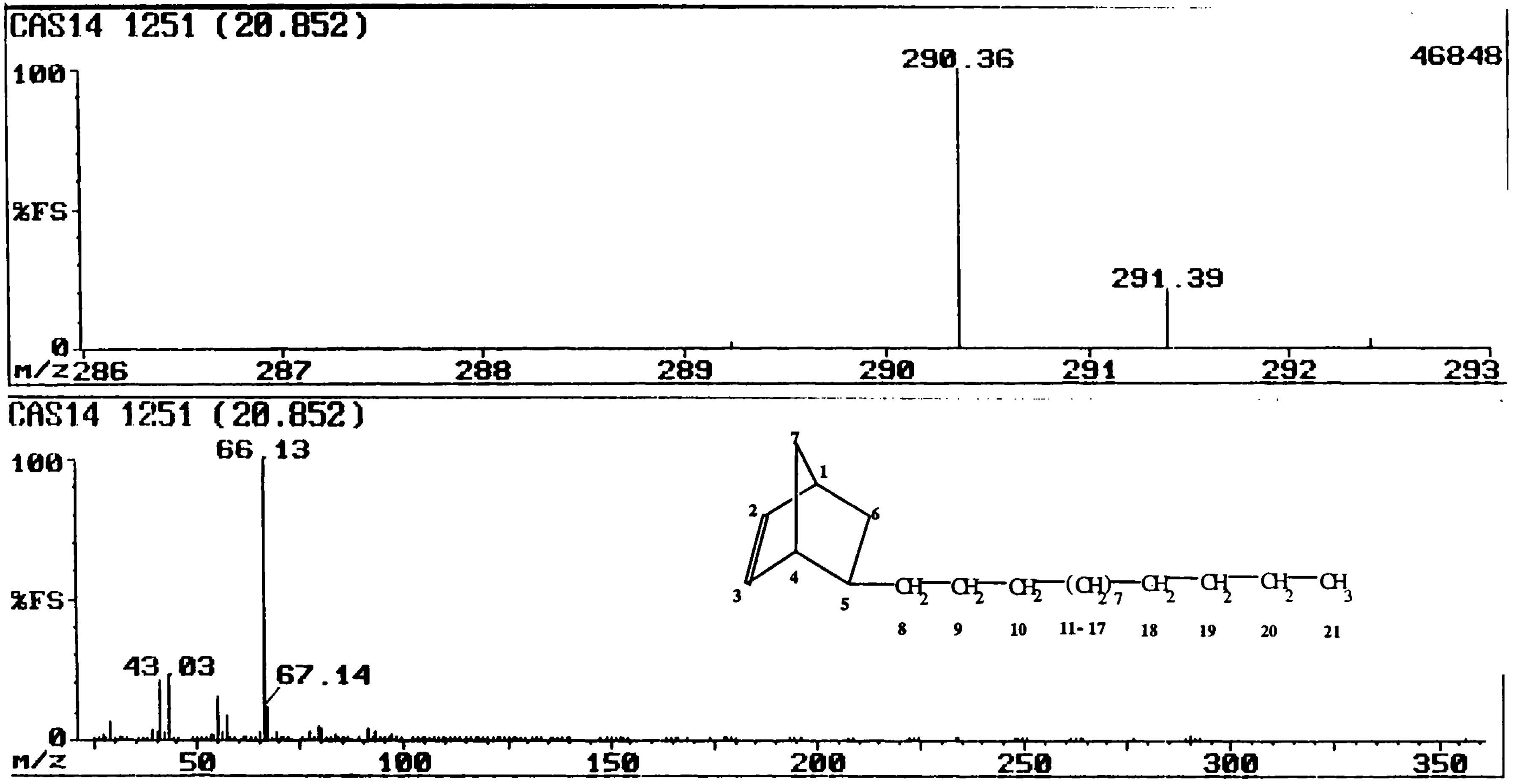
The molecular weight and the distribution of the acetate units in the resultant polymer would be controlled by the initial selection of the polyolefin and by the degree of epoxidation obtained. Several methods of polymer epoxidation have been reported in the literature.[111-113] The degree of conversion, of olefin units to epoxy units, being dependant upon the reagents used for epoxidation, reaction time, temperature and the microstructure of the polymer chain.

CONCLUDING REMARKS

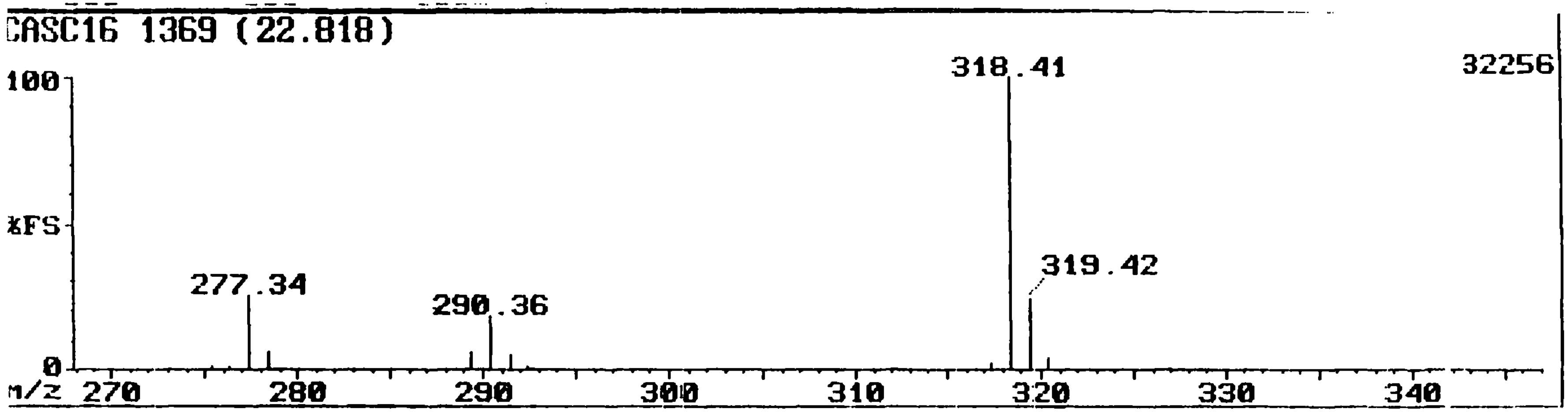
The synthesis of a range of comb polymers and co-polymers from the ring opening metathesis polymerisation of 5-substituted alkylnorbornenes has been achieved. Initial test results on a selection of comb polymers indicate that they show a degree of wax crystal modification in diesel fuel and merit more detailed testing.

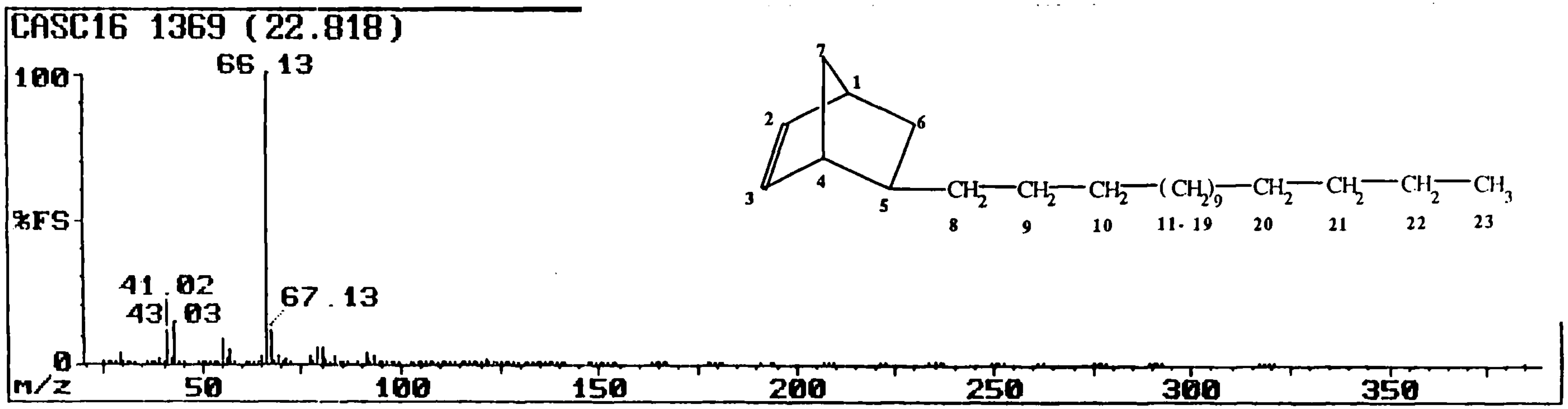
The preparation of a model EVA polymer from the ring opening metathesis polymerisation of 1-acetoxy-4,8-cyclododecadiene proved irreproducible. However, a through examination of the experimental parameters may yield a reproducible procedure for the polymerisation of this monomer. Alternatively the epoxidation and acetylation of a poly(olefin) may be a feasible experimental procedure to yield a model EVA polymer.

APPENDIX A

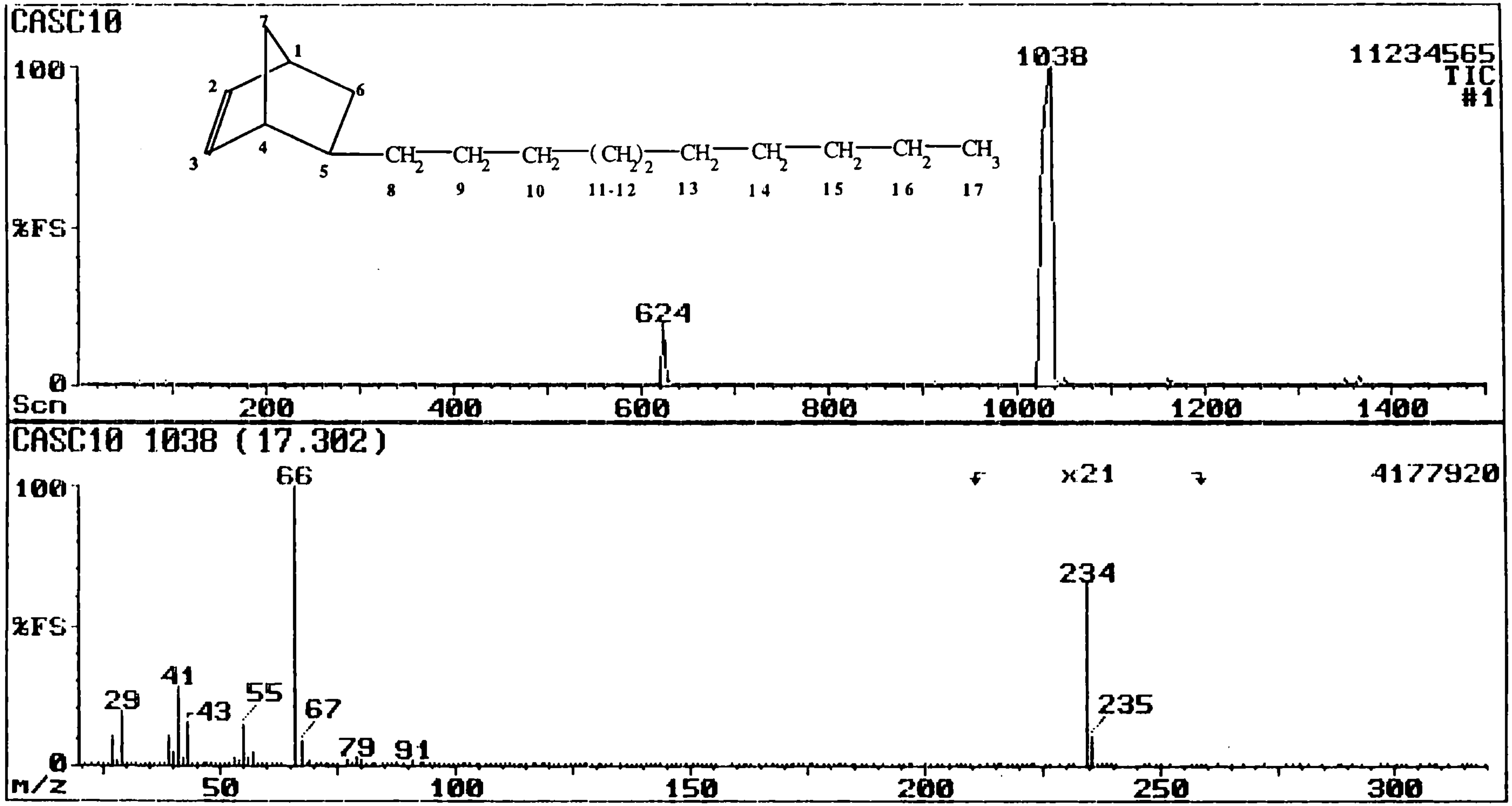


APPENDIX A1 MS of (±)-*exo*/*endo*-5-tetradecylnorbornene

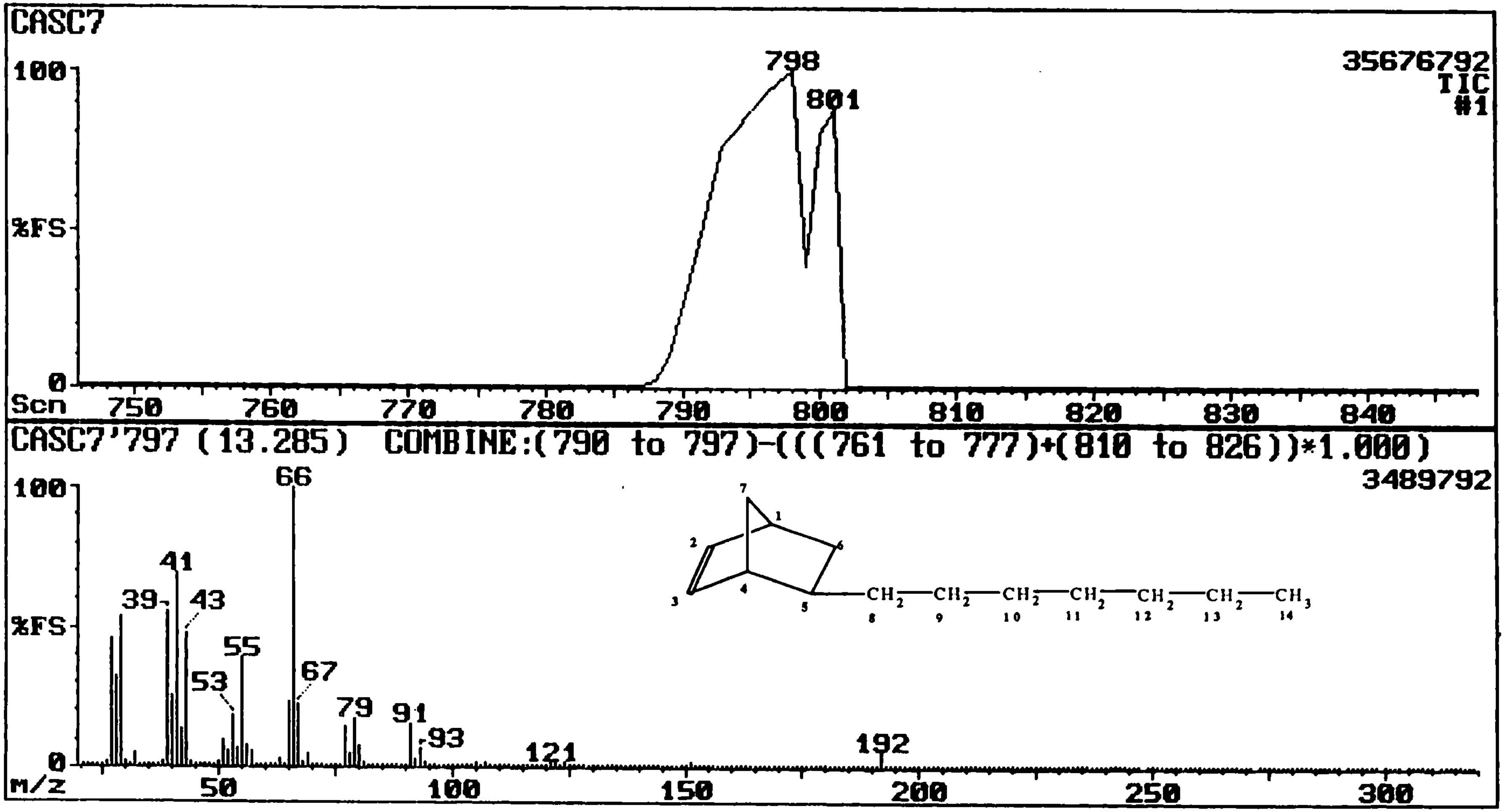




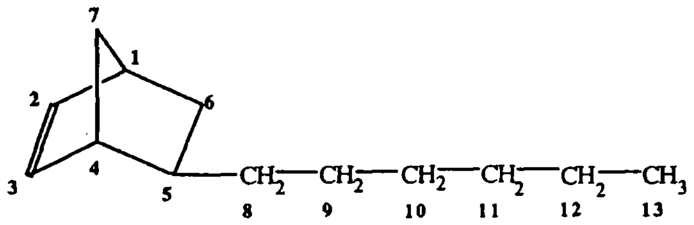
APPENDIX A2 MS of (±)-*exo*/*endo*-5-hexadecylnorbornene

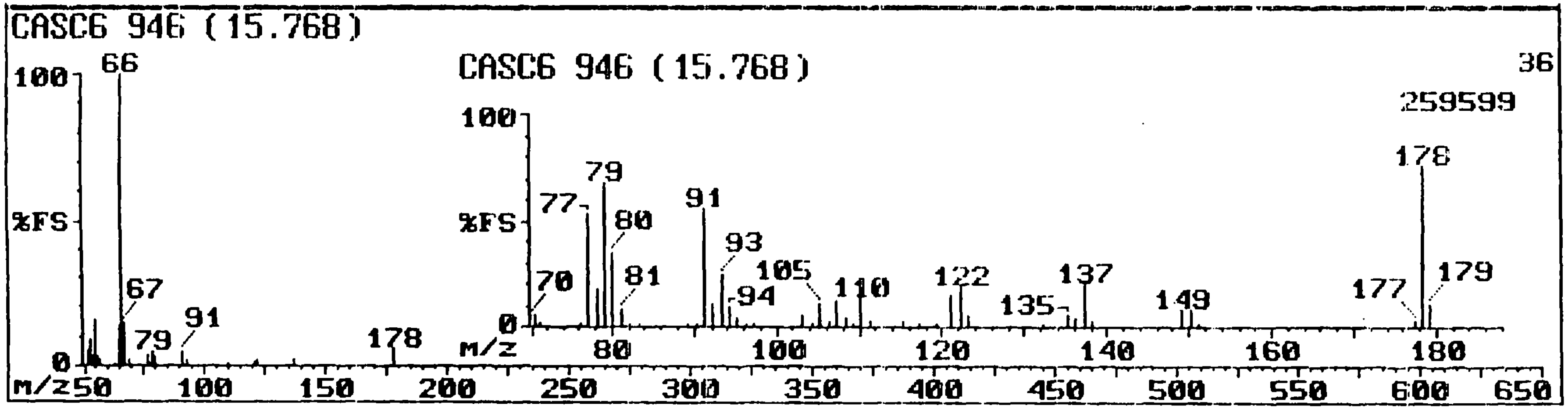


APPENDIX A3 GC/MS of (±)-*exo*/*endo*-5-decylnorbornene

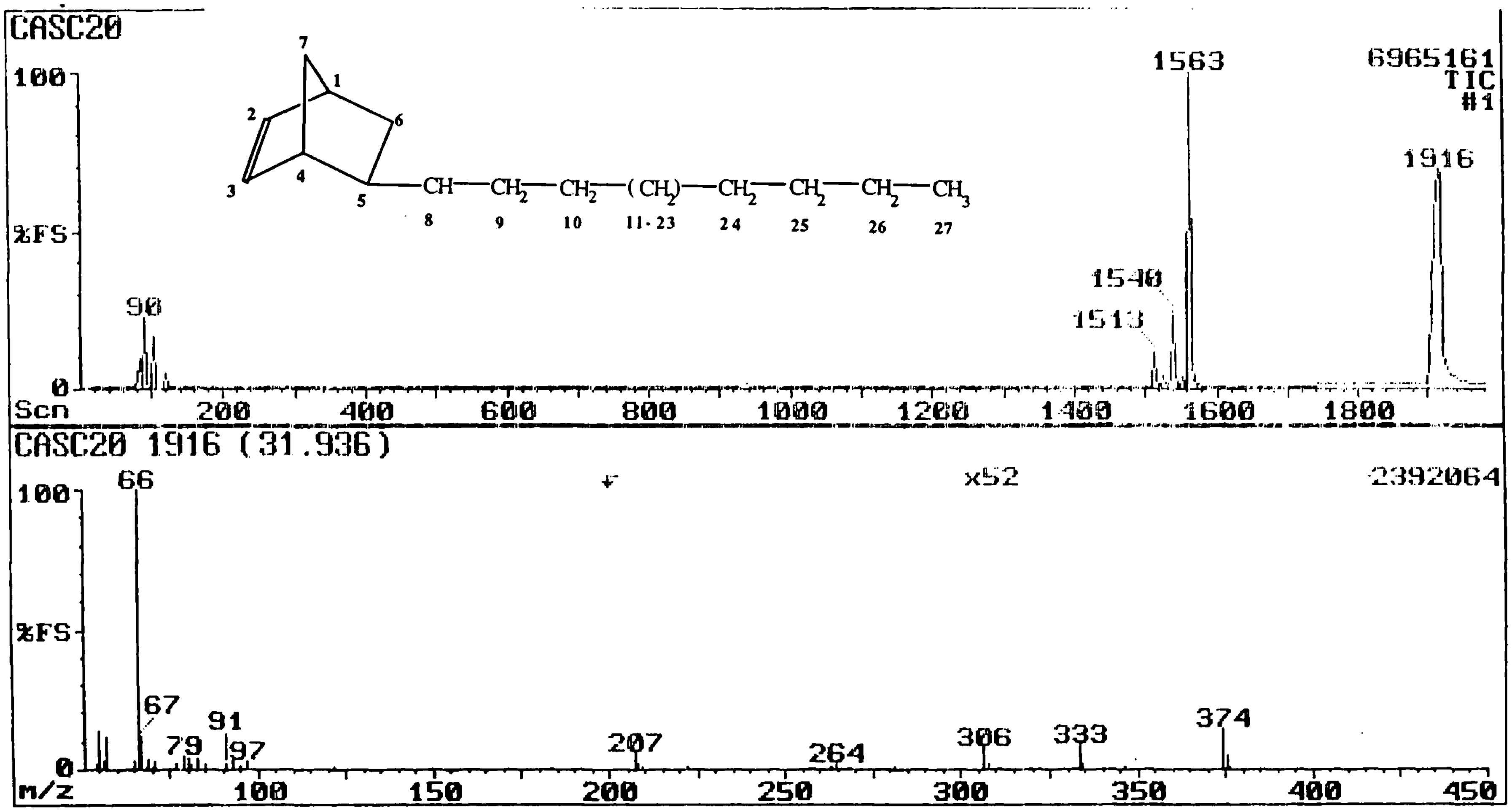


APPENDIX A4 GC/MS of (±)-*exo*/*endo*-5-heptylnorbornene

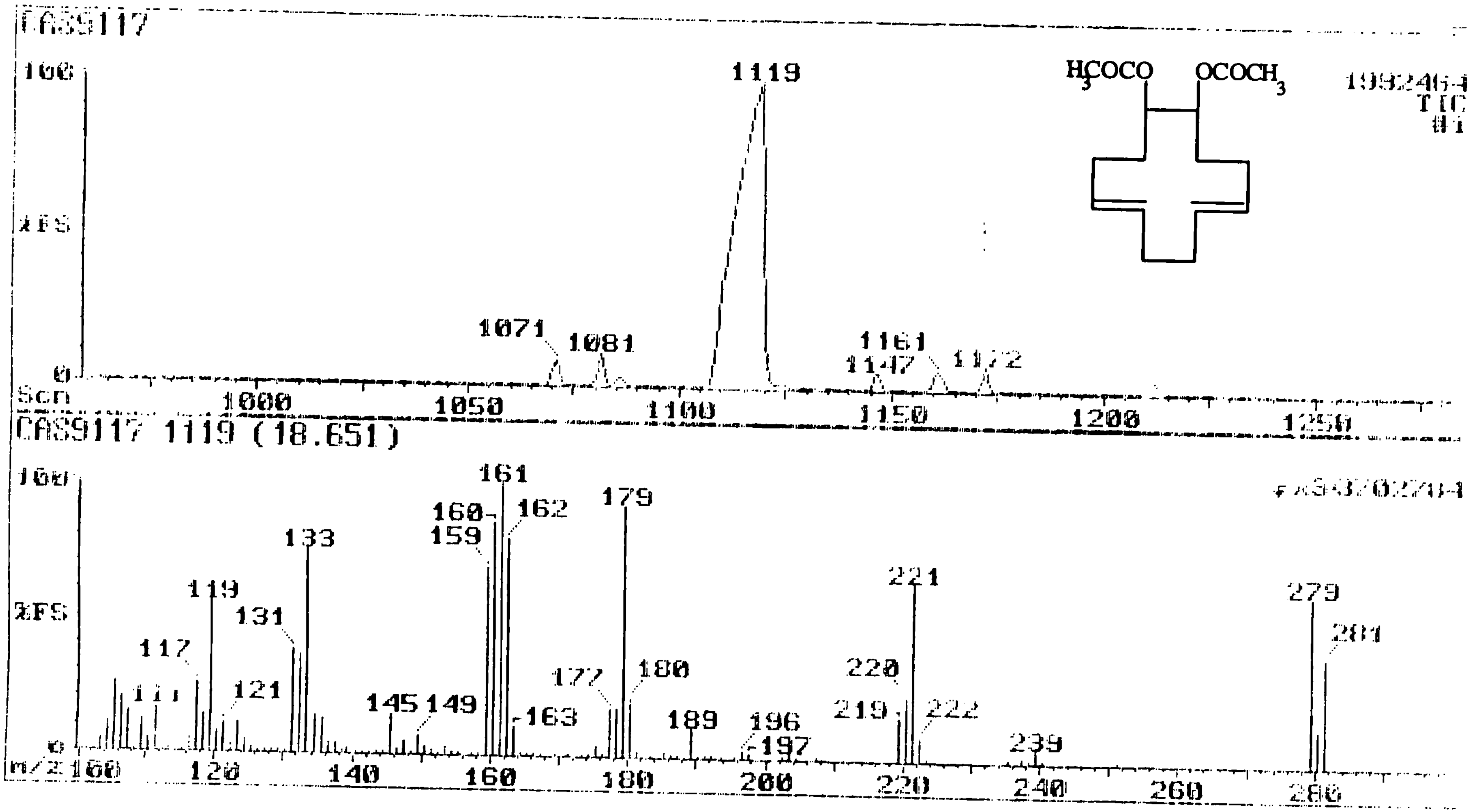




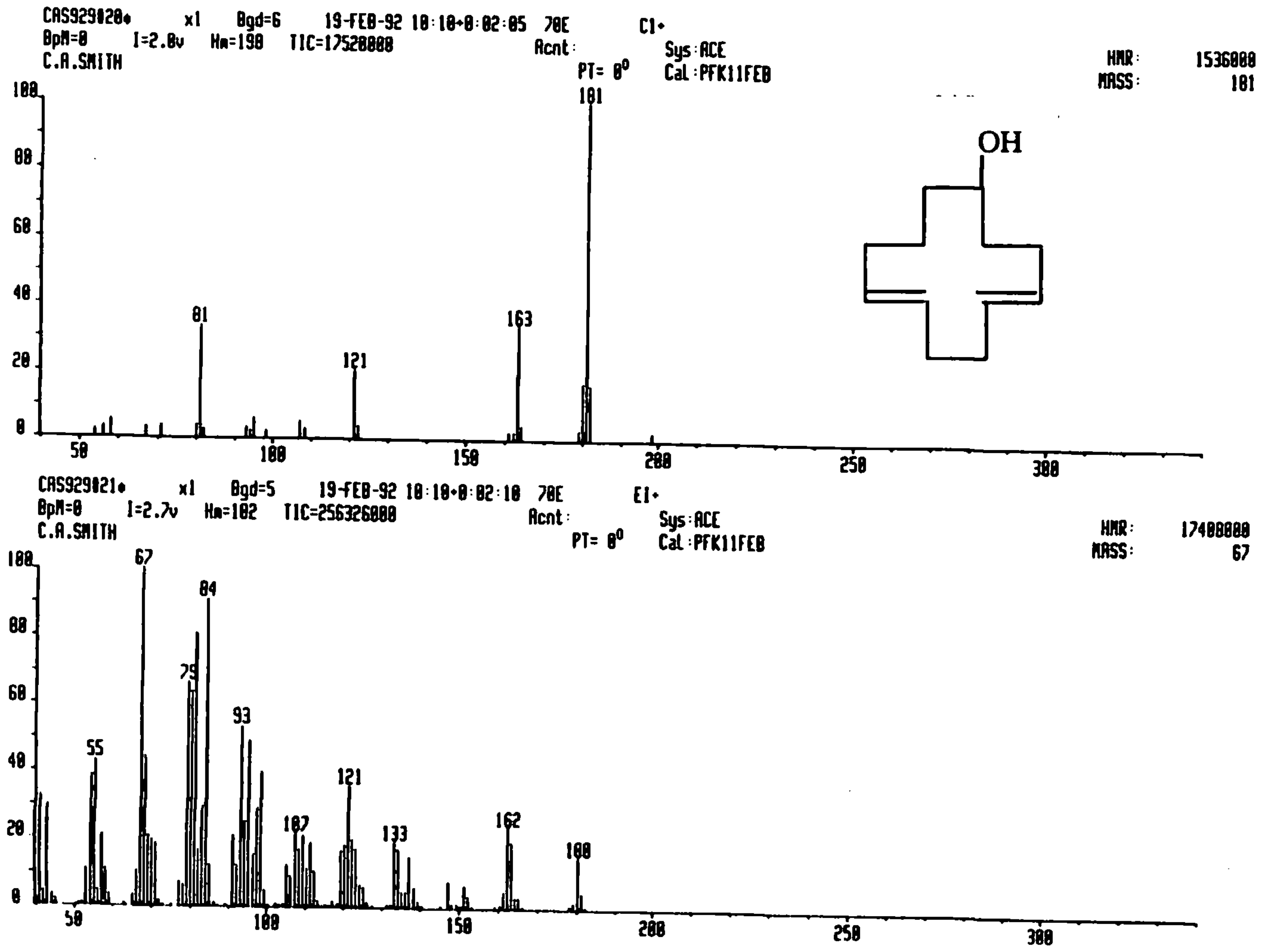
APPENDIX A5 MS of (±)-*exo*/*endo*-5-hexylnorbornene



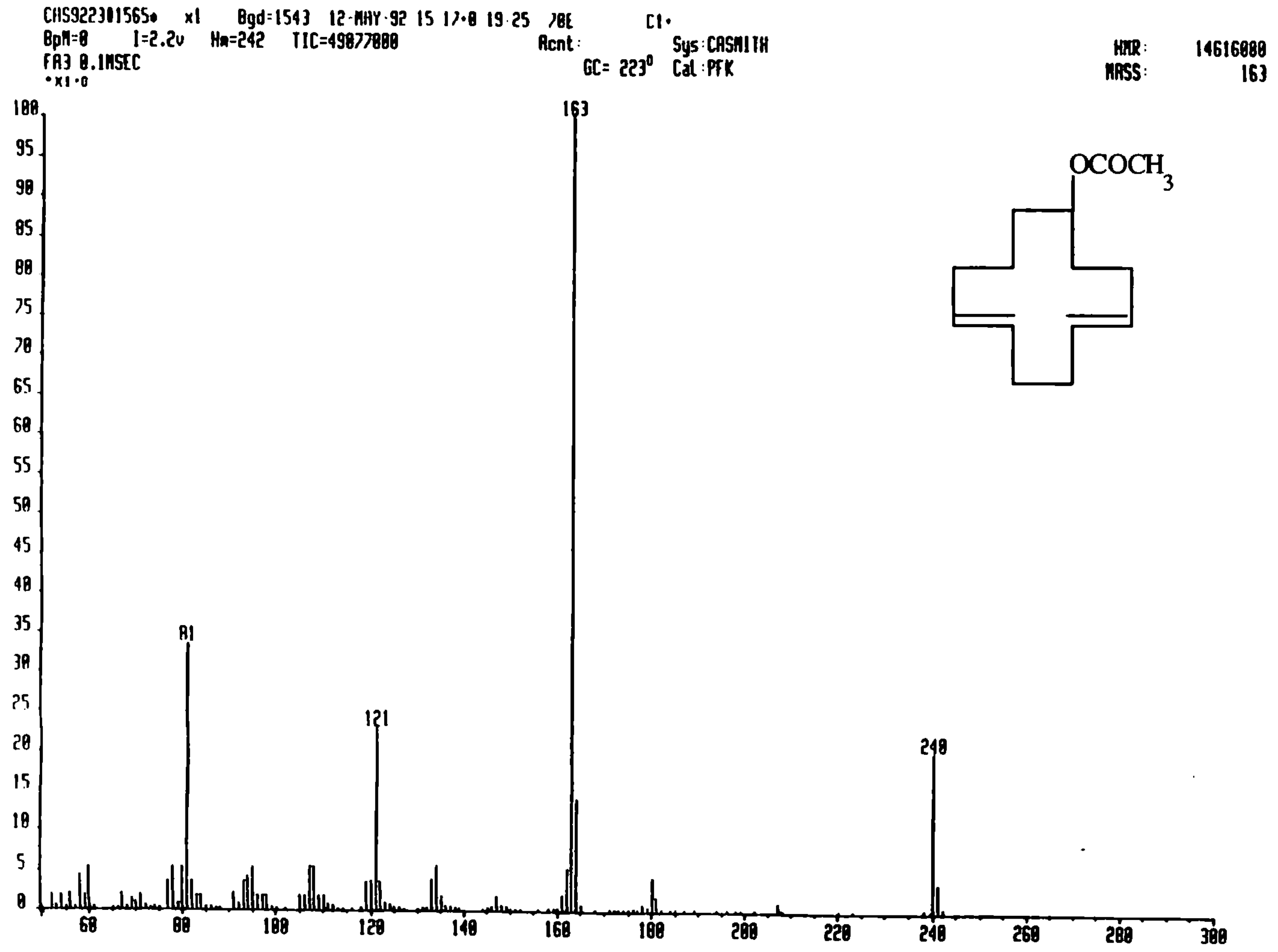
APPENDIX A6 GC/MS of (±)-*exo/endo*-5-eicosylnorbornene



APPENDIX A7 GC/MS of 1,2-diacetoxy-5,9-cyclododecadiene

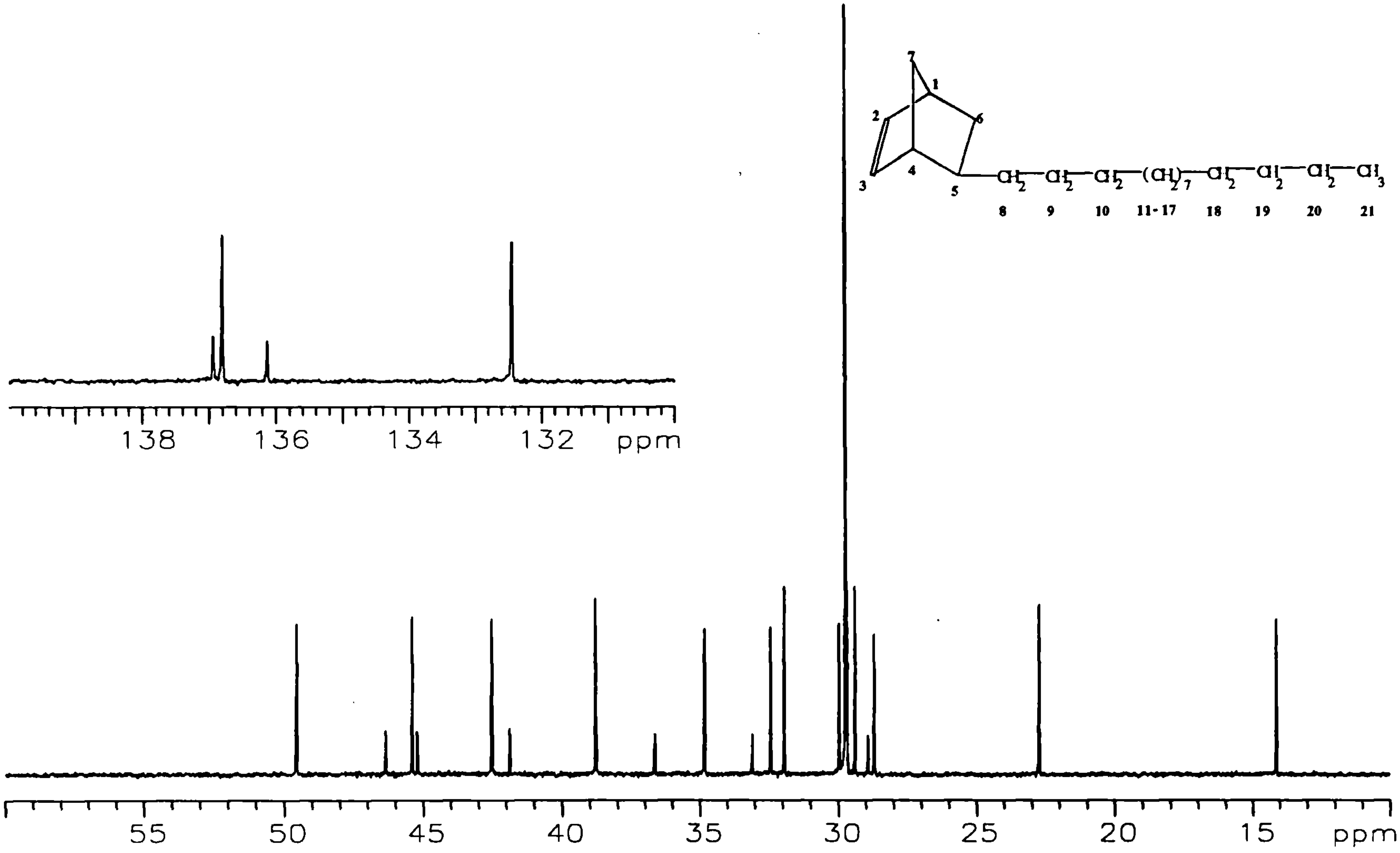


APPENDIX A8 MS of 1-hydroxy-4,8-cyclododecadiene

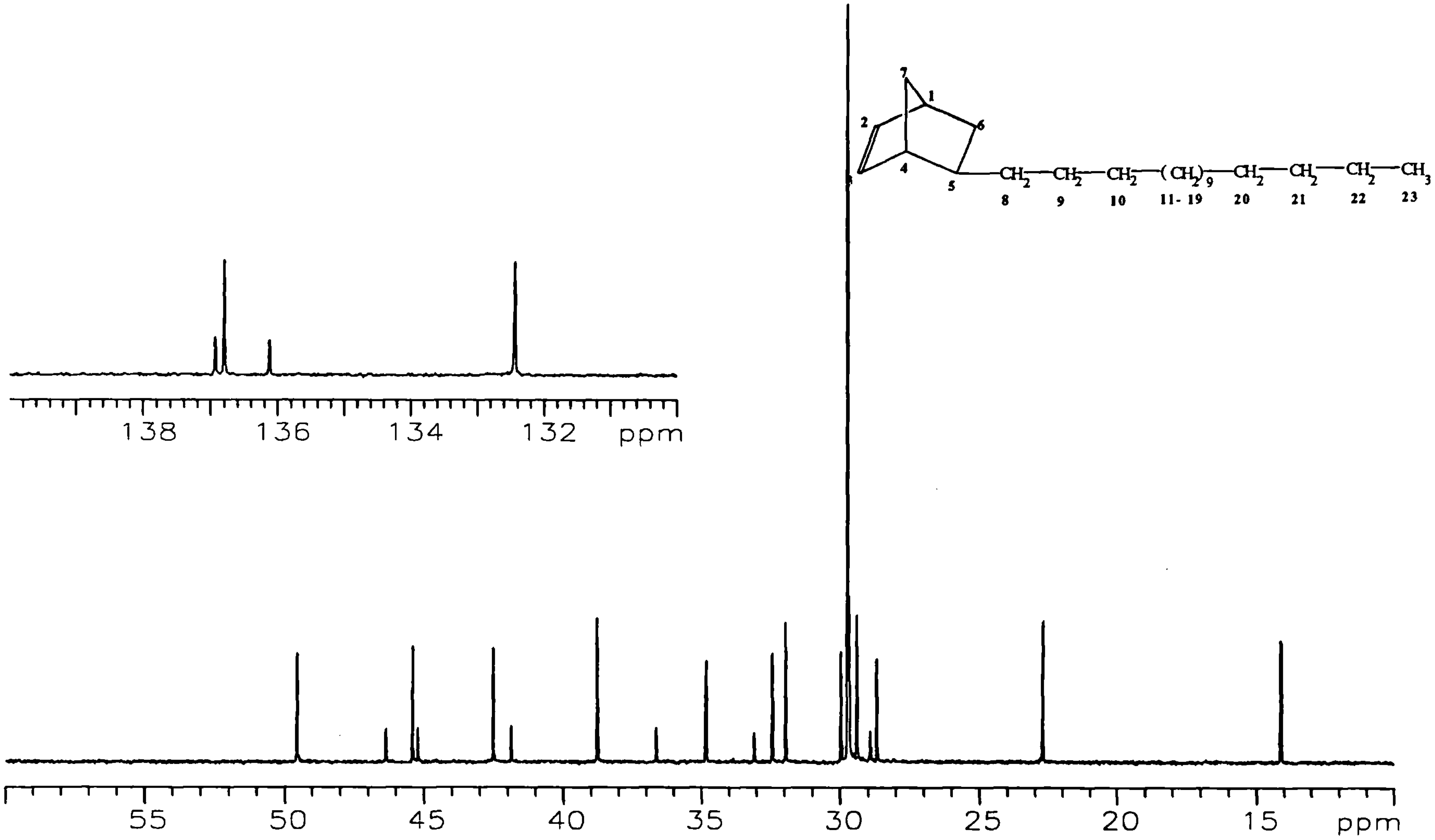


APPENDIX A9 MS of 1-acetoxy-4,8-cyclododecadiene

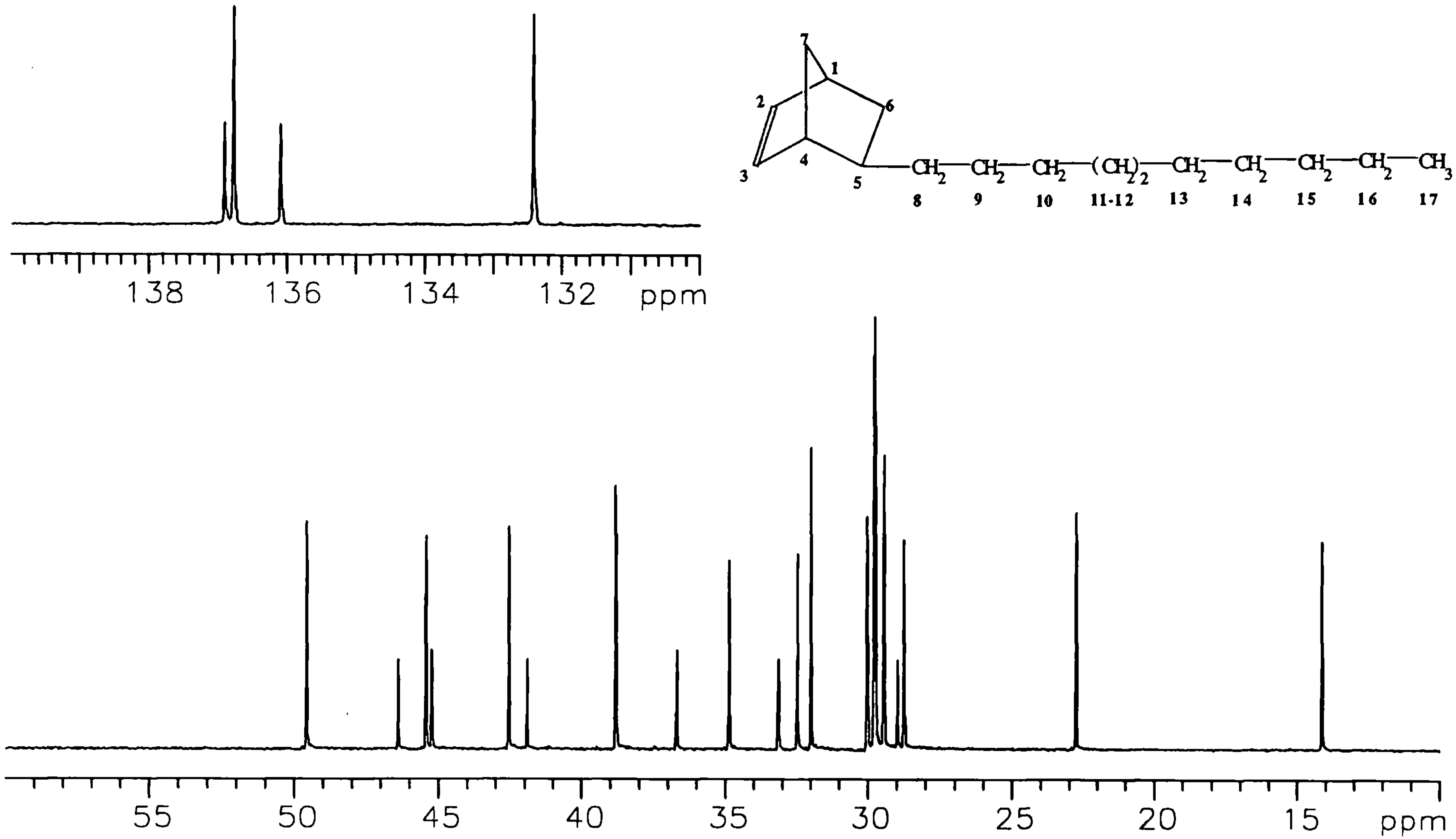
APPENDIX B



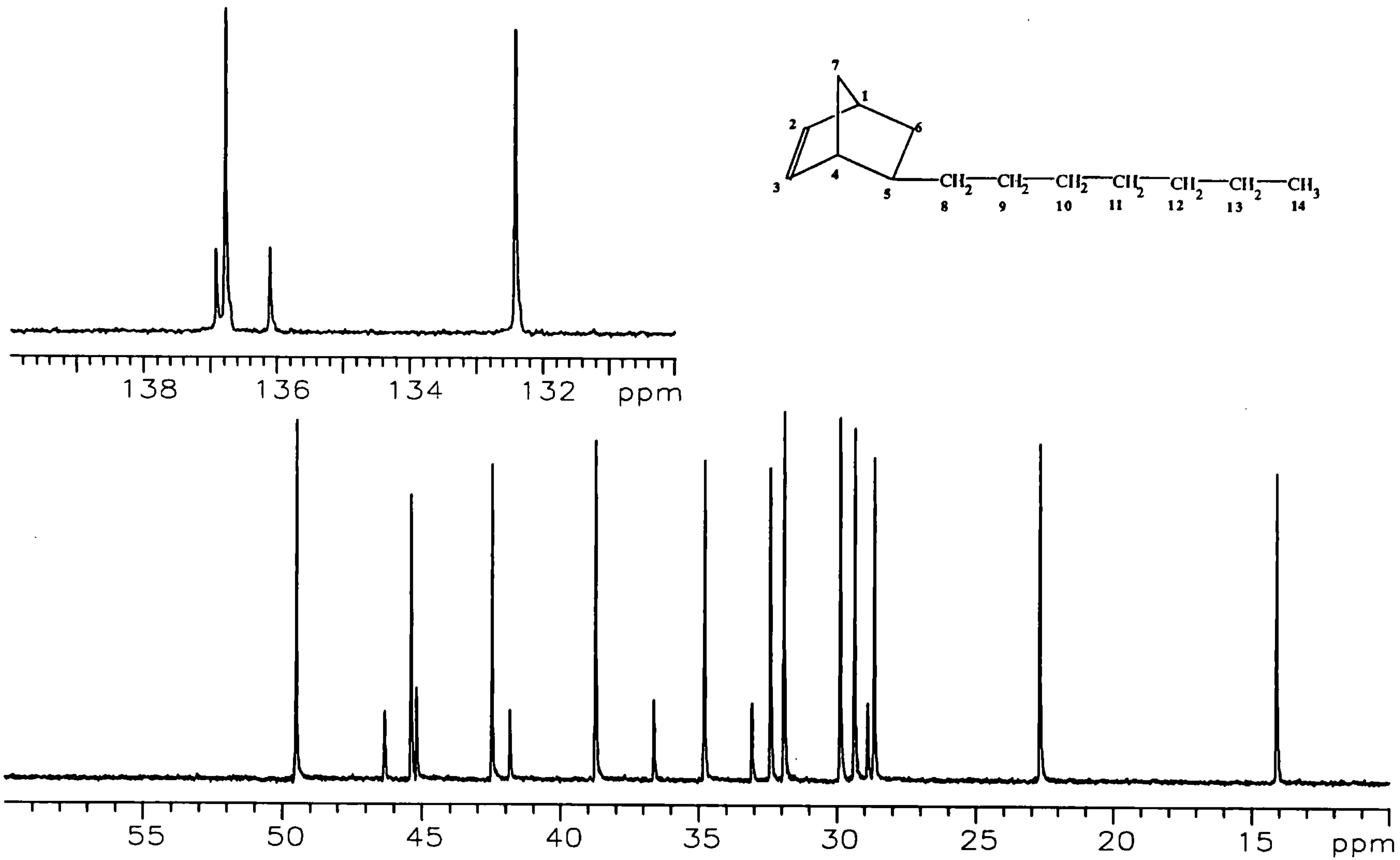
APPENDIX B1 ^{13}C NMR Spectrum of (±)-*exo*/*endo*-5-tetradecylnorbornene



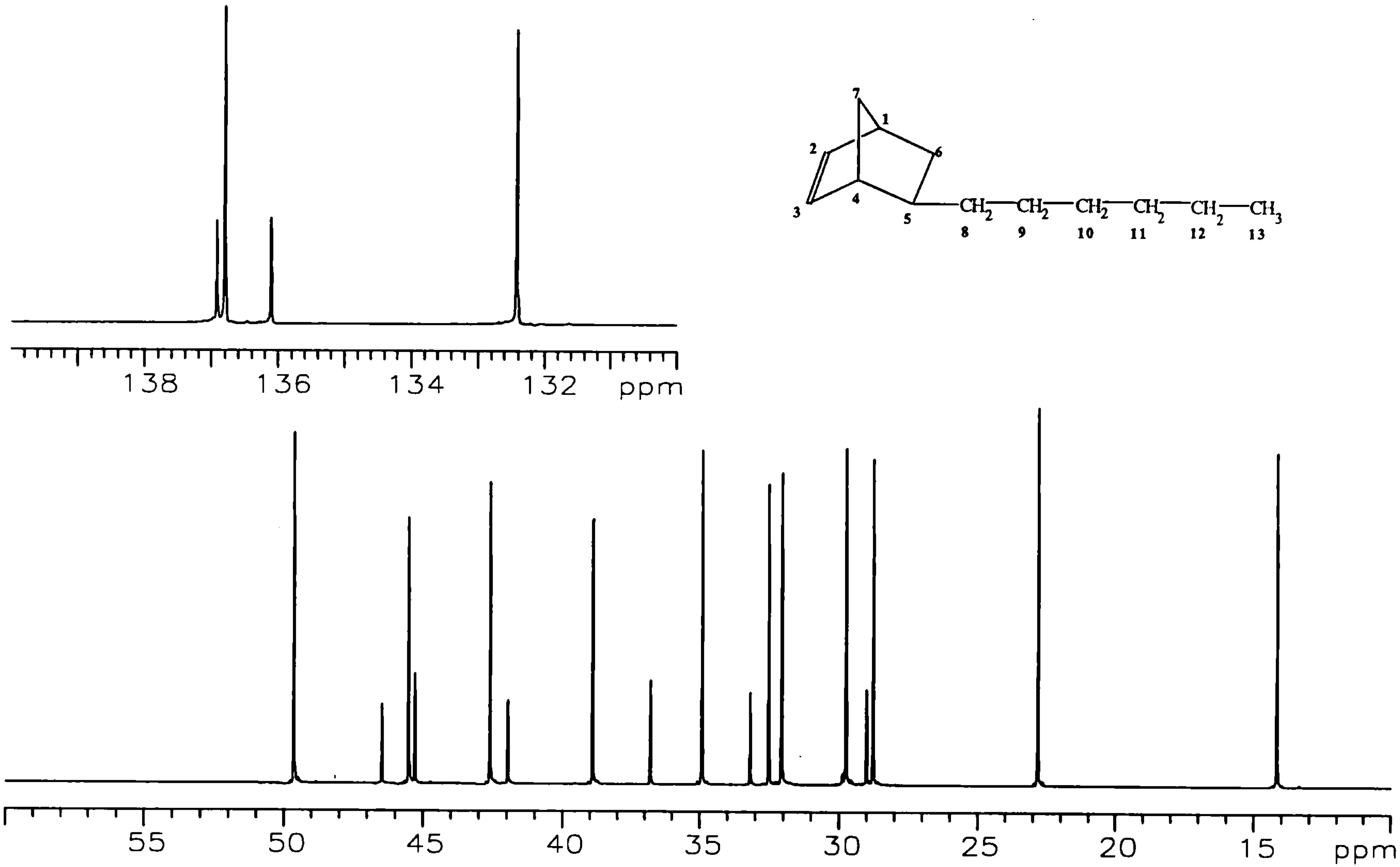
APPENDIX B2 ^{13}C NMR Spectrum of (±)-*exo*/*endo*-5-hexadecylnorbornene



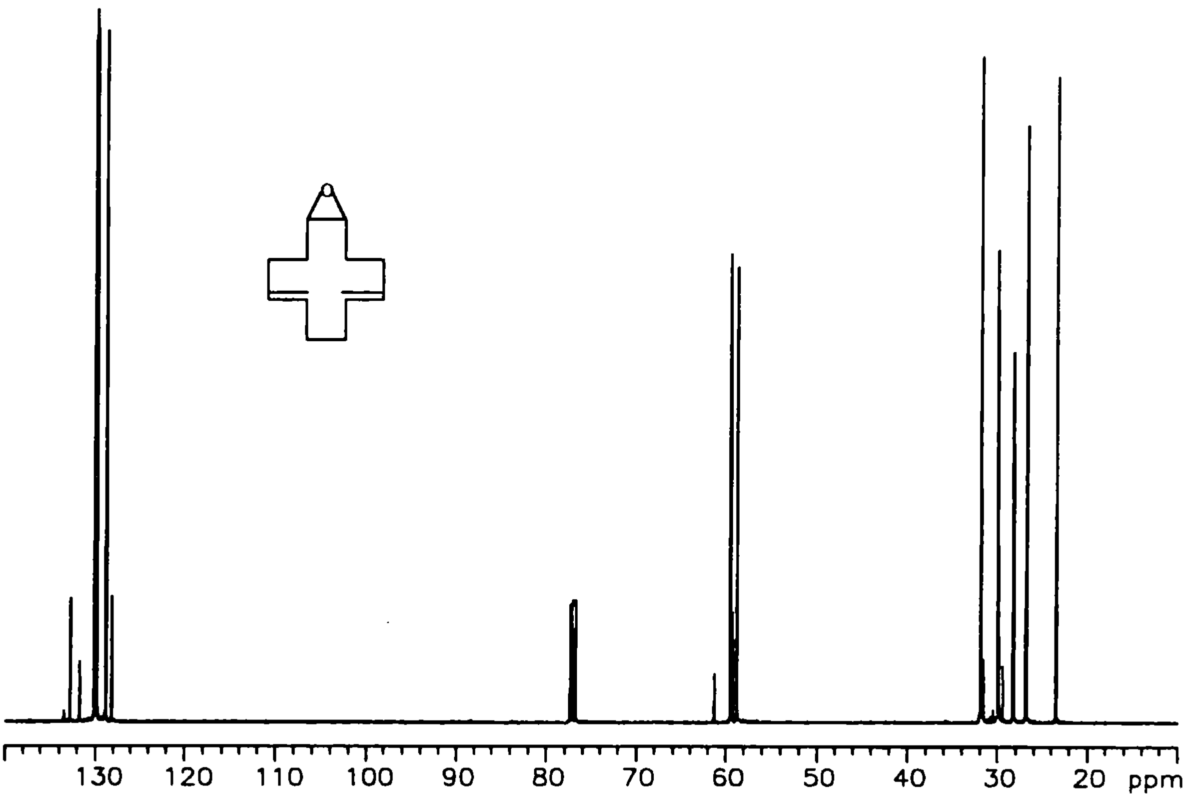
APPENDIX B3 ^{13}C NMR Spectrum of (±)-*exo*/*endo*-5-decylnorbornene



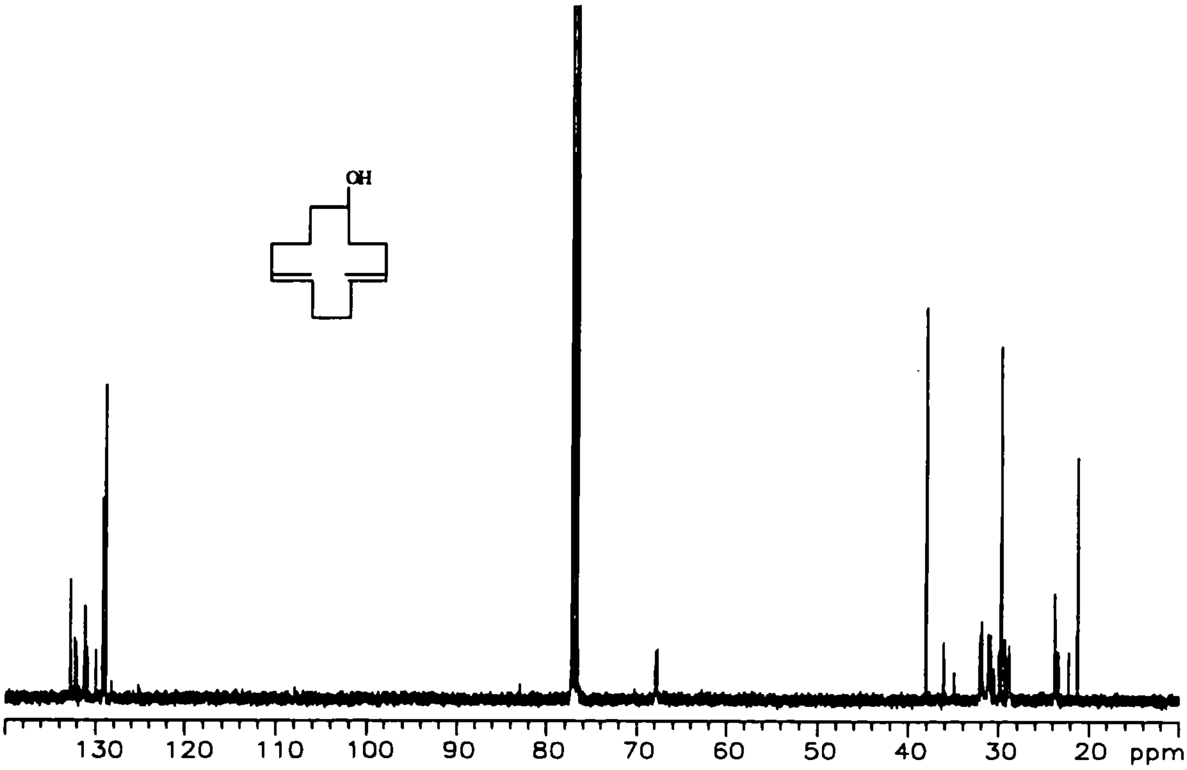
APPENDIX B4 ^{13}C NMR Spectrum of (±)-*exo/endo*-5-heptylnorbornene



APPENDIX B5 ^{13}C NMR Spectrum of (±)-*exo/endo*-5-hexylnorbornene

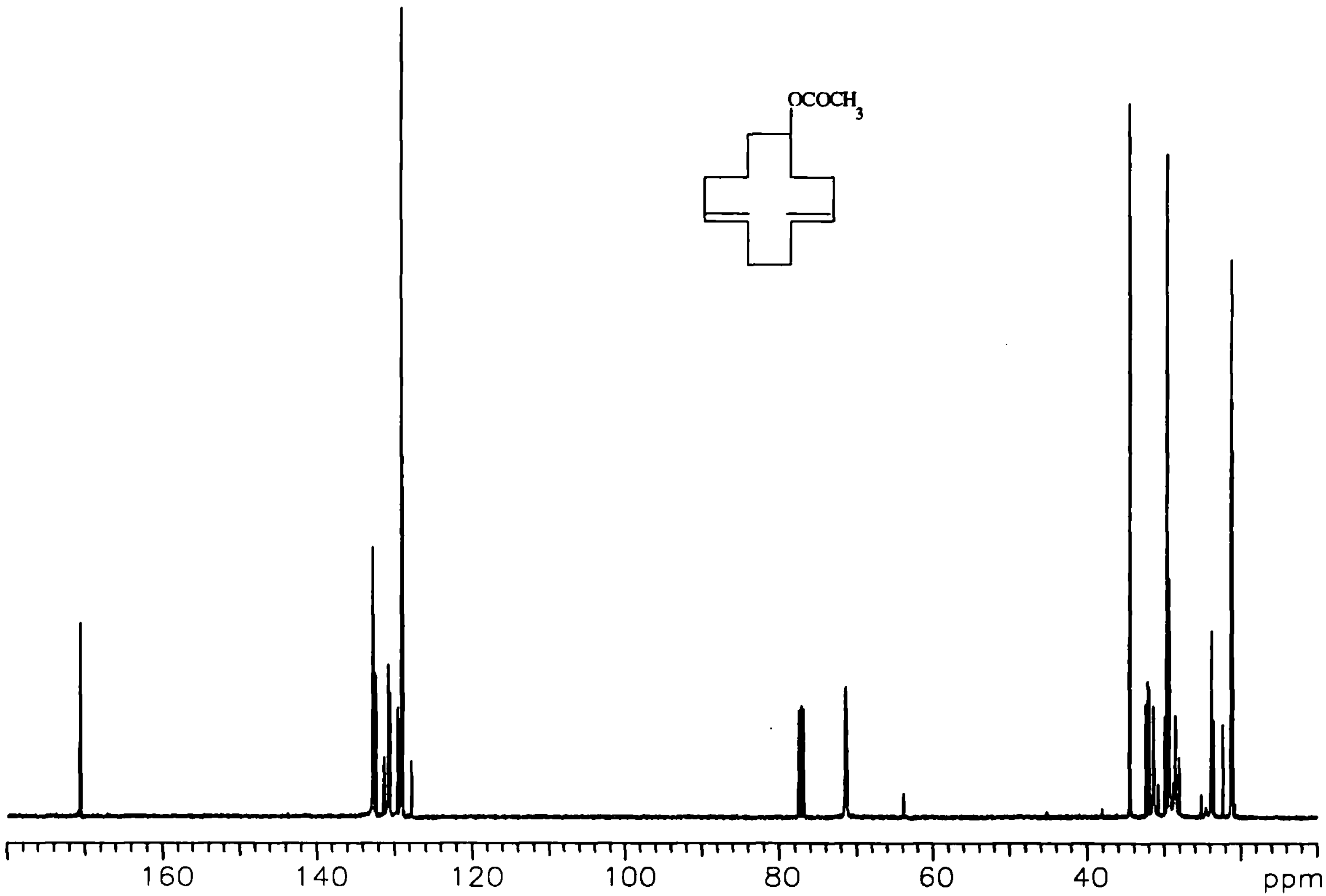


i) ^{13}C NMR Spectrum of 1,2-epoxy-5,9-cyclododecadiene

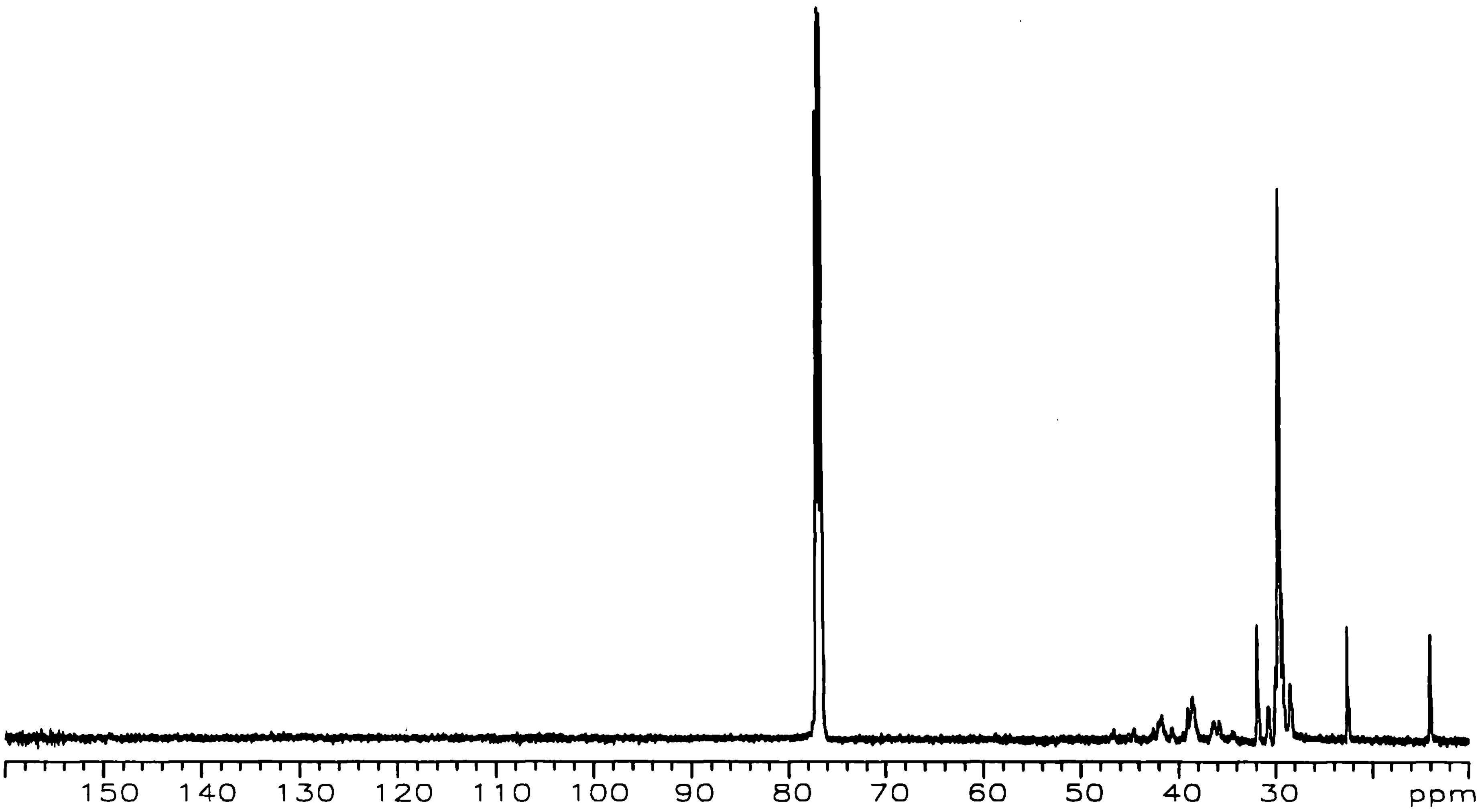


(ii) ^{13}C NMR Spectrum of 1-hydroxy-4,8-cyclododecadiene

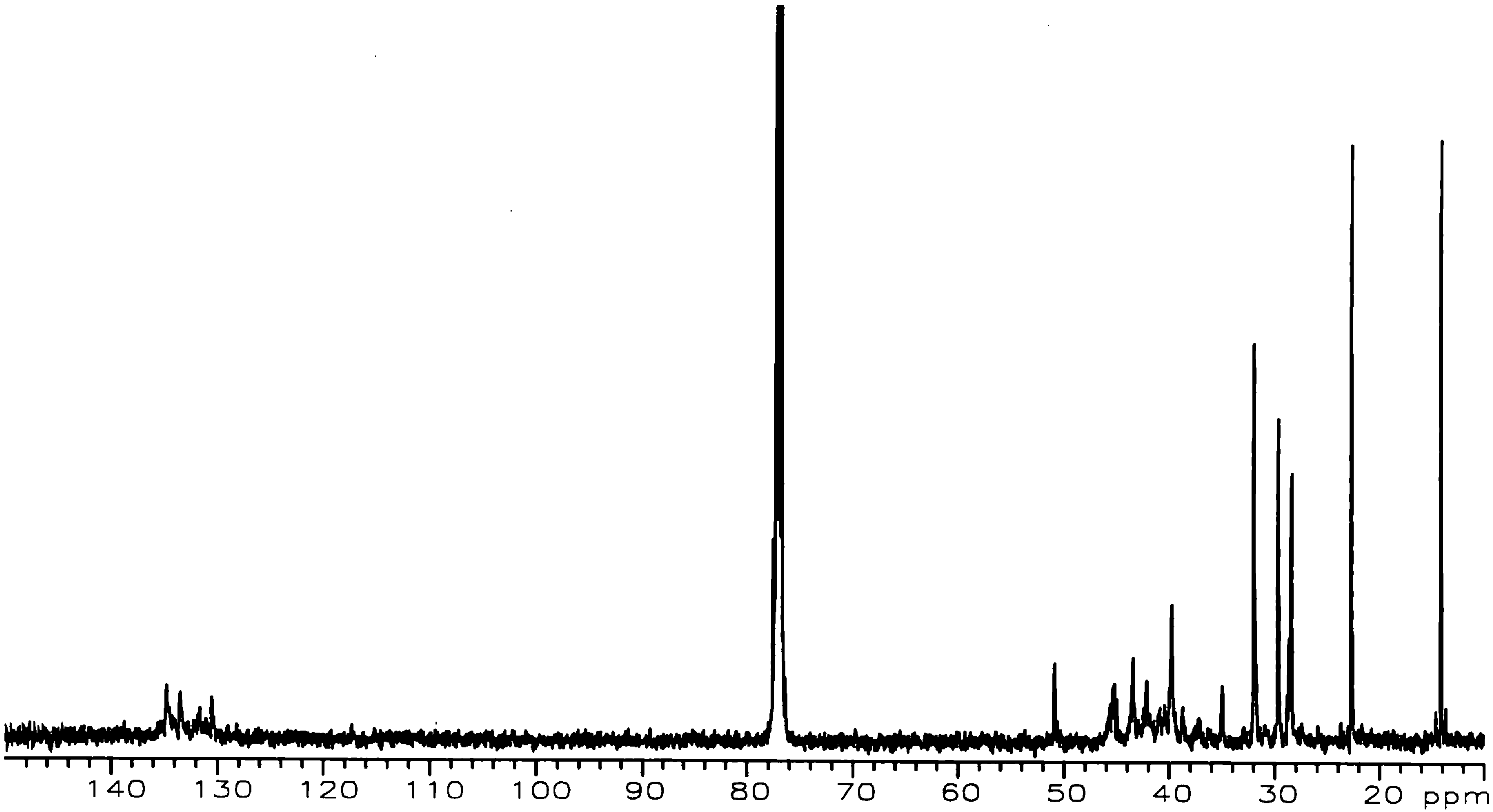
APPENDIX B6



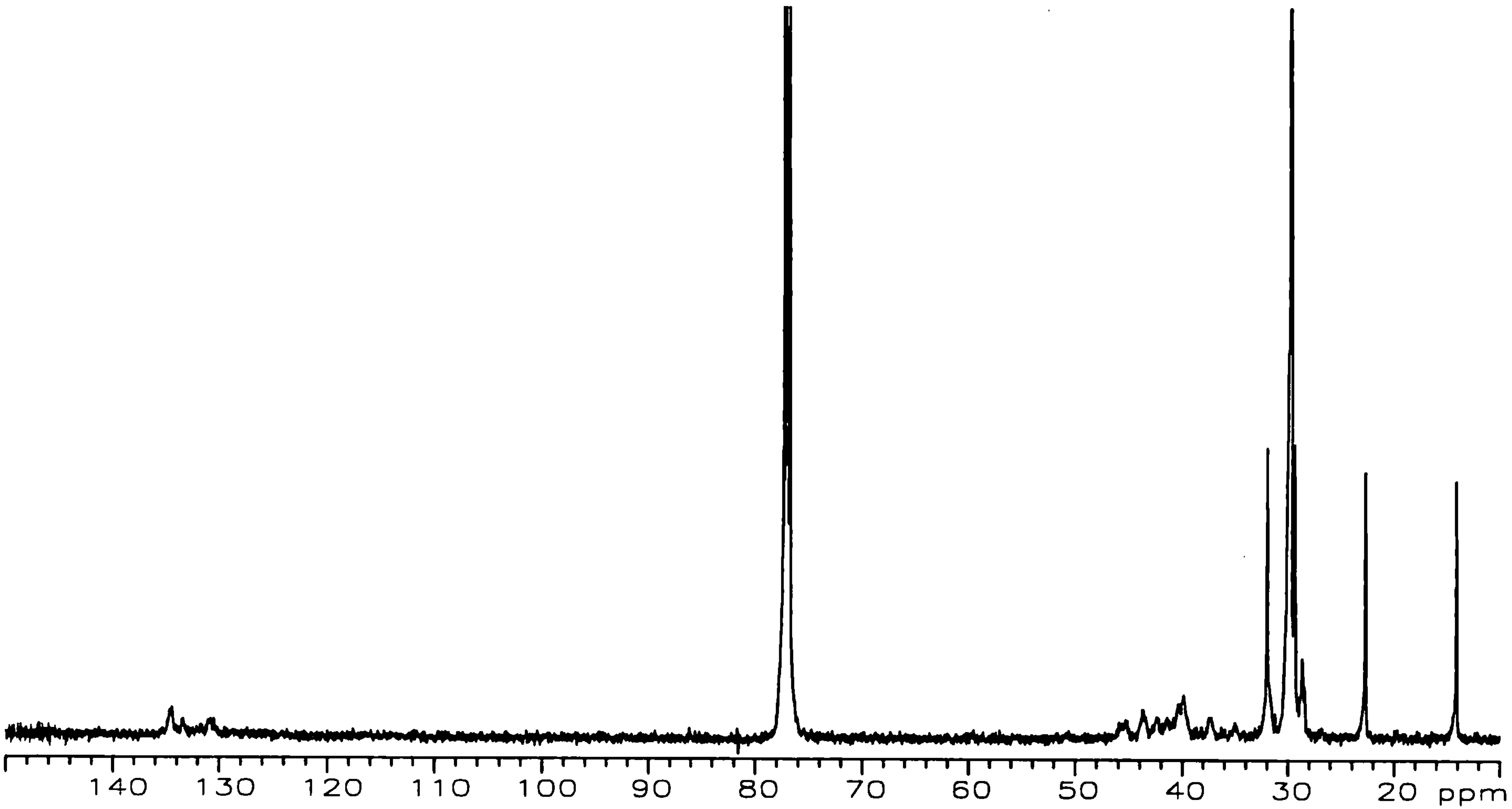
APPENDIX B7 ^{13}C NMR Spectrum of 1-acetoxy-4,8-cyclododecadiene



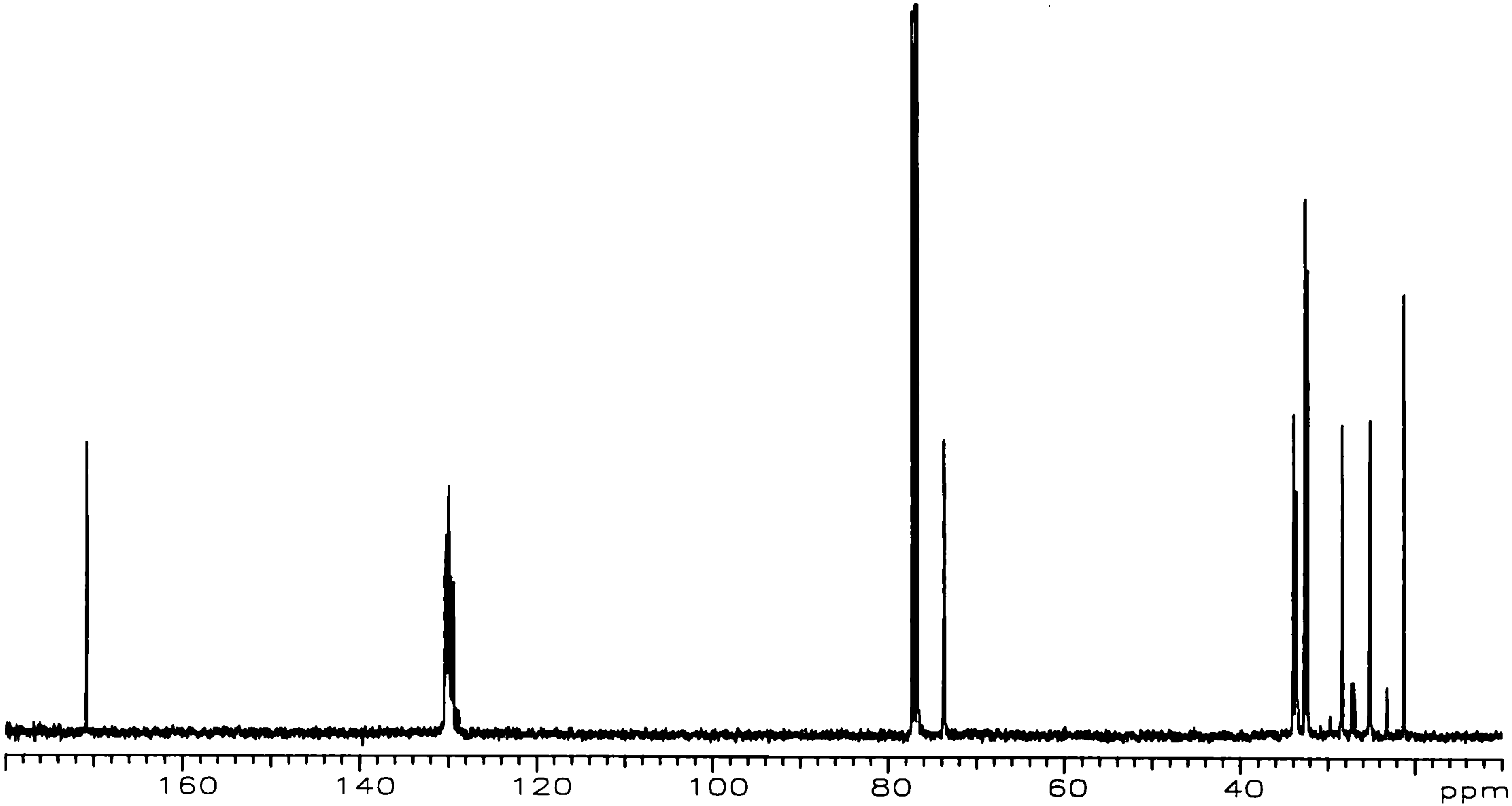
APPENDIX B8 ^{13}C NMR Spectrum of hydrogenated poly(5-tetradecylnorbornene)



APPENDIX B9 ^{13}C NMR Spectrum of non-hydrogenated poly(5-hexylnorbornene)

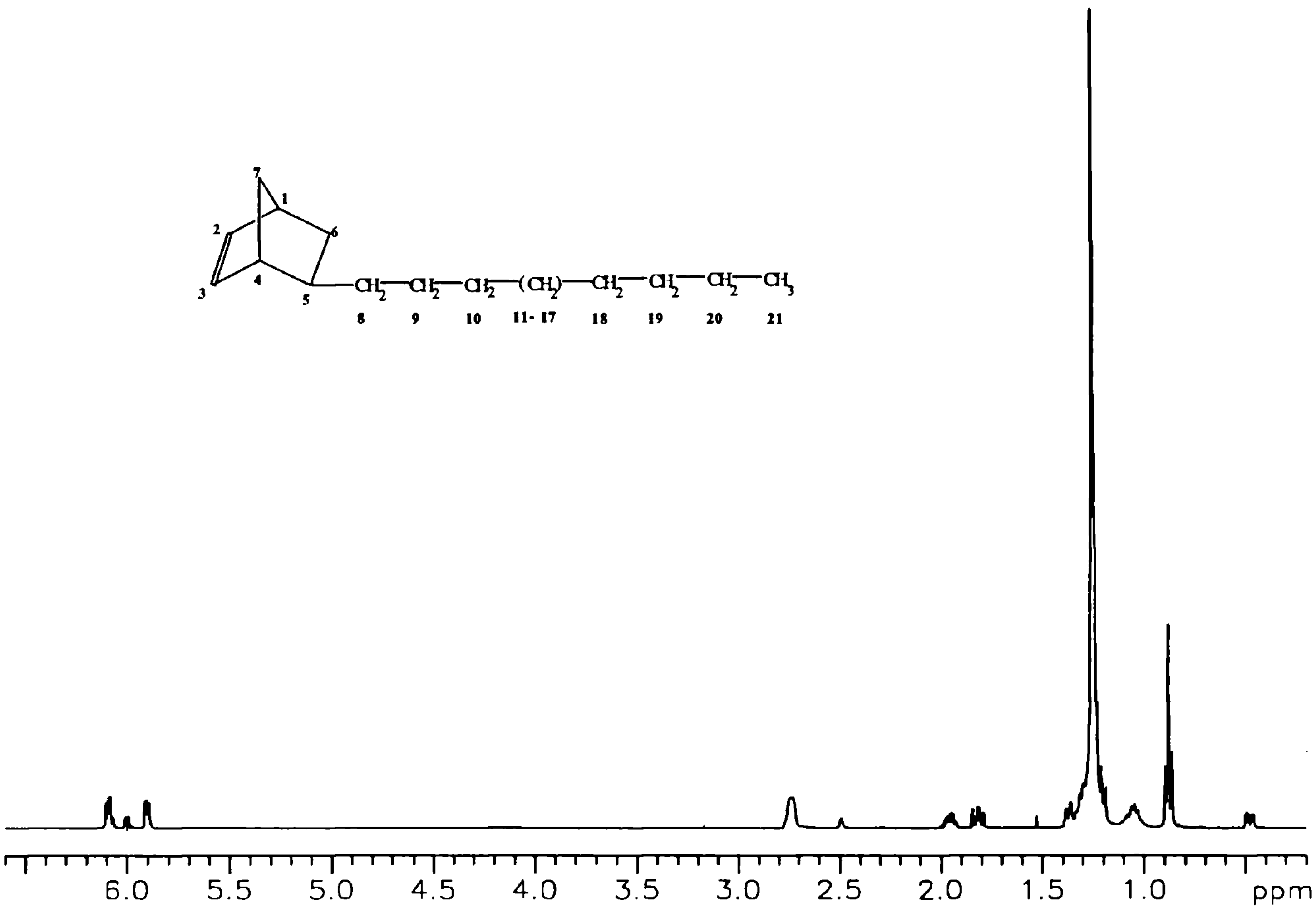


APPENDIX B10 ^{13}C NMR Spectrum of non-hydrogenated poly(5-hexadecylnorbornene)

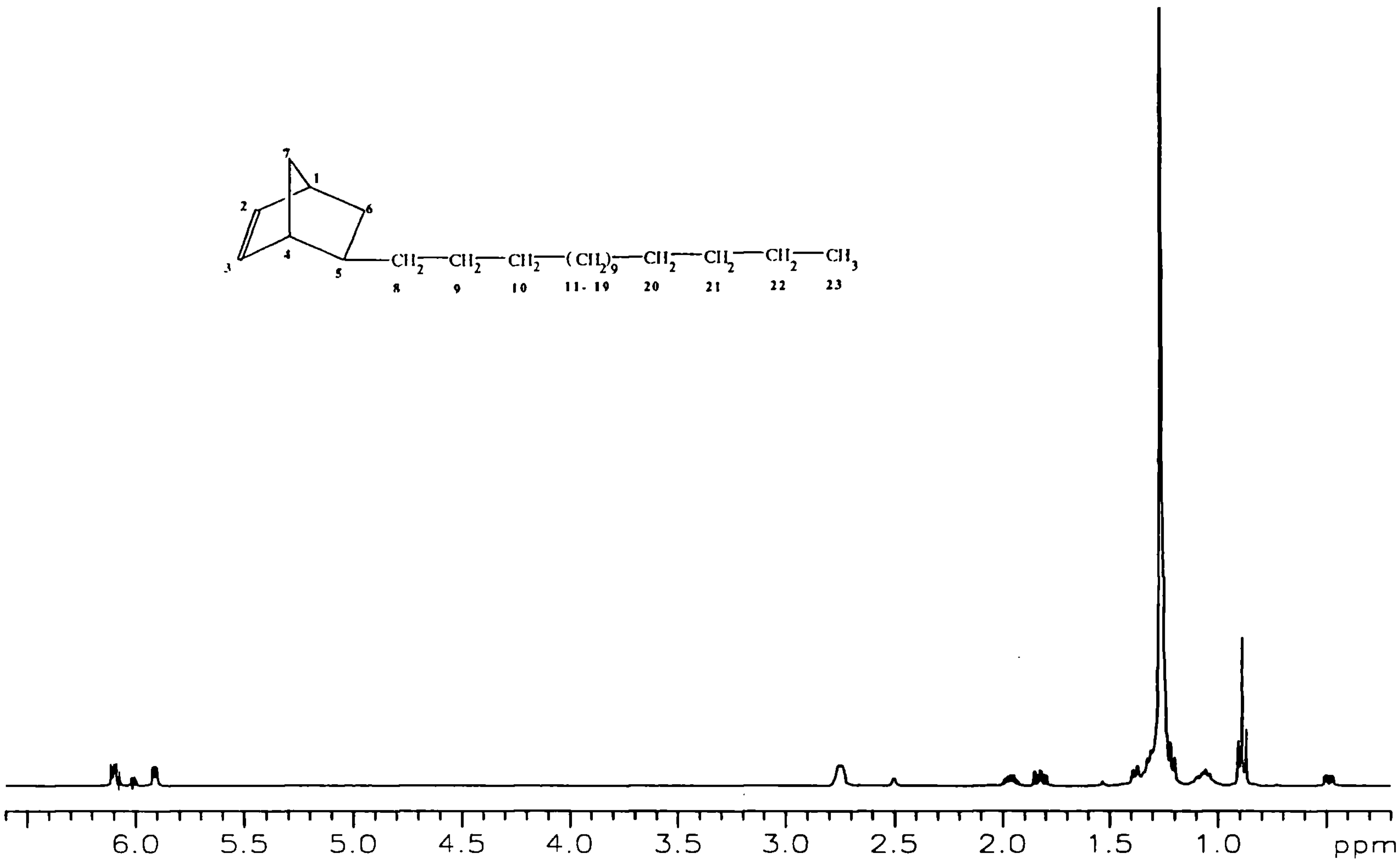


APPENDIX B11 ^{13}C NMR Spectrum of poly(acetoxycyclododecadiene)

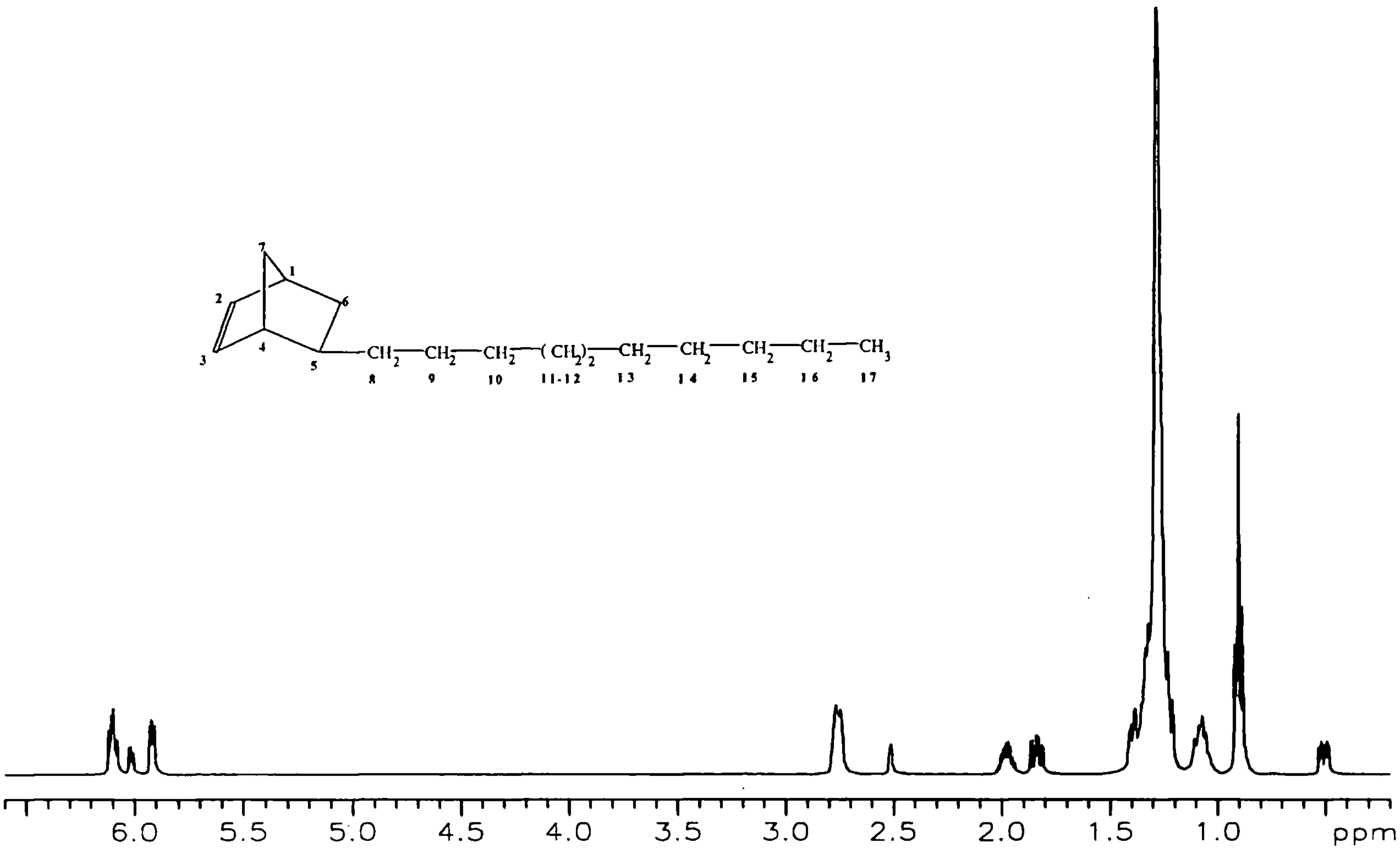
APPENDIX C



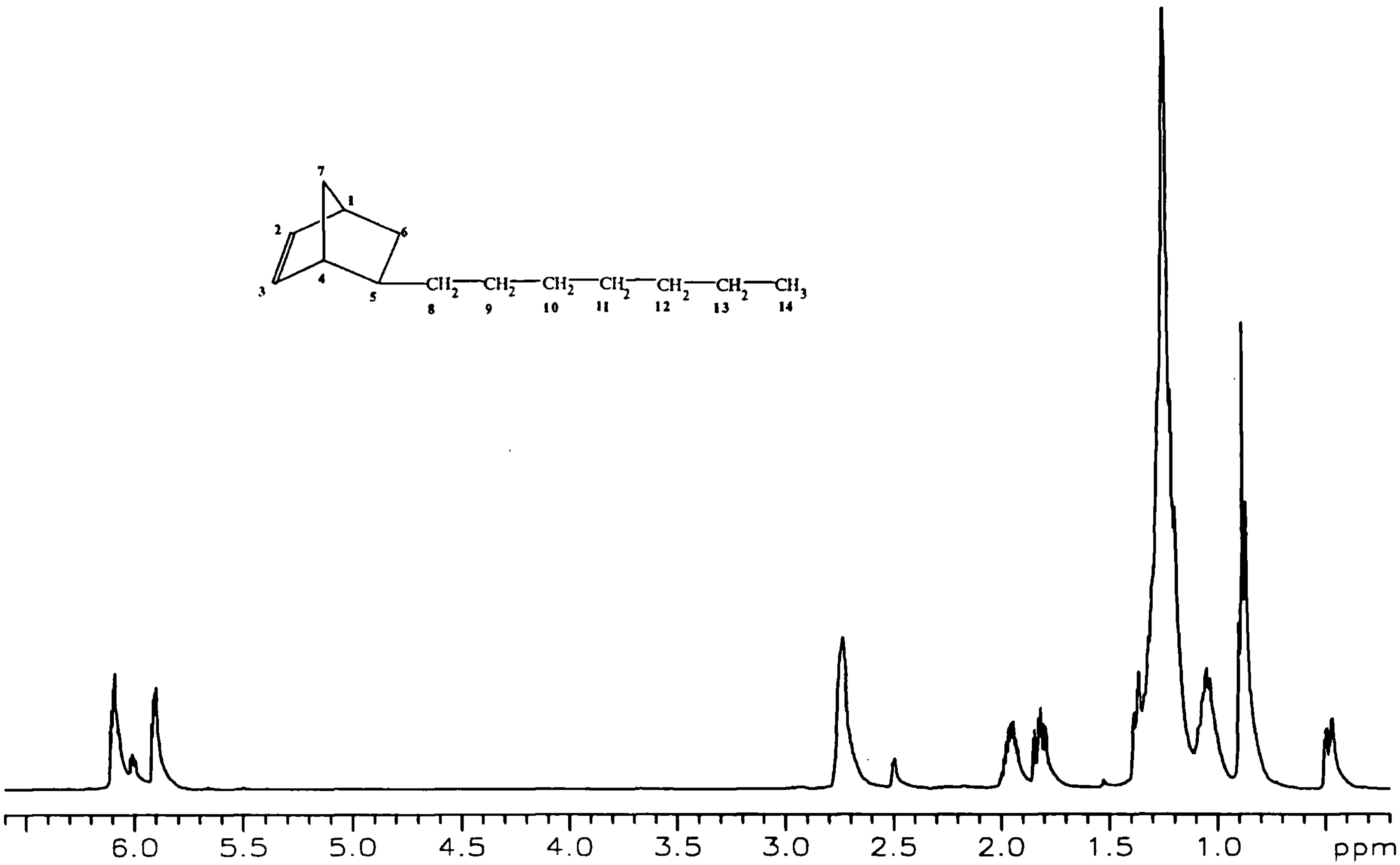
APPENDIX C1 ^{1}H NMR Spectrum of (±)-*exo/endo*-5-tetradecylnorbornene



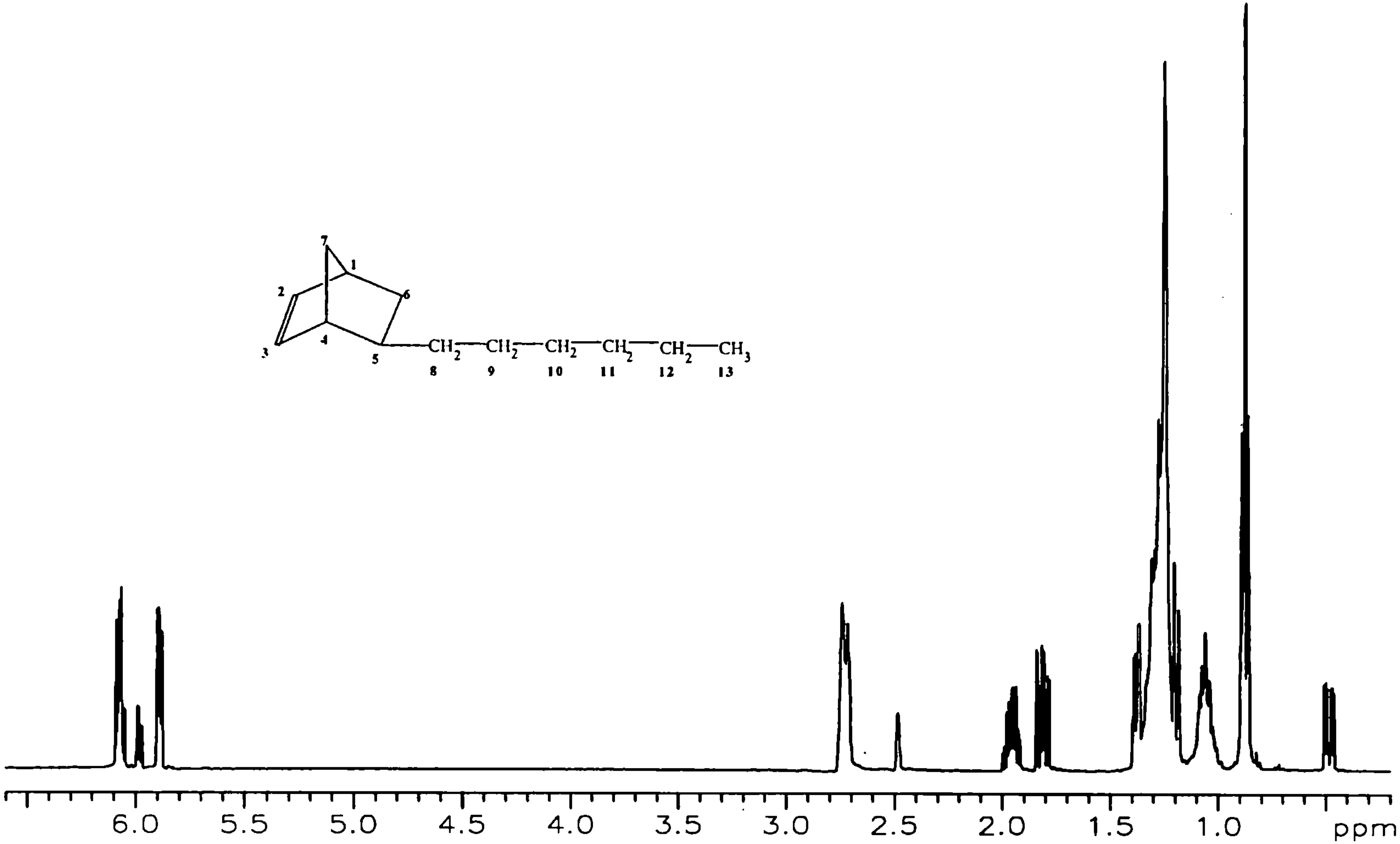
APPENDIX C2 ^{1}H NMR Spectrum of (±)-*exo/endo*-5-hexadecylnorbornene



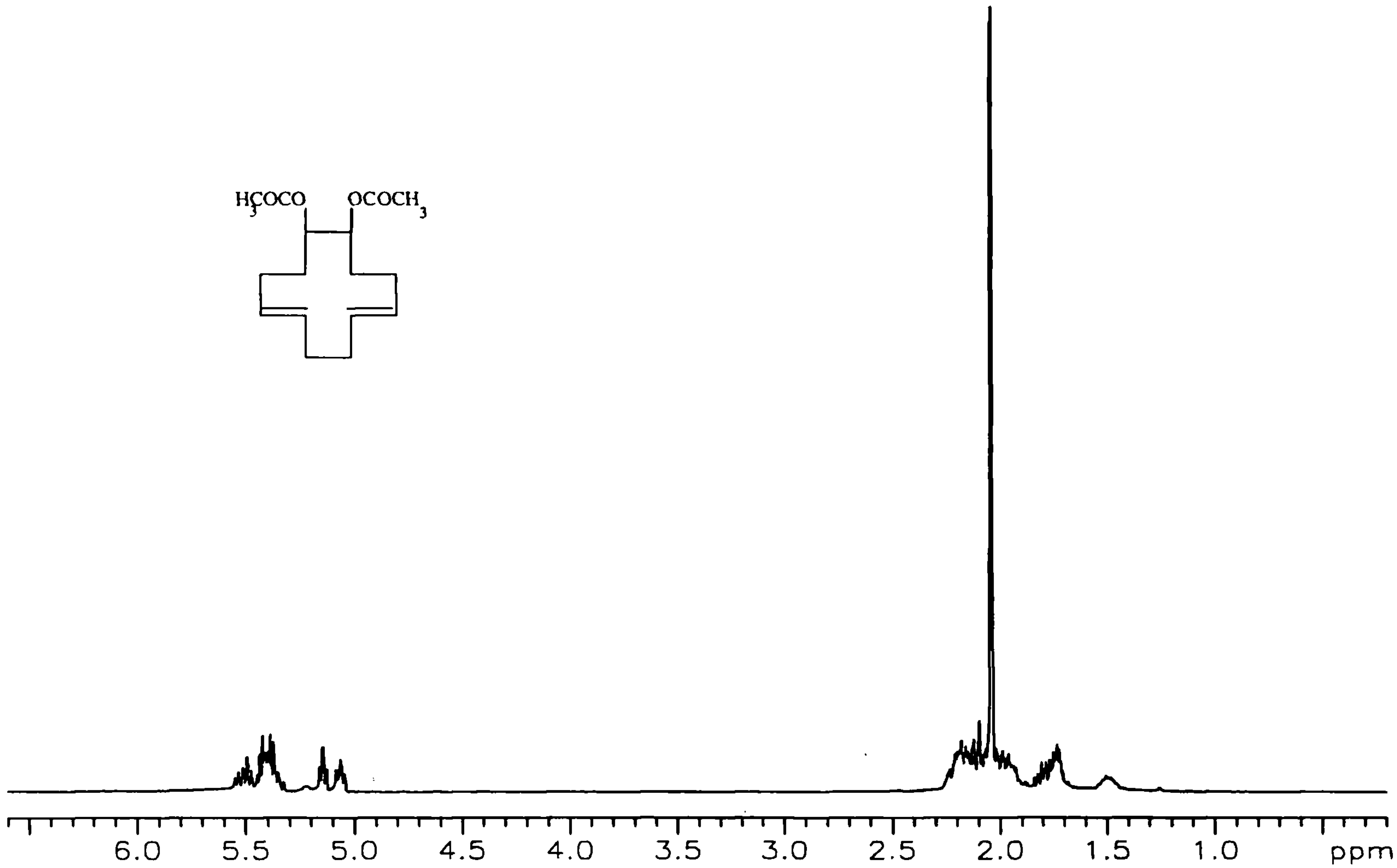
APPENDIX C3 ^{1}H NMR Spectrum of (±)-*exo*/*endo*-5-decylnorbornene



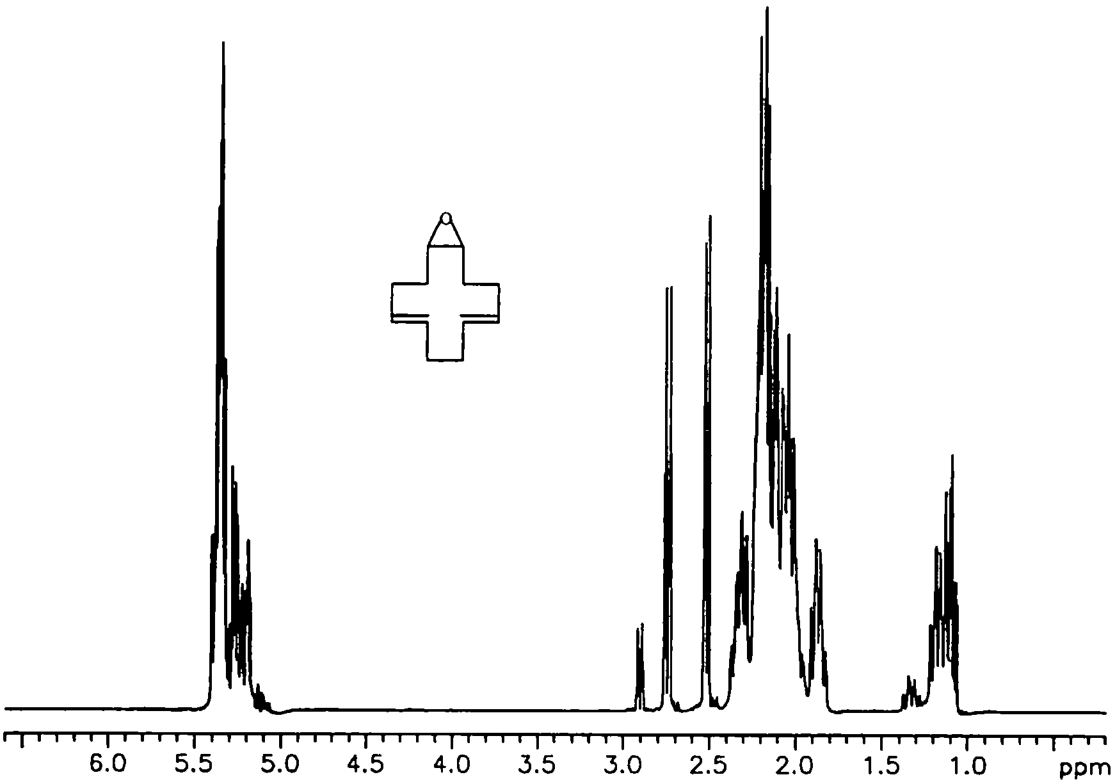
APPENDIX C4 ^{1}H NMR Spectrum of (±)-*exo/endo*-5-heptyl norbornene



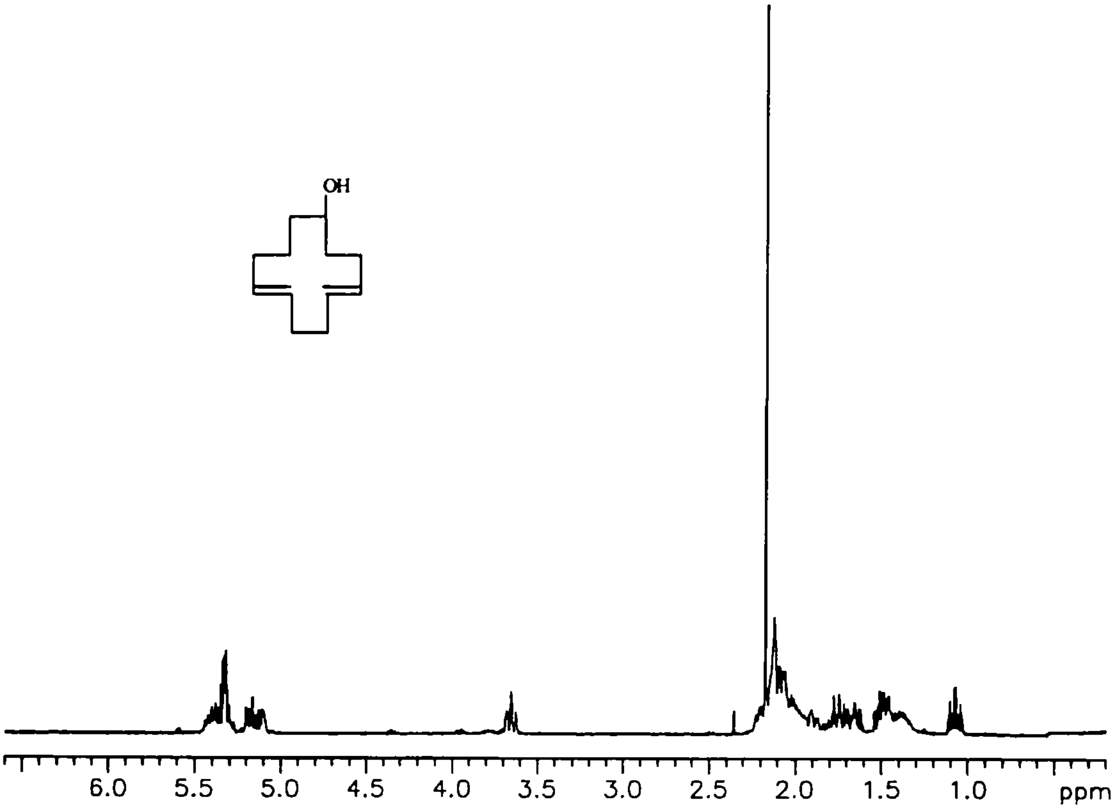
APPENDIX C5 ^{1}H NMR Spectrum of (±)-*exo/endo*-5-hexylnorbornene



APPENDIX C6 ^{1}**H NMR Spectrum of 1,2-diacetoxy-5,9-cyclododecadiene**

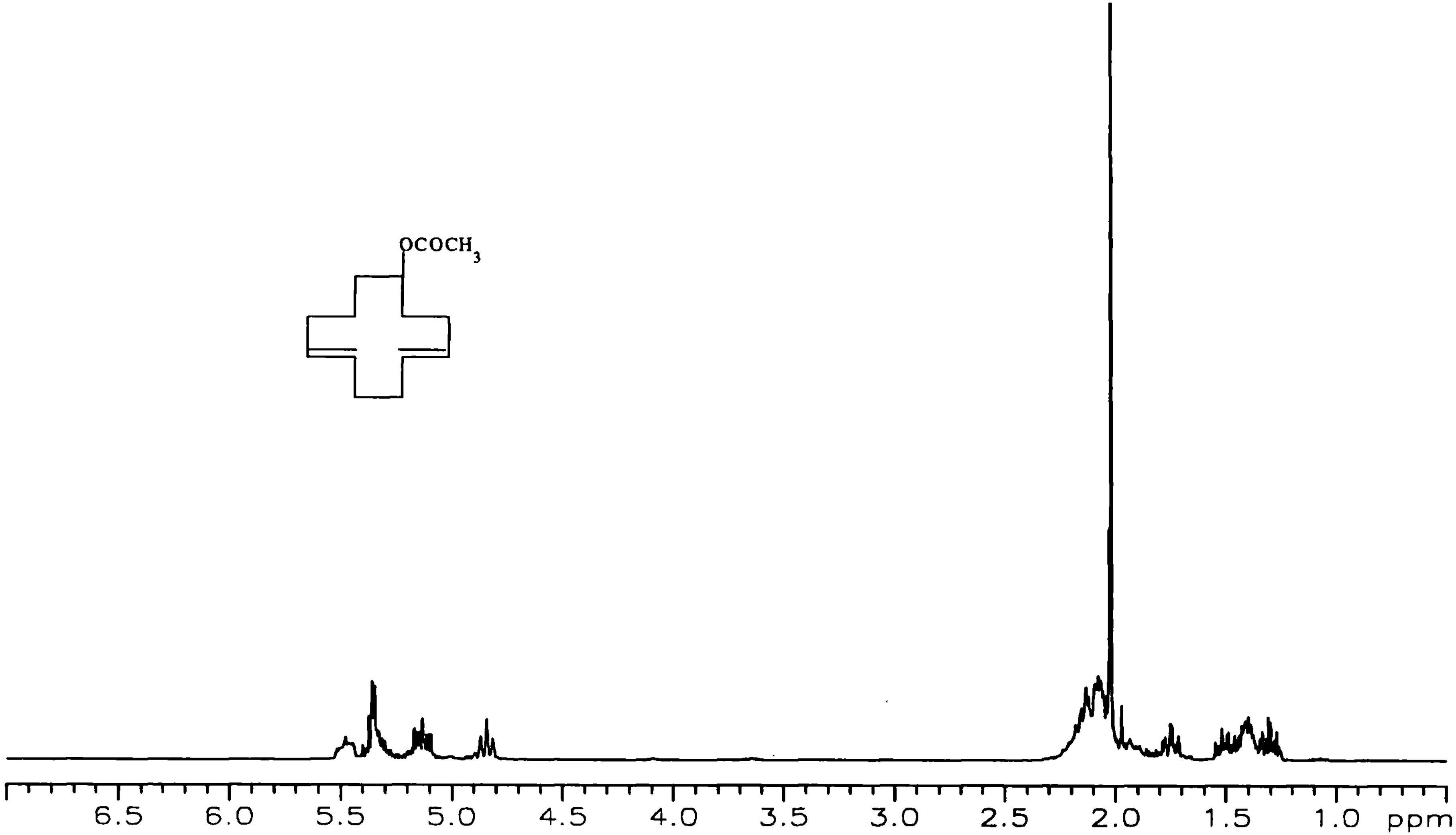


(i) ^{1}H NMR Spectrum of 1,2-diacetoxy-5,9-cyclododecadiene

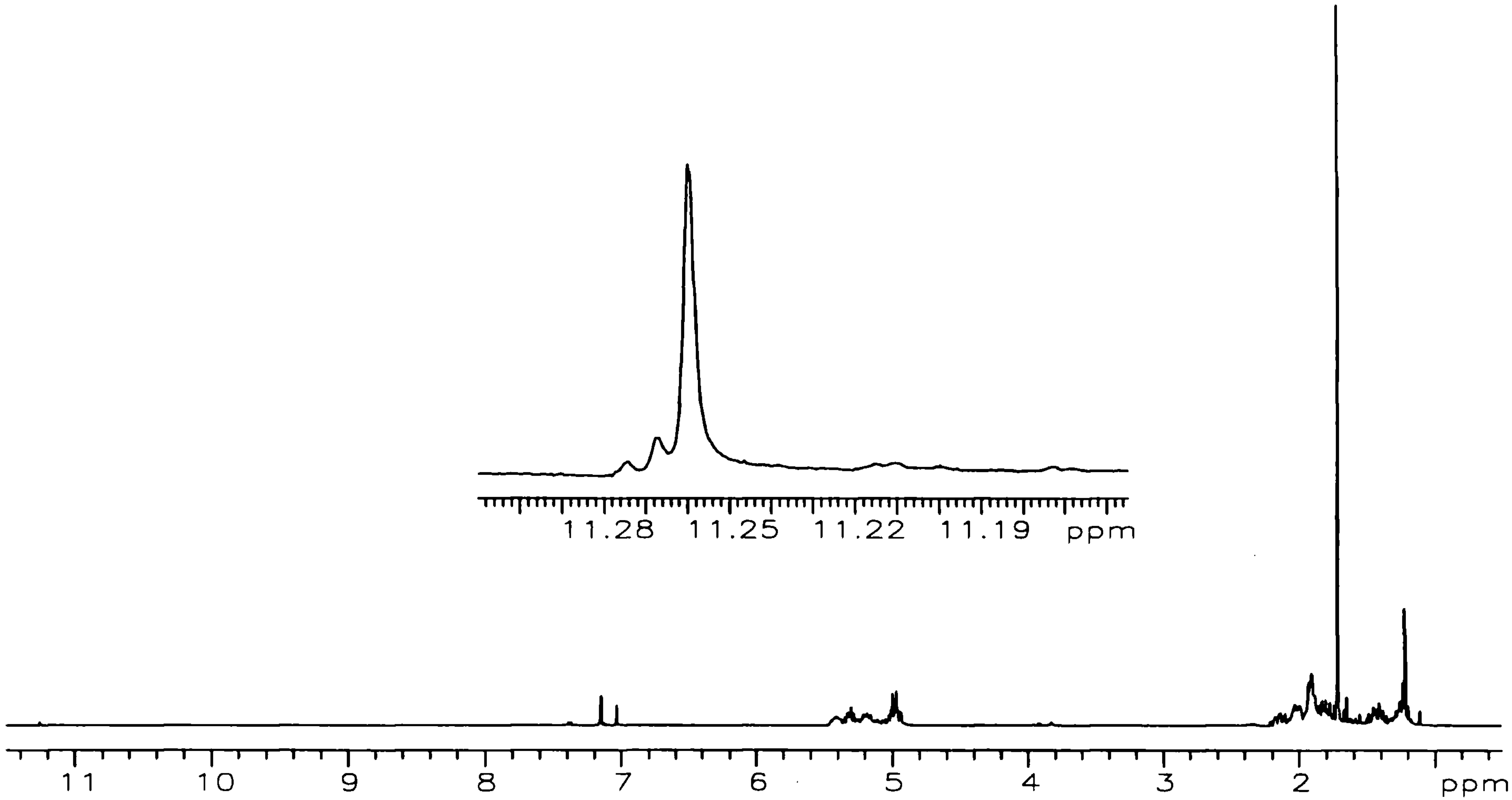


(ii) ^{1}H NMR Spectrum of 1-hydroxy-4,8-cyclododecadiene

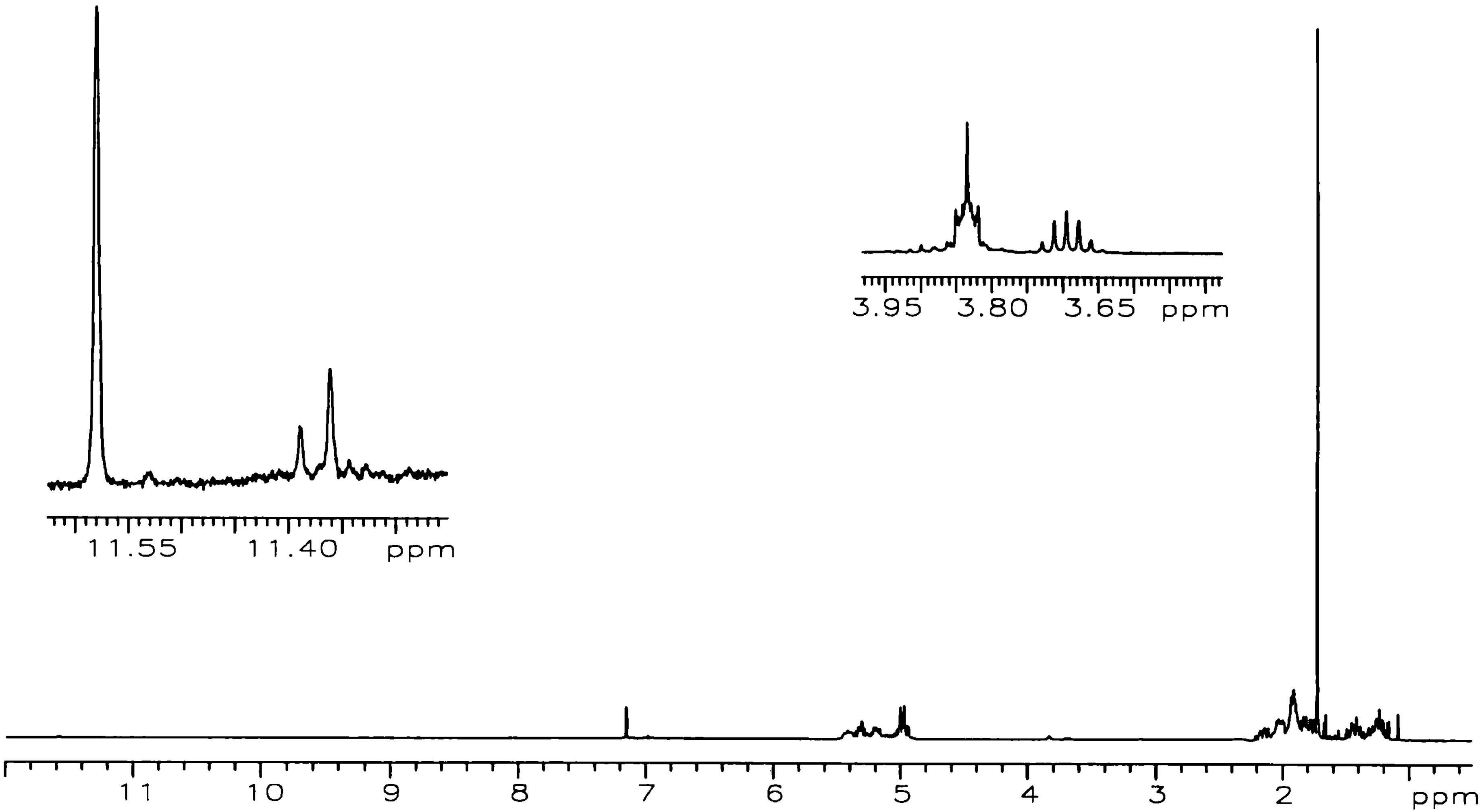
APPENDIX C7



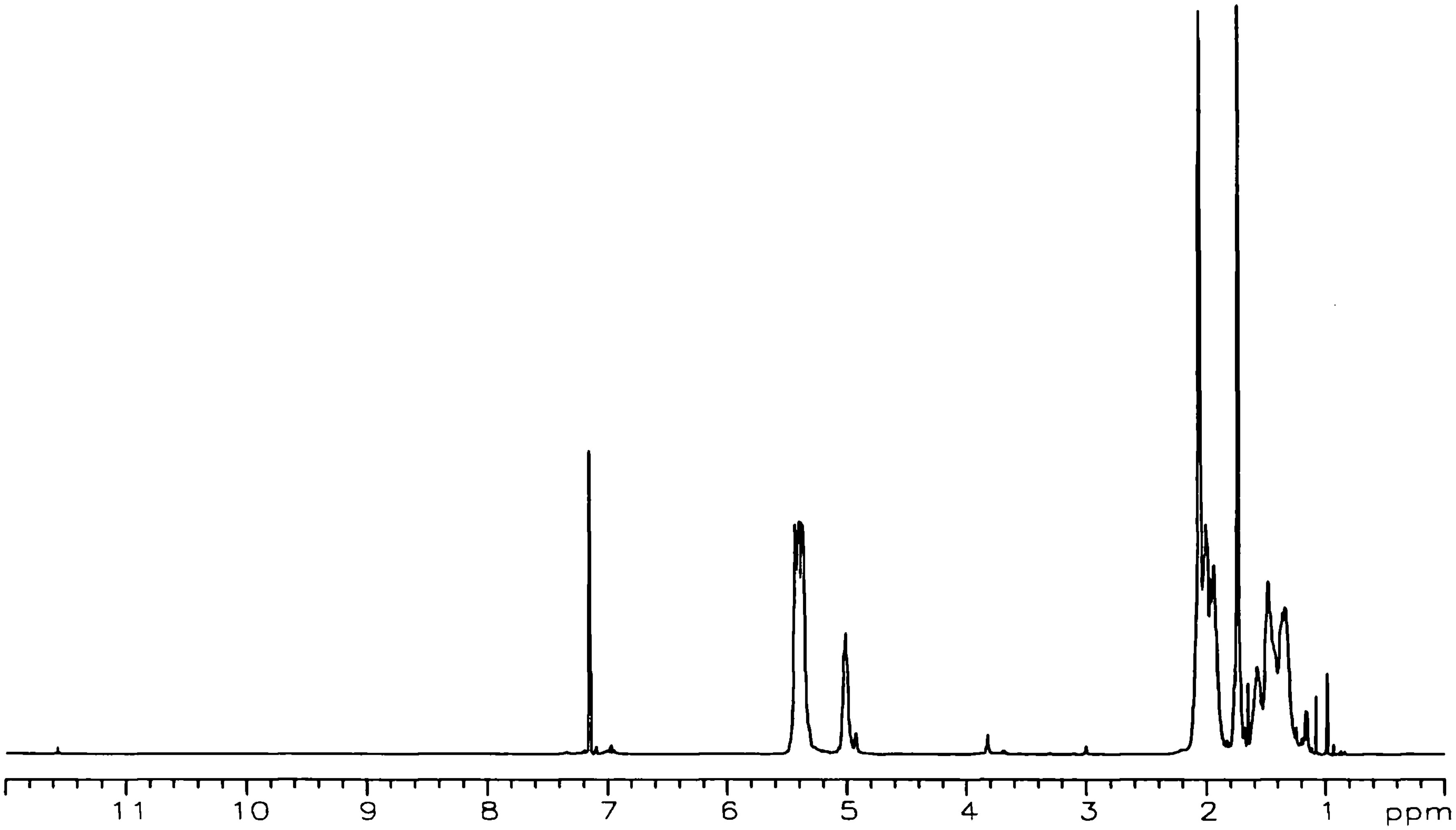
APPENDIX C8 ^{1}H NMR Spectrum of 1-acetoxy-4,8-cyclododecadiene



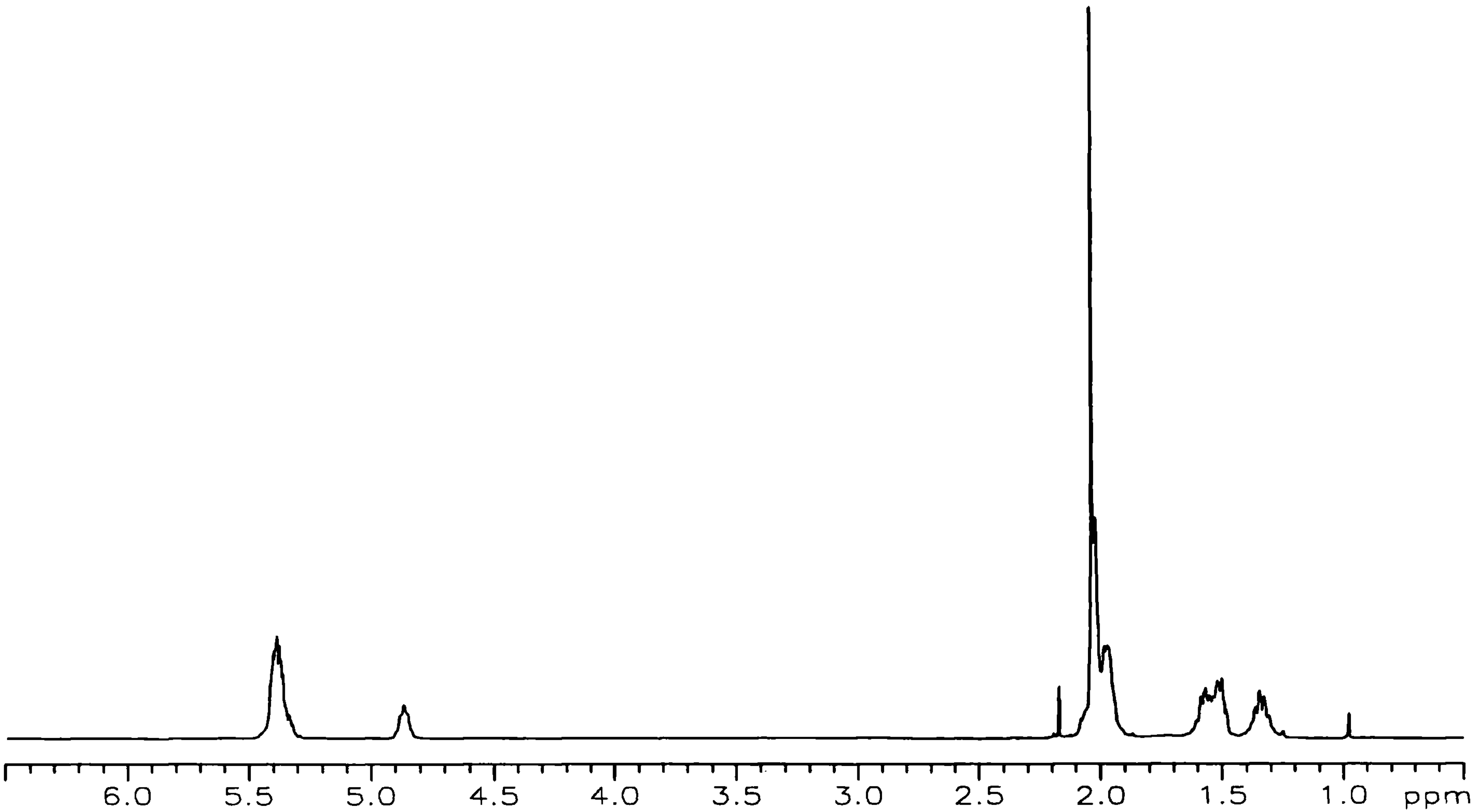
APPENDIX C9 ^1H NMR Spectrum of the polymerisation of 1-acetoxy-4,8-cyclododecadiene (in progress)



APPENDIX C10 ^{1}H NMR Spectrum of the polymerisation of 1-acetoxy-4,8-cyclododecadiene (in progress) (Expt. No. 81)

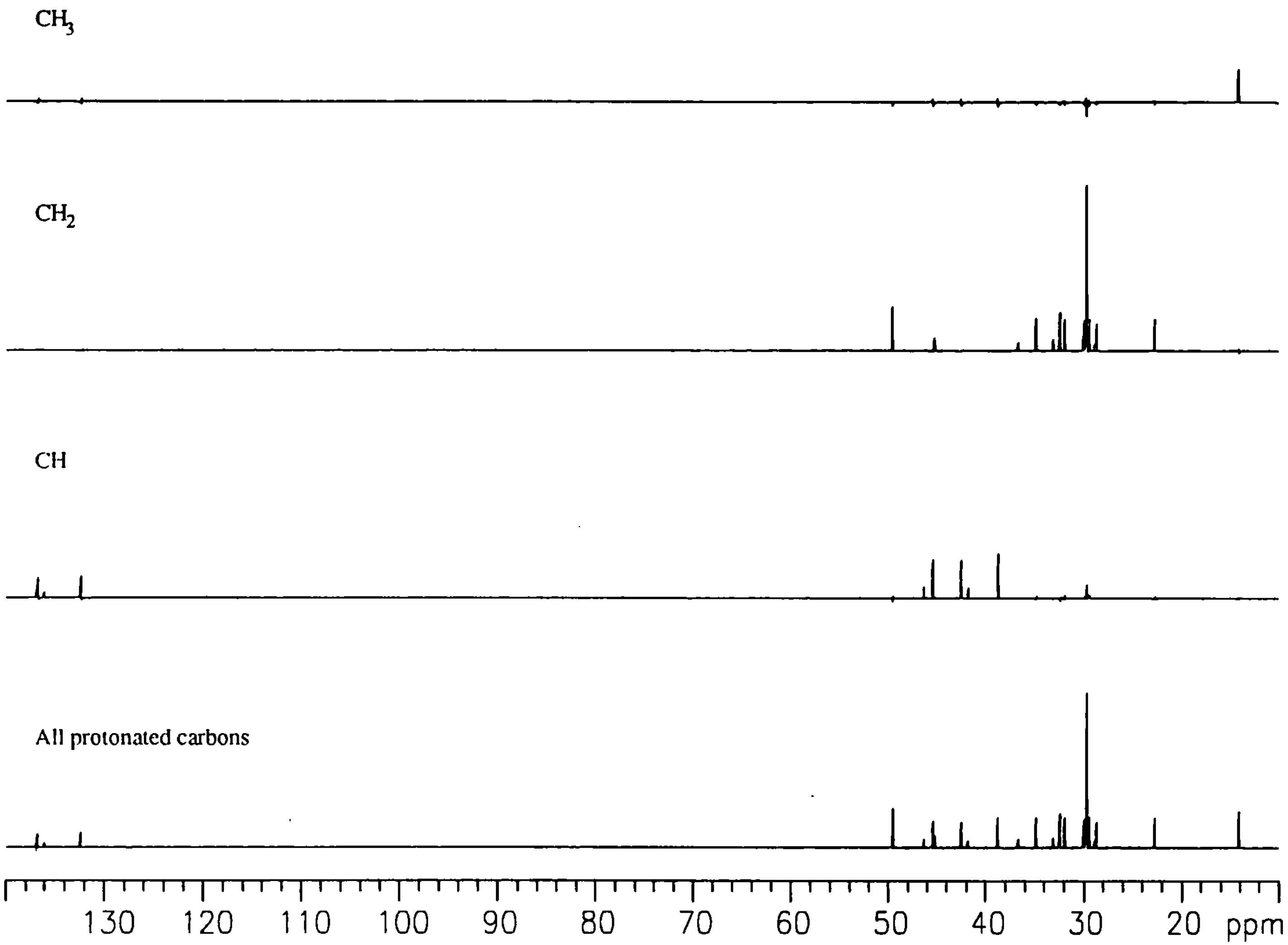


APPENDIX C11 ^{1}H NMR Spectrum of the polymerisation of 1-acetoxy-4,8-cyclododecadiene (in progress-after 24hrs) (Expt. No. 81)

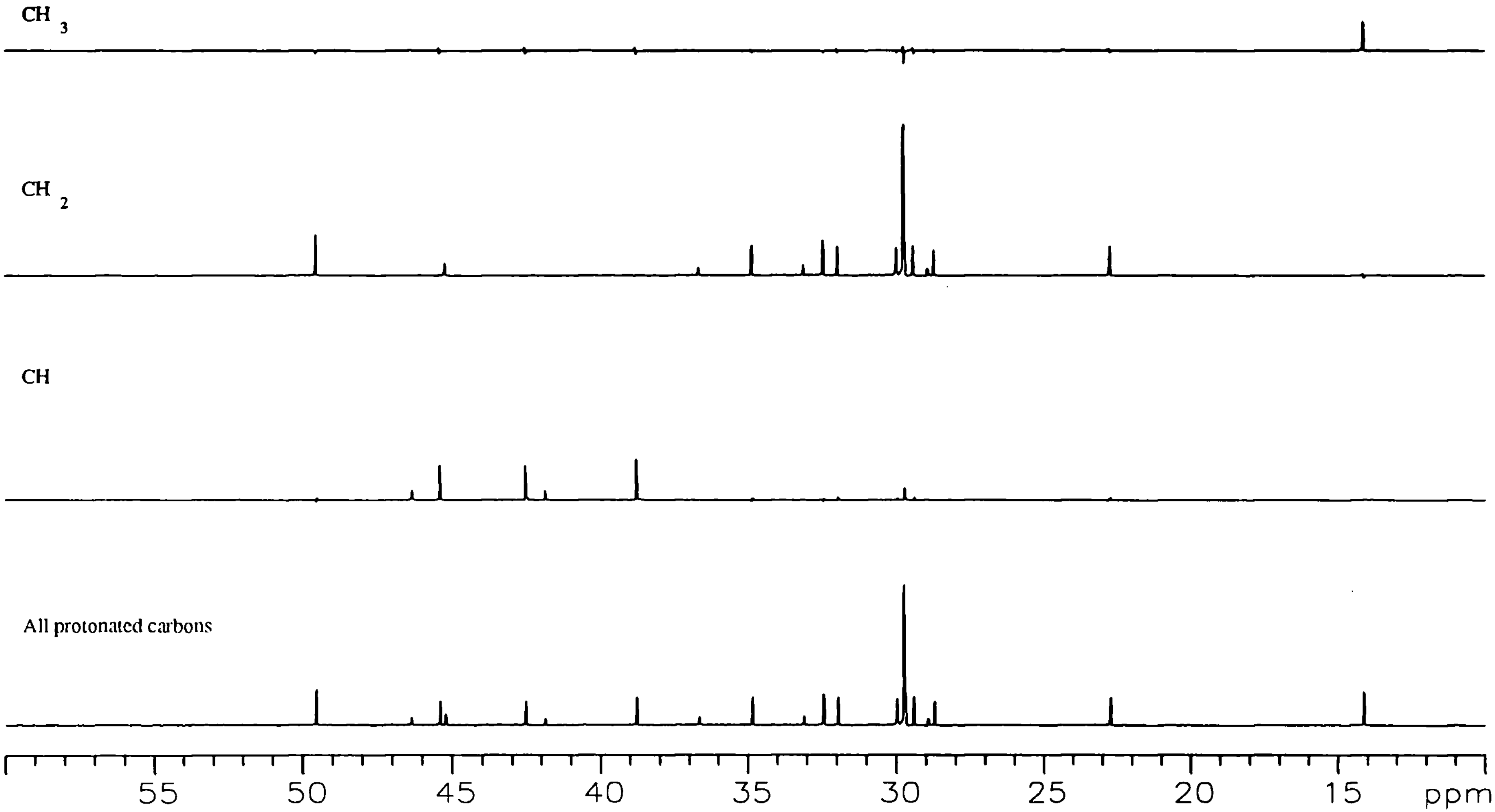


APPENDIX C12 ^{1}H NMR Spectrum of poly(acetoxycyclododecadiene)

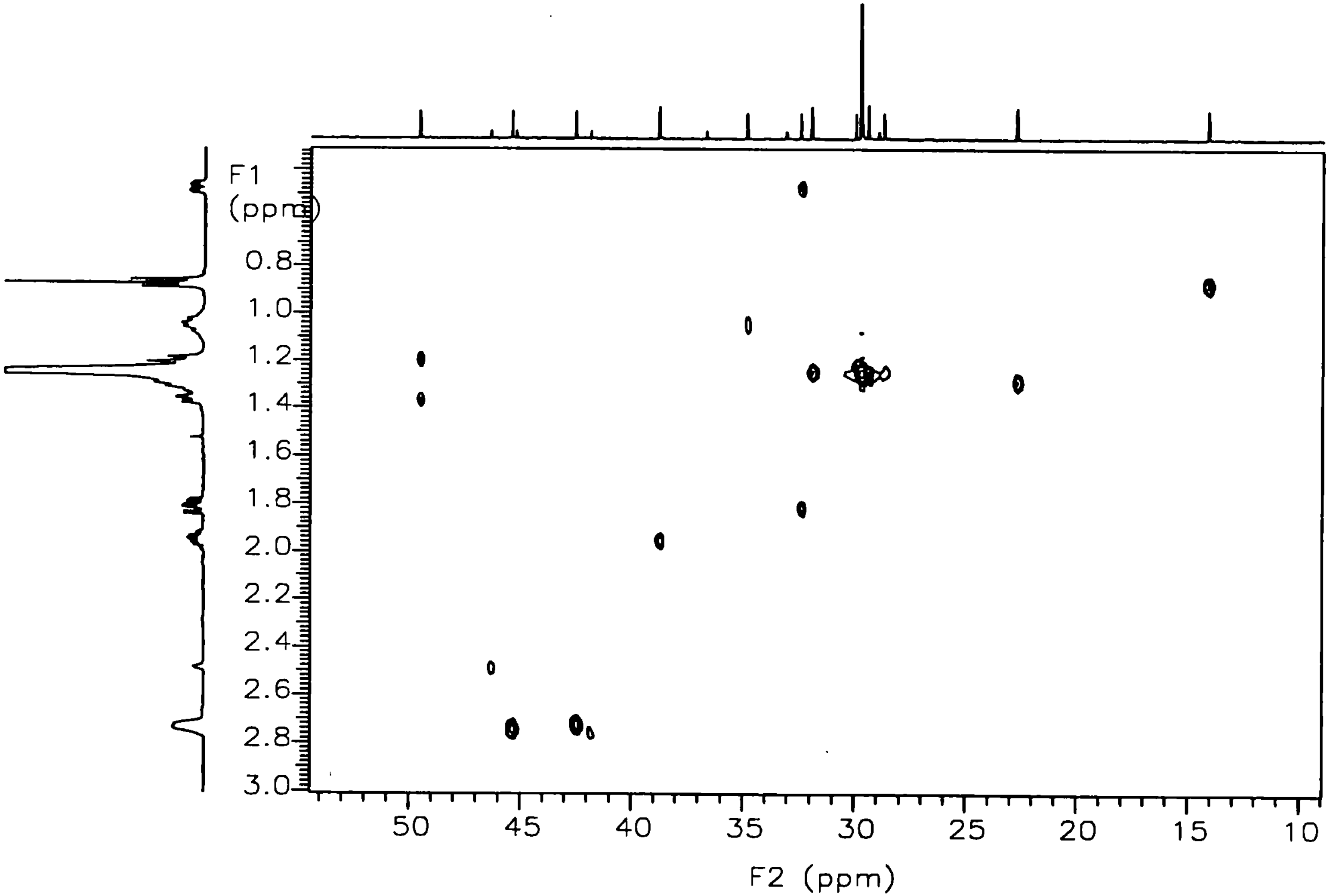
APPENDIX D



APPENDIX D1 DEPT Spectrum of (±)-*exo/endo*-5-tetradecylnorbornene

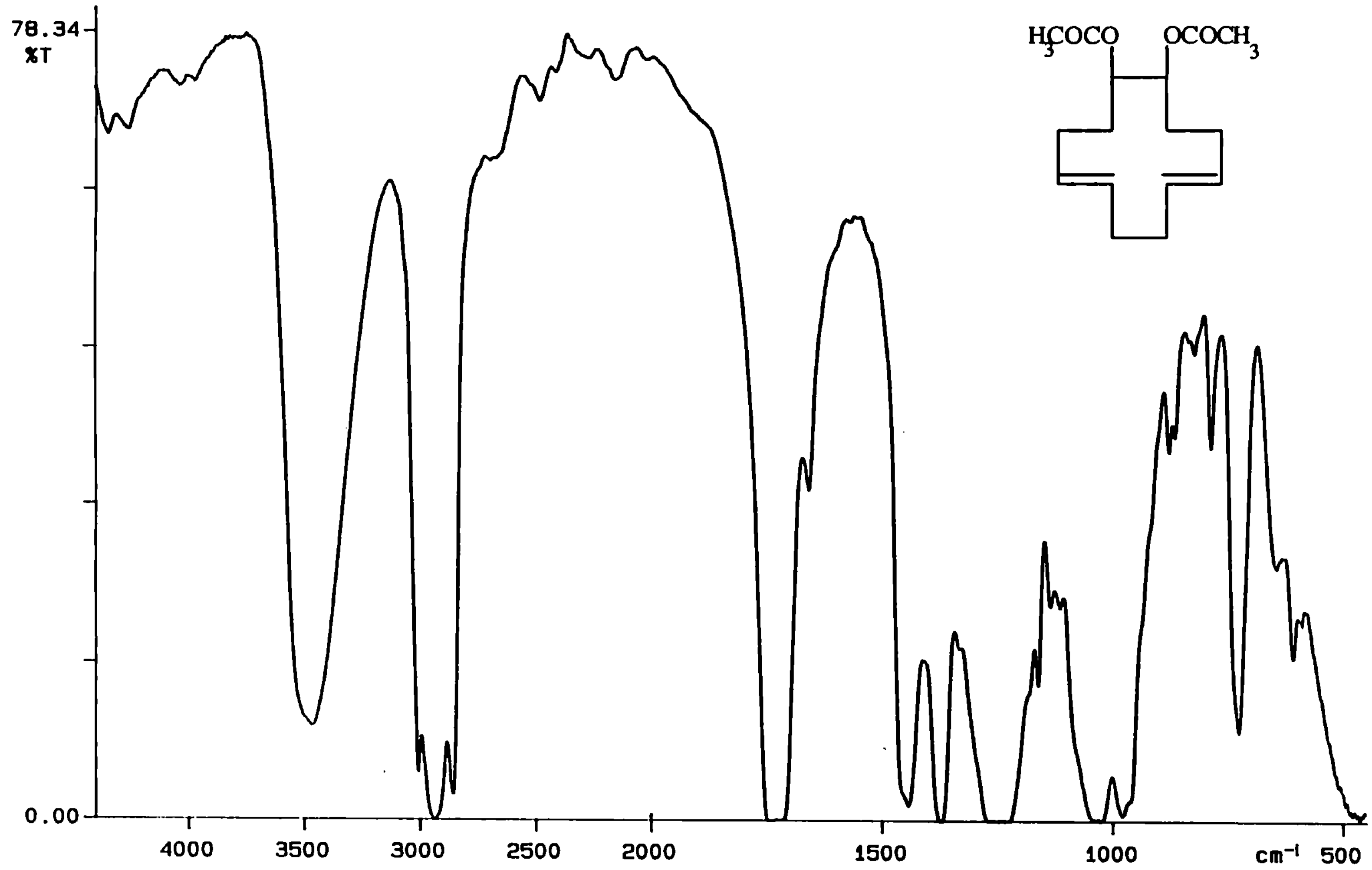


APPENDIX D2 Expanded DEPT Spectrum of (±)-*exo*/*endo*-5-tetradecylnorbornene

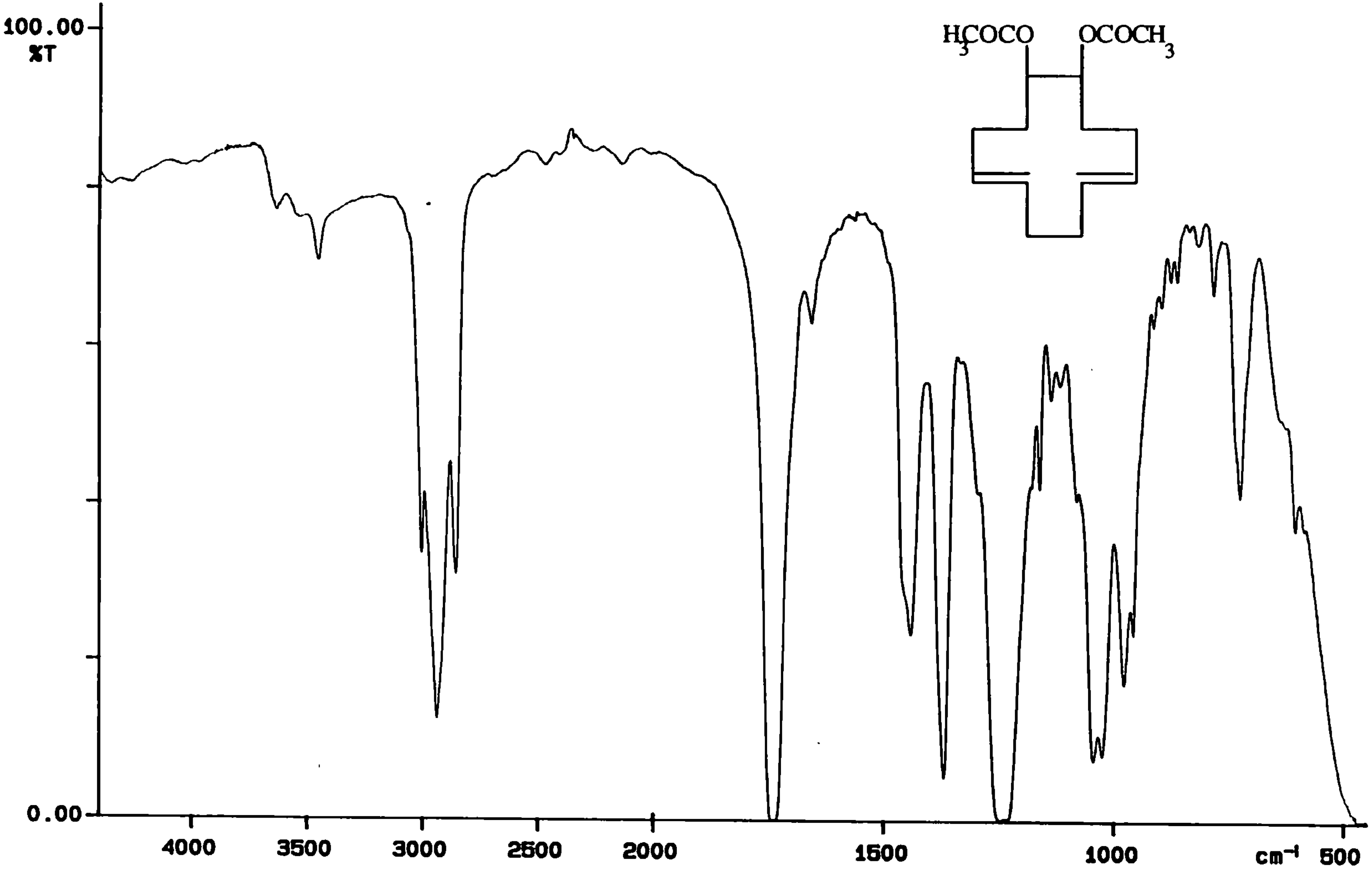


APPENDIX D3 HETCOR Spectrum of (±) *exo/endo*-5-tetradecylnorbornene

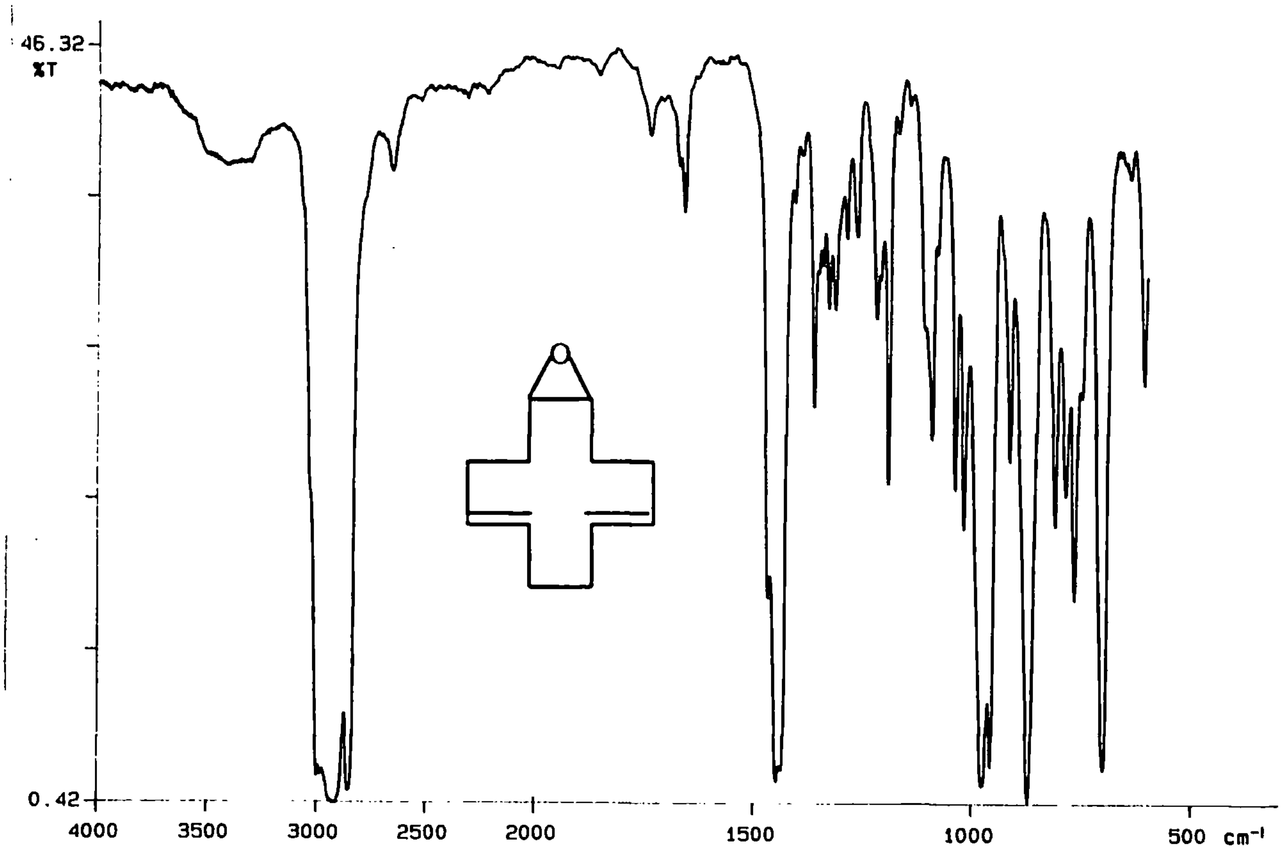
APPENDIX E

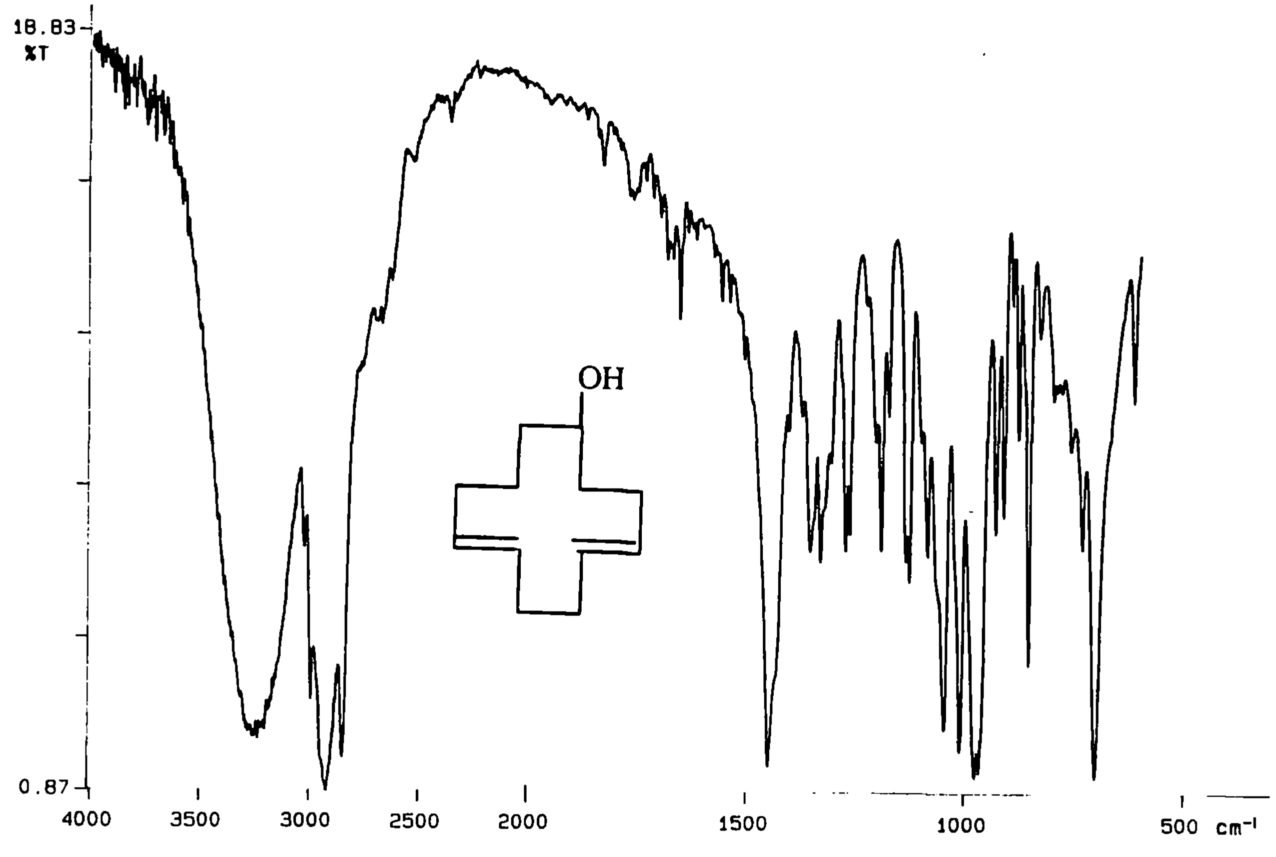


APPENDIX E1 FTIR spectrum of impure 1,2-diacetoxy-5,9-cyclododecadiene



APPENDIX E2 FTIR spectrum of 1,2-diacetoxy-5,9-cyclododecadiene

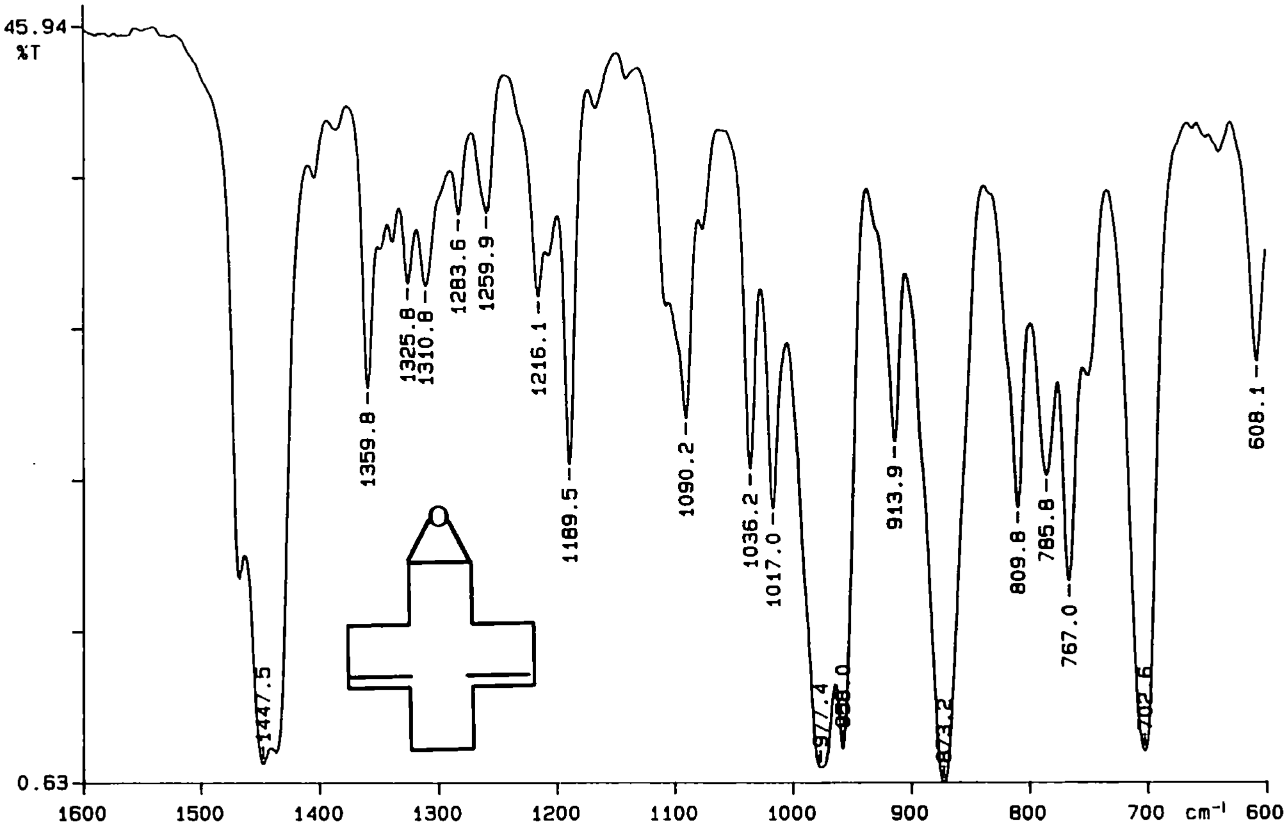


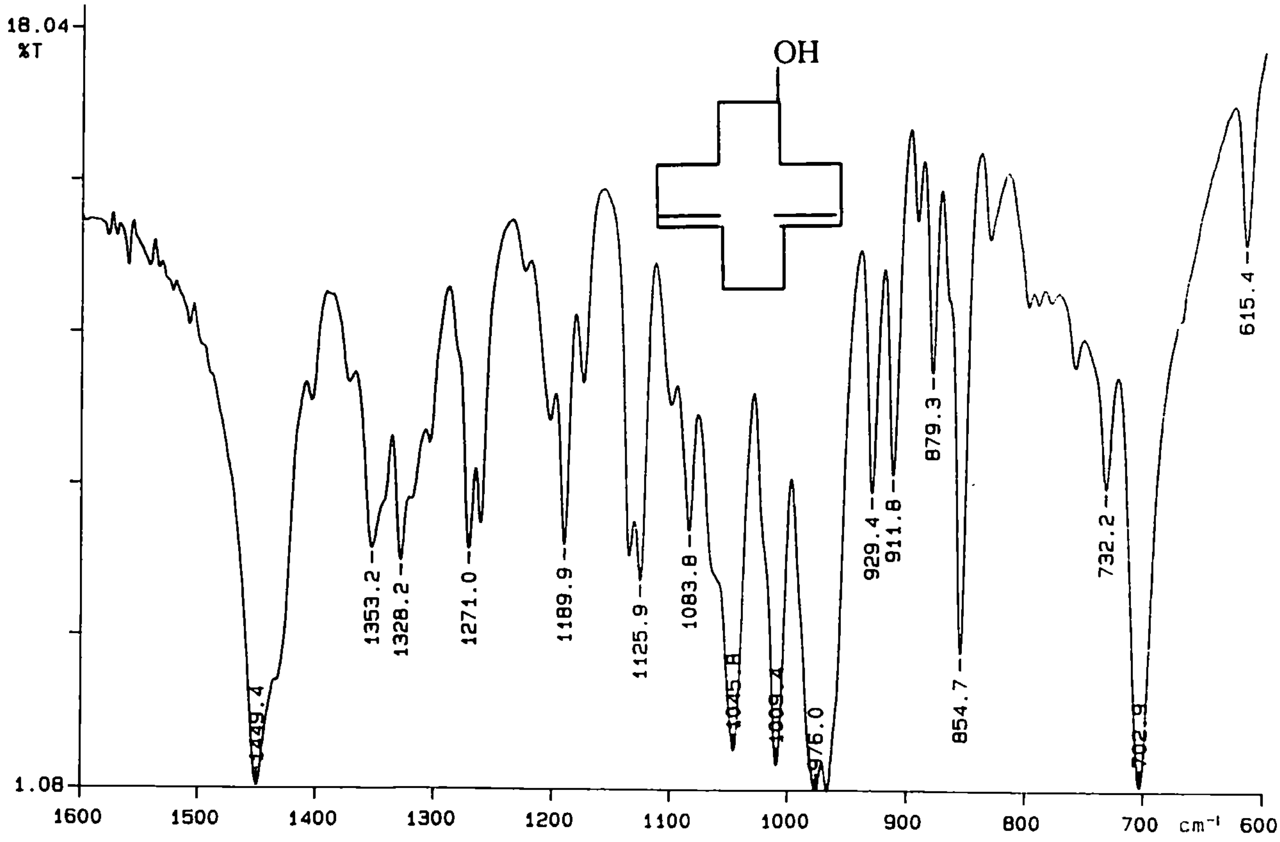


(i) FTIR spectrum of 1,2-epoxy-5,9-cyclododecadiene

(ii) FTIR spectrum of 1-hydroxy-4,8-cyclododecadiene

APPENDIX E3

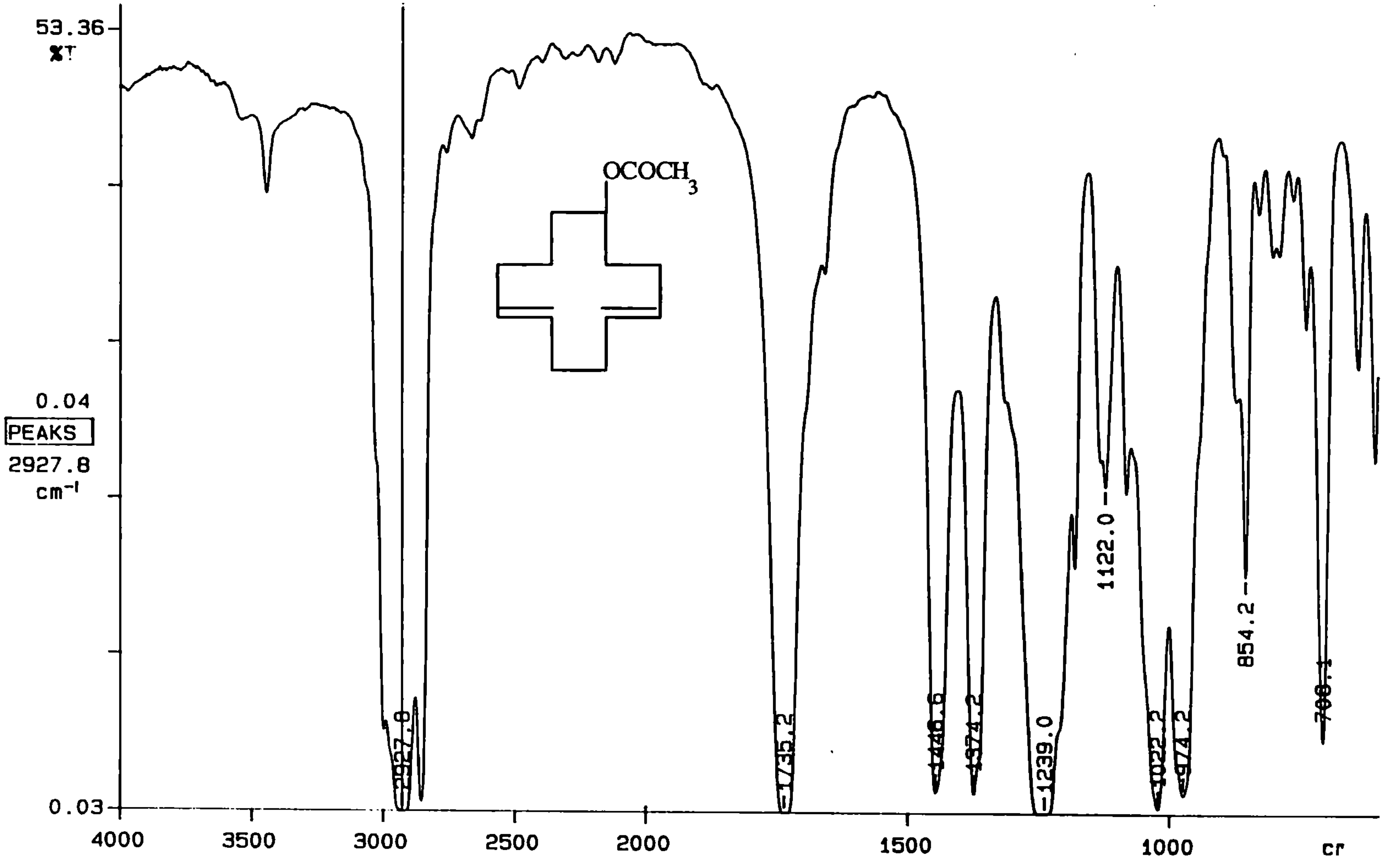




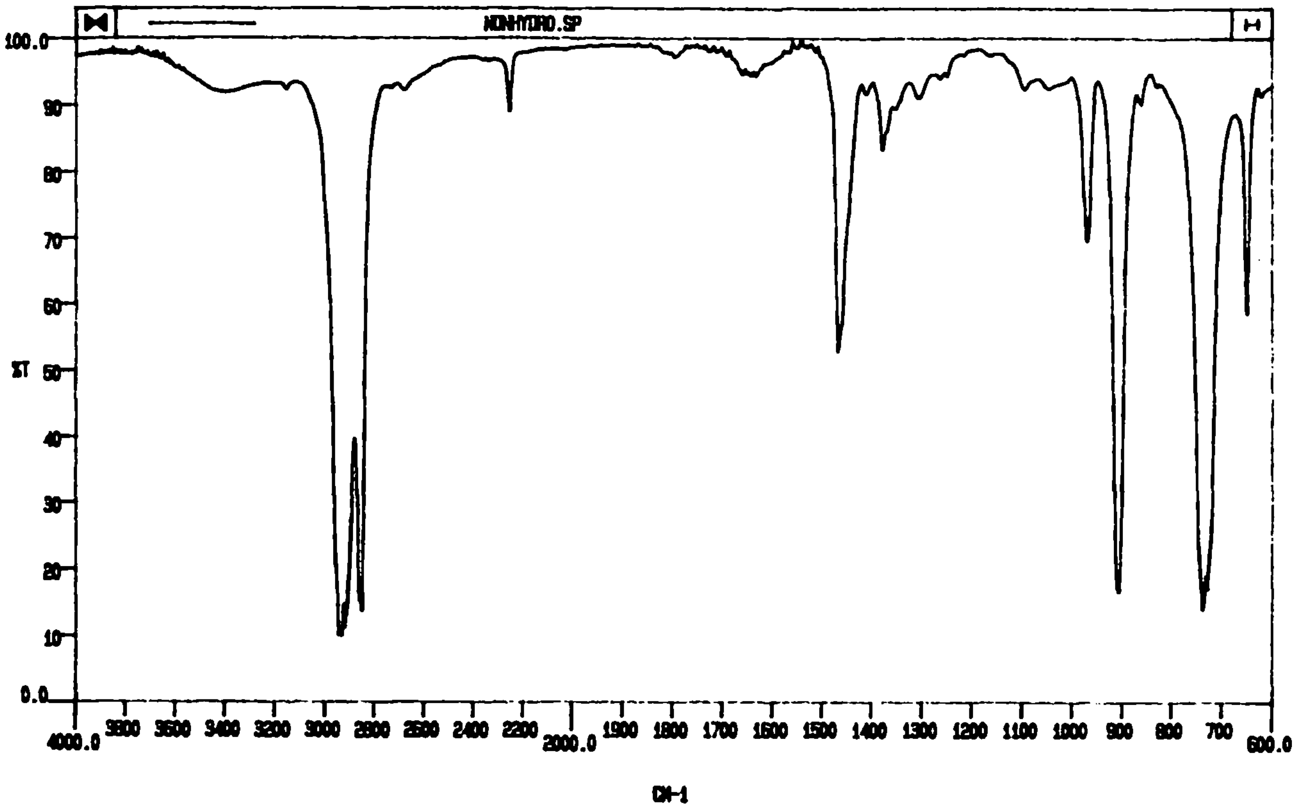
(i) Expanded FTIR spectrum of 1,2-epoxy-5,9-cyclododecadiene

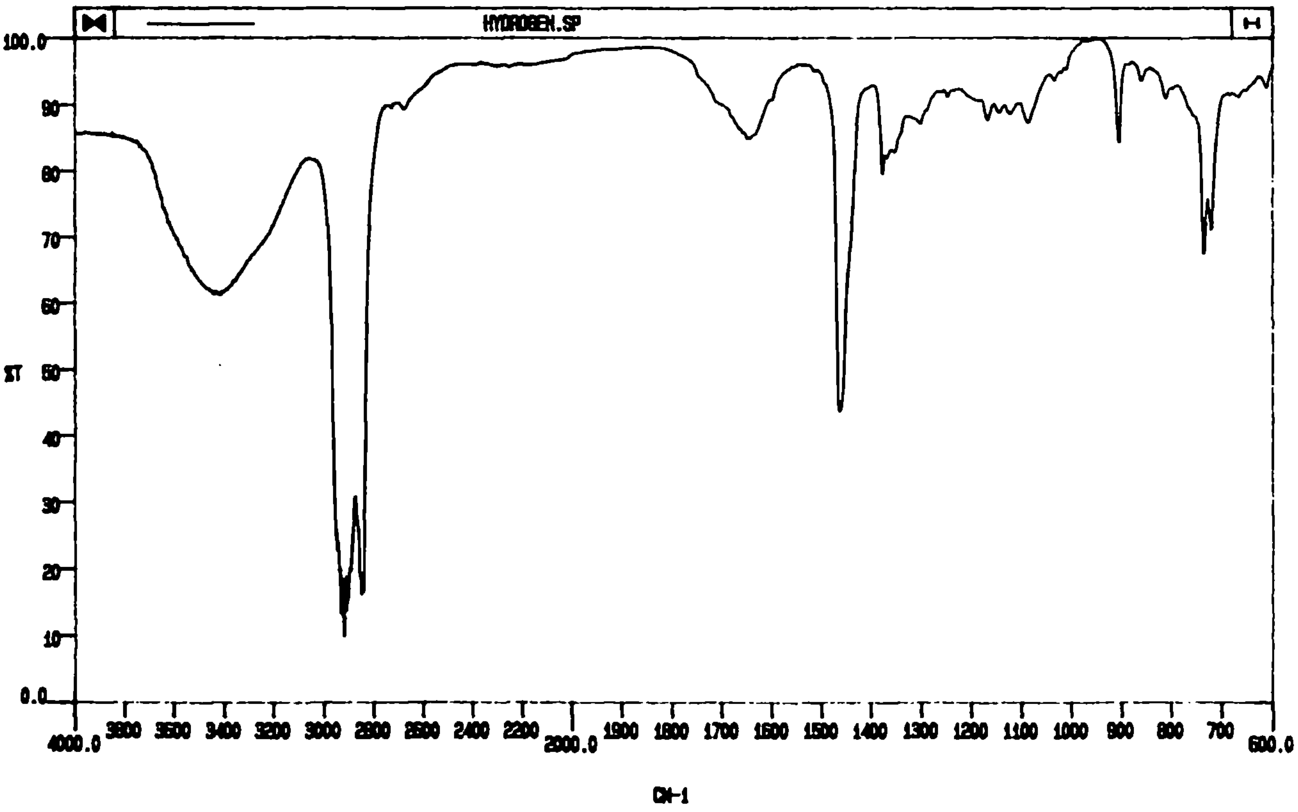
(ii) Expanded FTIR spectrum of 1-hydroxy-4,8-cyclododecadiene

APPENDIX E4



APPENDIX E5 FTIR spectrum of 1-acetoxy-4,8-cyclododecadiene

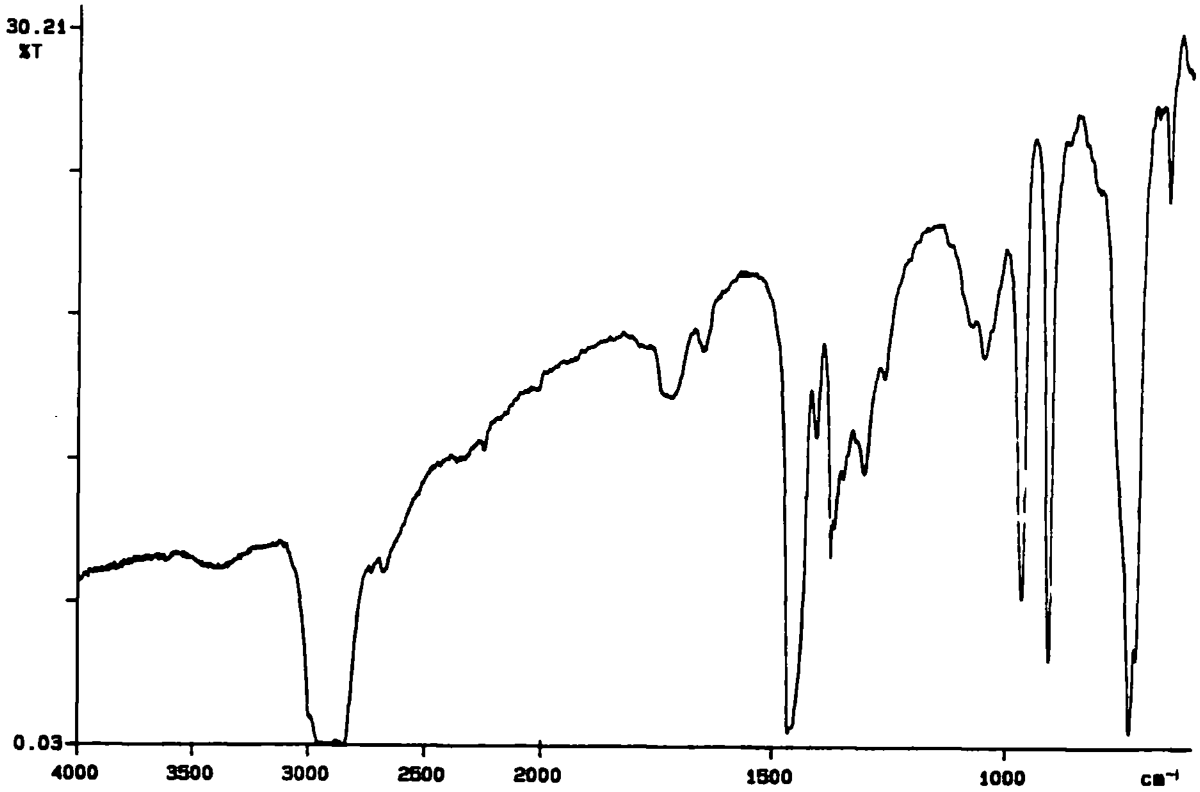


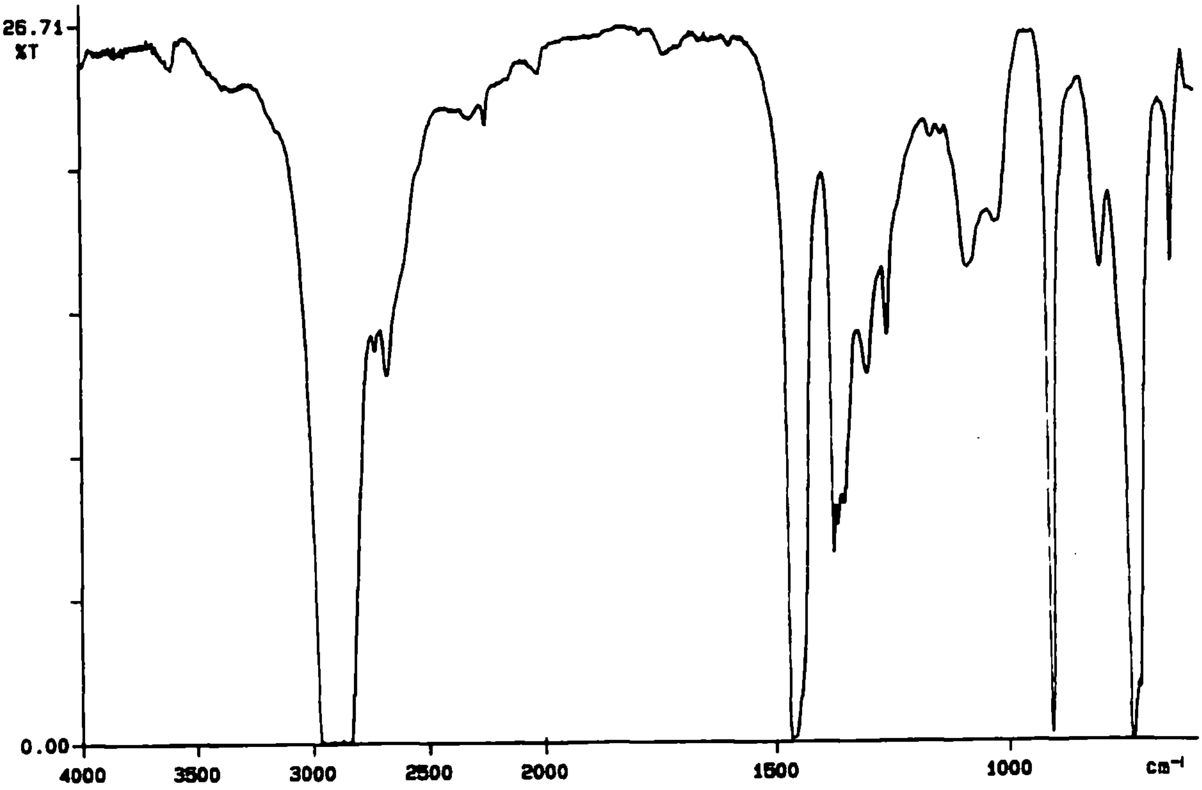


(i) FTIR Spectrum of non-hydrogenated poly(5-tetradecylnorbornene)

(ii) FTIR Spectrum of hydrogenated poly(5-tetradecylnorbornene)

APPENDIX E6



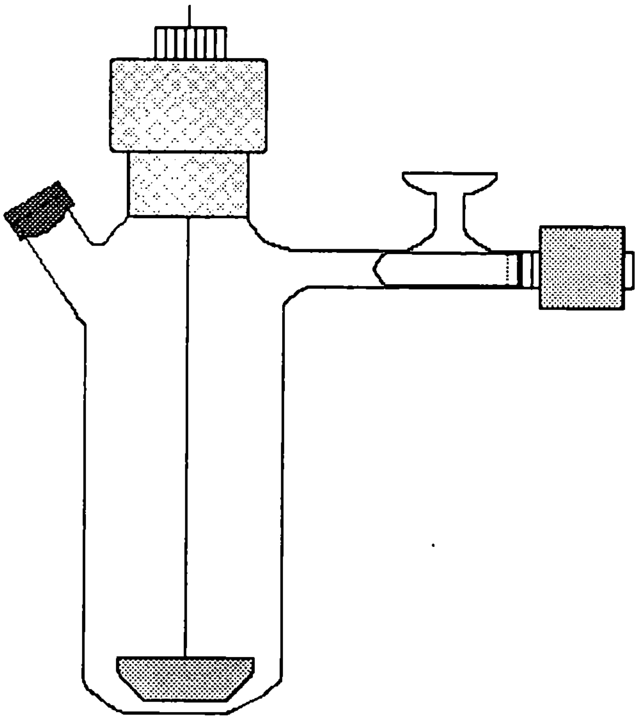


(i) FTIR Spectrum of non-hydrogenated poly(5-hexadecylnorbornene)

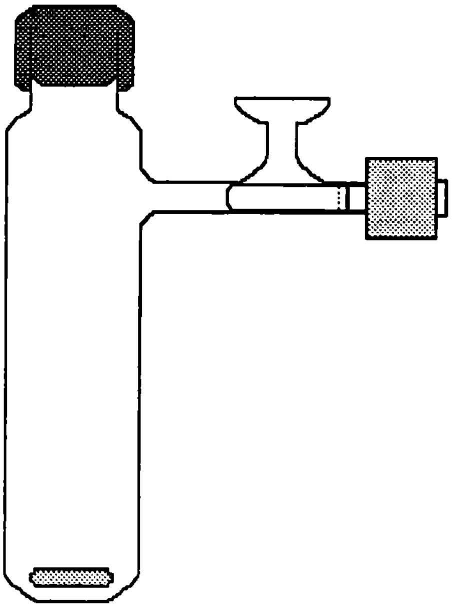
(ii) FTIR Spectrum of hydrogenated poly(5-hexadecylnorbornene)

APPENDIX E7

APPENDIX F



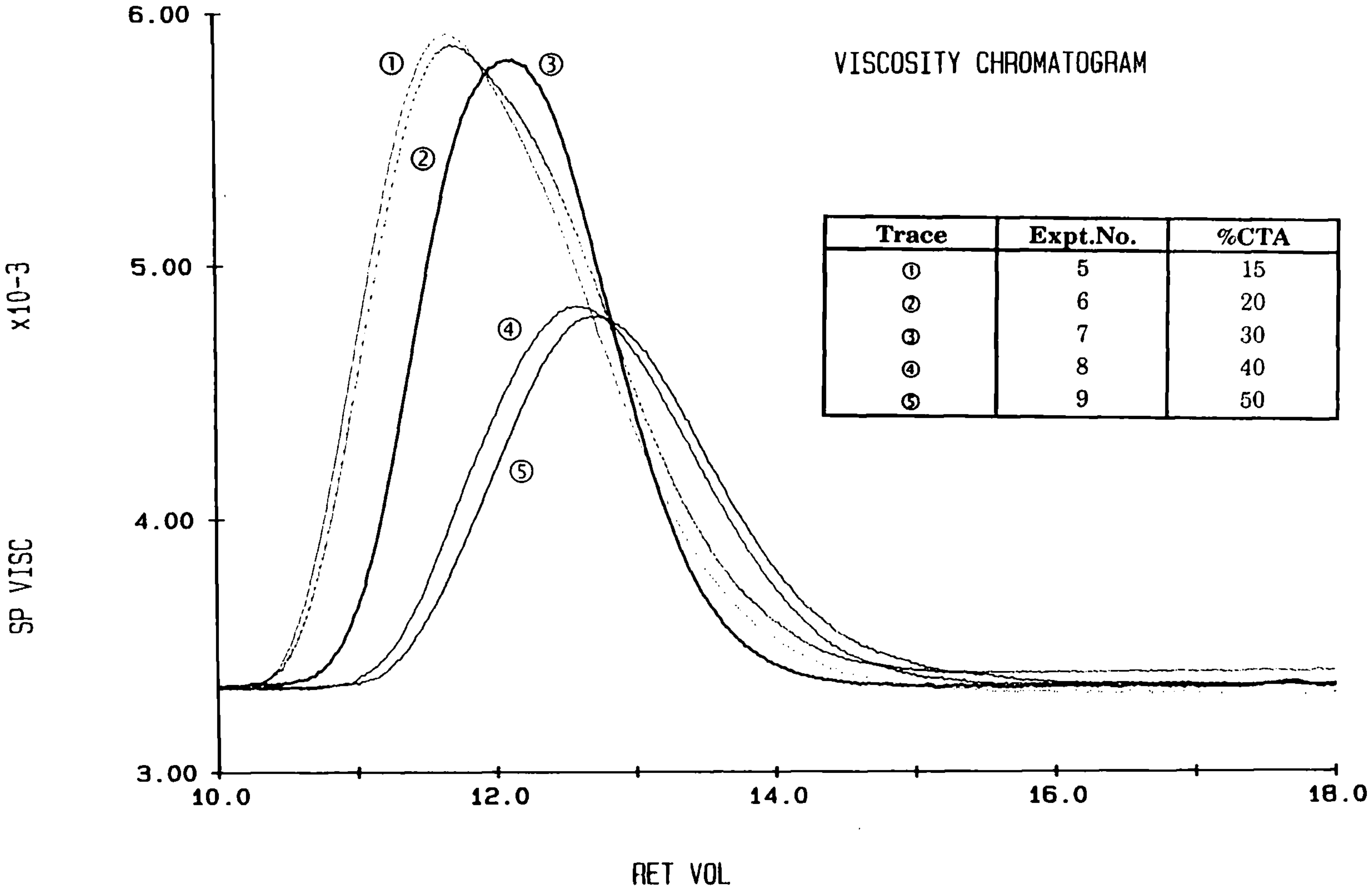
(i)



(ii)

APPENDIX F

APPENDIX G



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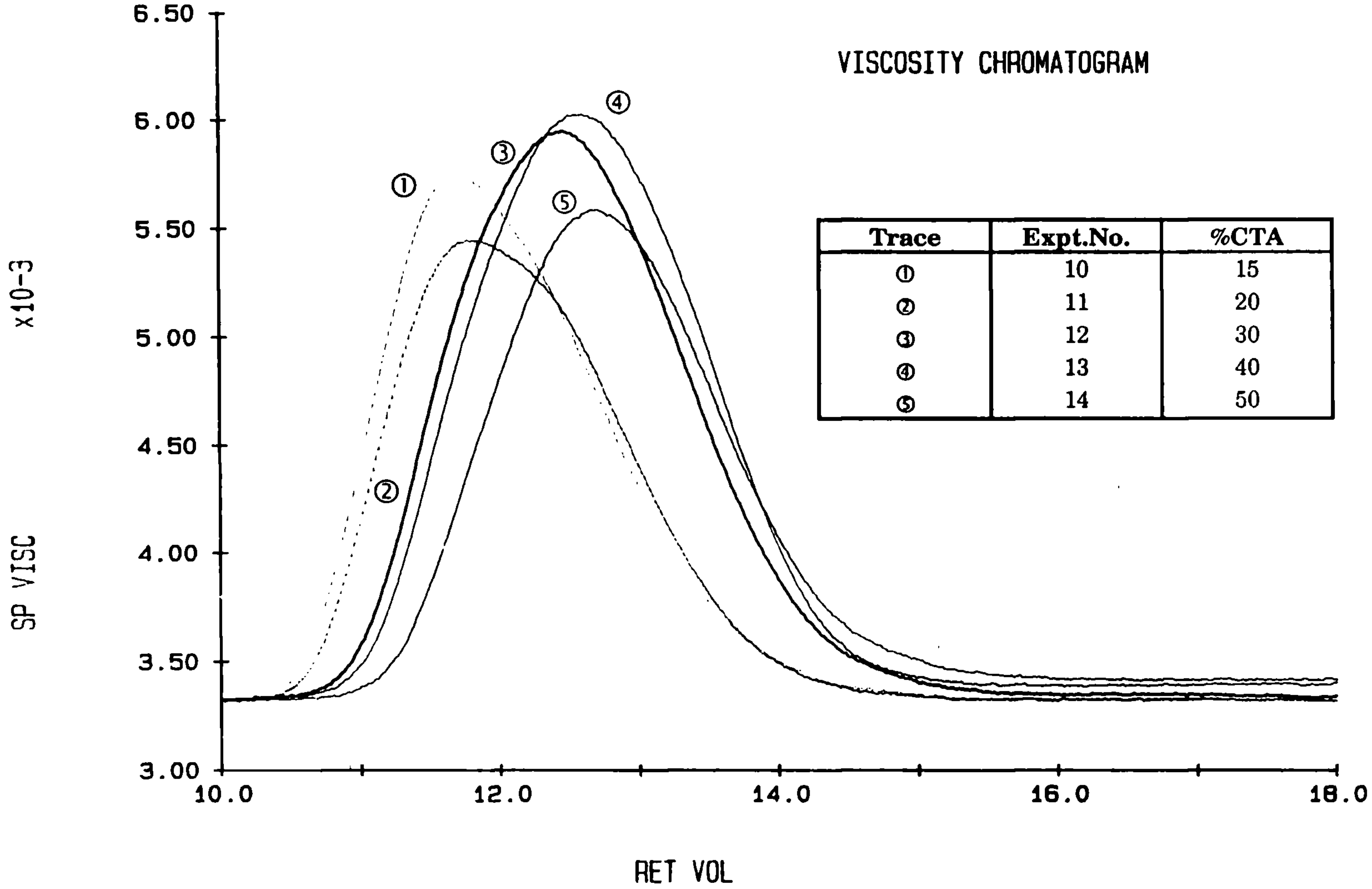
④	8	40
⑤	9	50

APPENDIX G1 GPC Traces for chain transfer studies on poly(5-tetradecylnorbornene)



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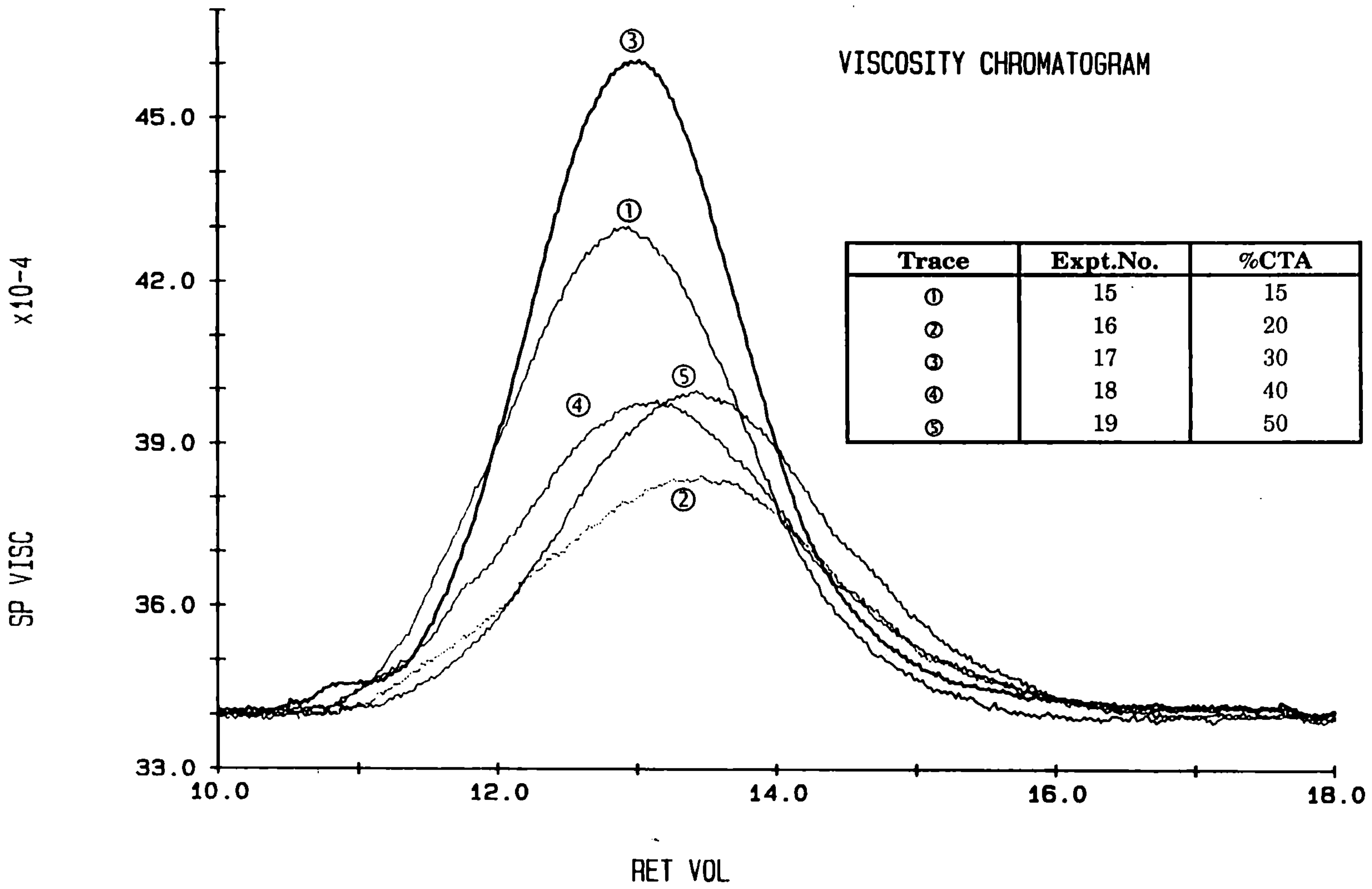
⑤	14	50

APPENDIX G2 GPC Traces for chain transfer studies on poly(5-tetradecylnorbornene)



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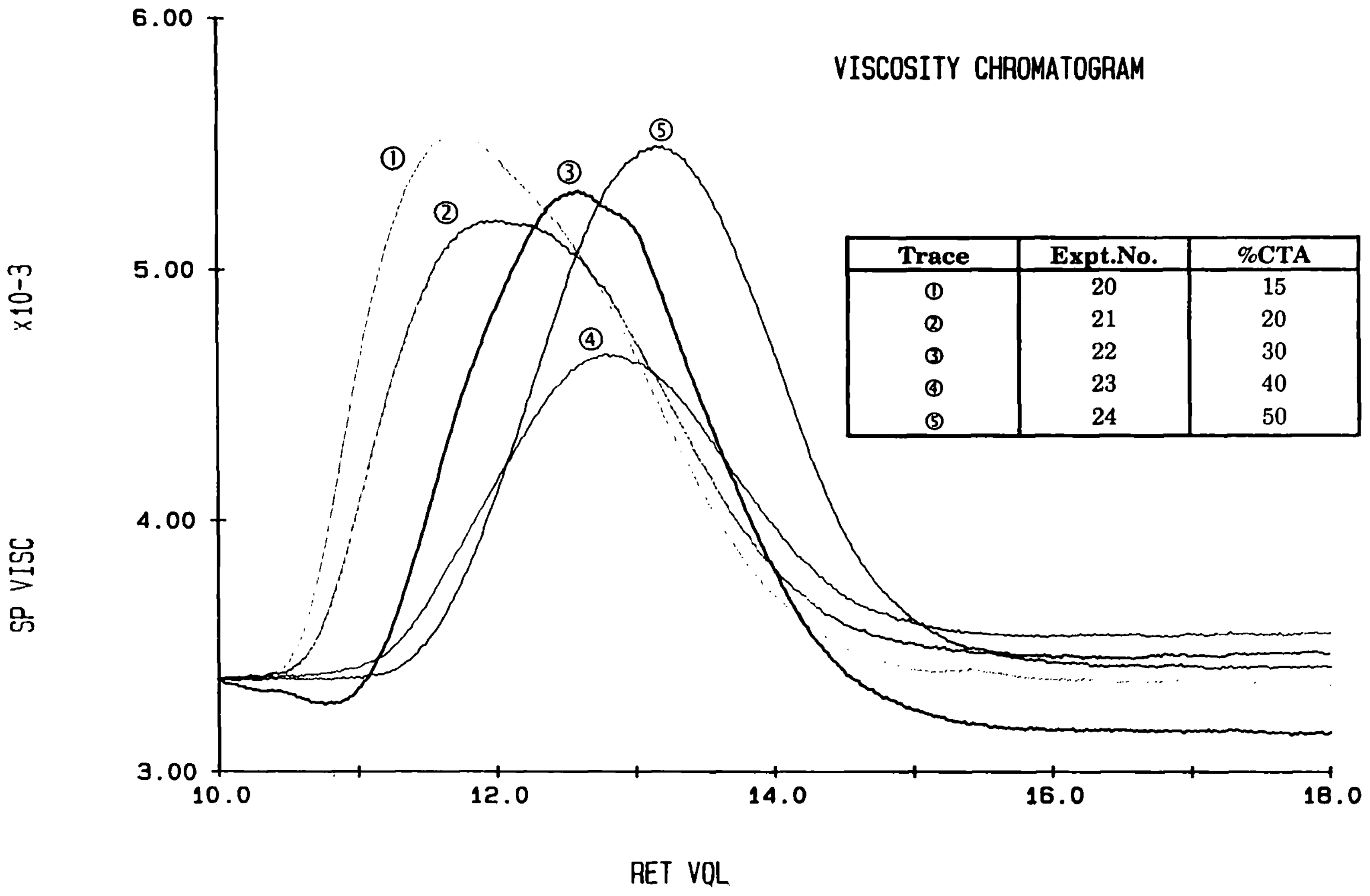
⑤	19	50

APPENDIX G3 GPC Traces for chain transfer studies on poly(5-hexylnorbornene)



Trace	Expt.No.	%CTA
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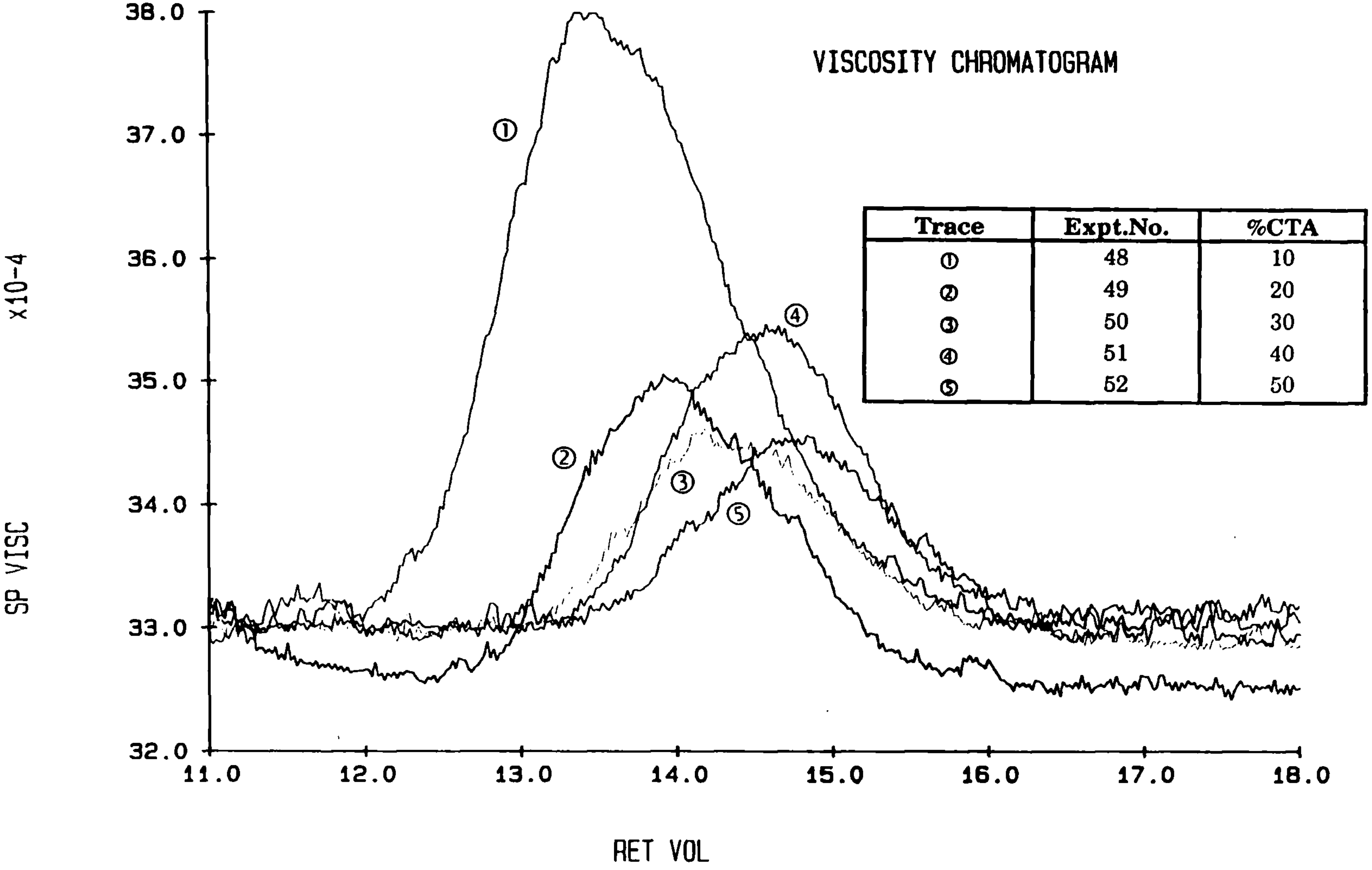
⑤	24	50

APPENDIX G4 GPC Traces for chain transfer studies on poly(5-hexylnorbornene)



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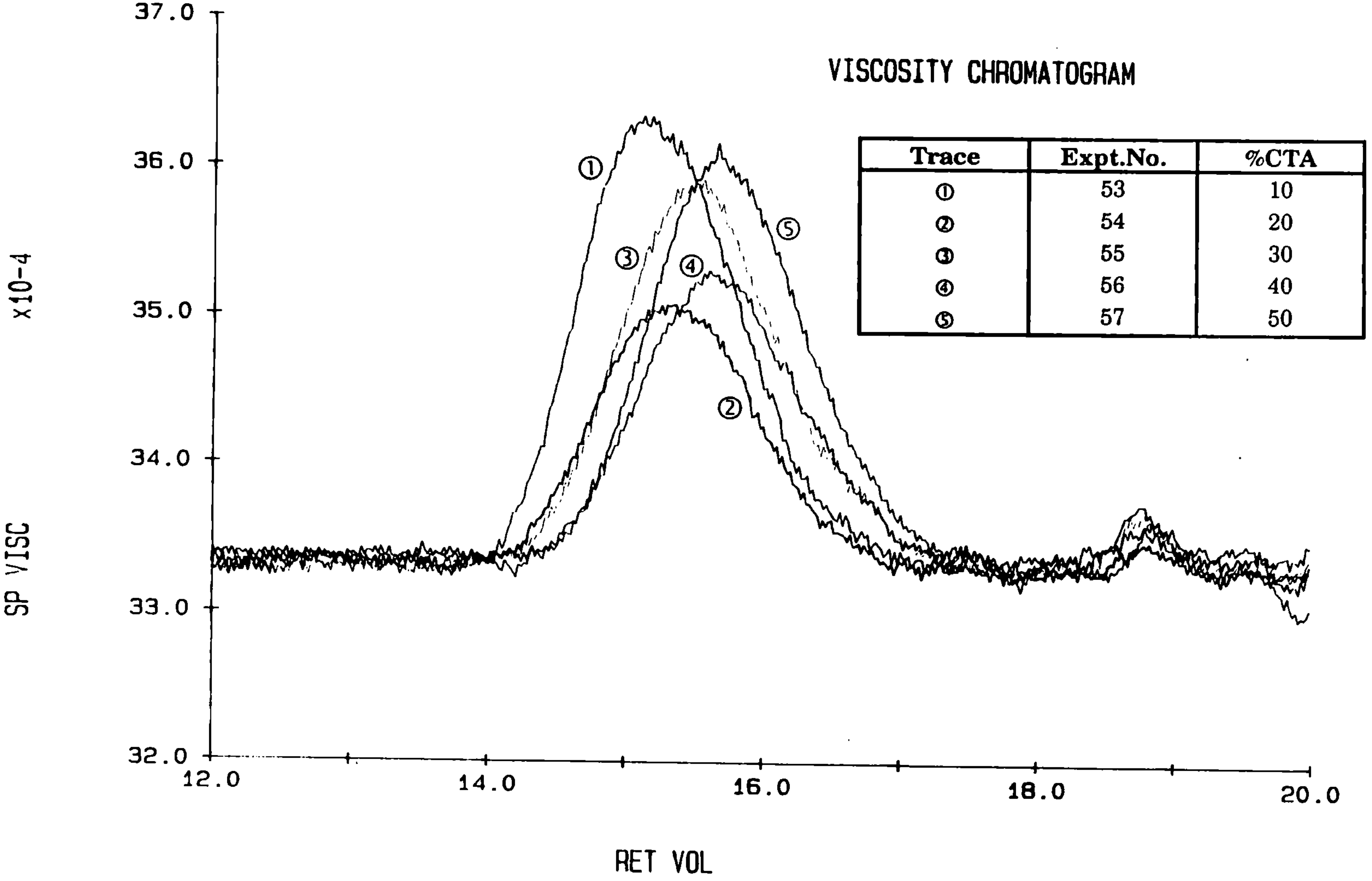
④	51	40
⑤	52	50

APPENDIX G5 GPC Traces for chain transfer studies on poly(5-tetradecylnorbornene)



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④	56	40
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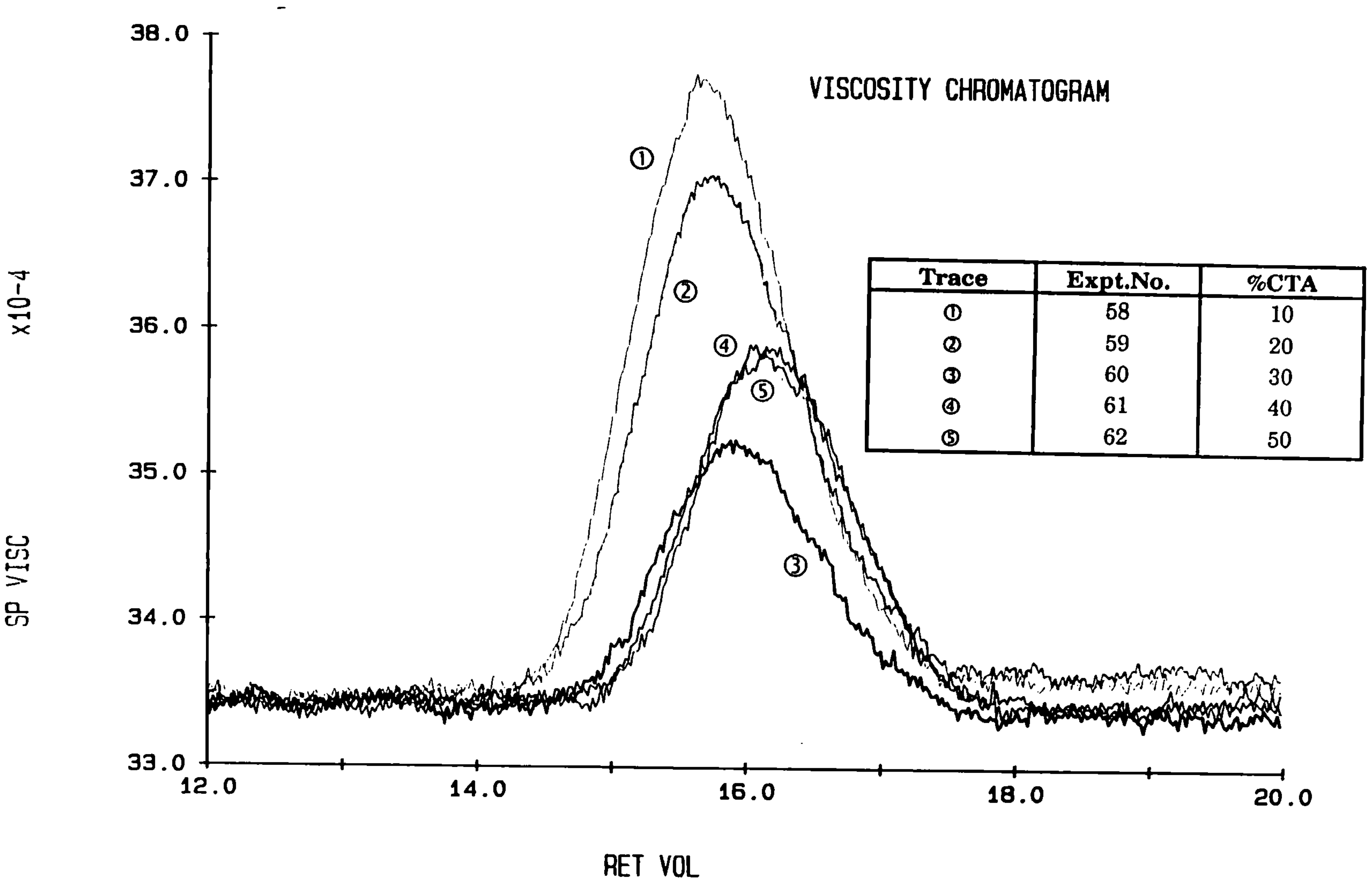
APPENDIX G6 GPC Traces for chain transfer studies on poly(5-tetradecylnorbornene)



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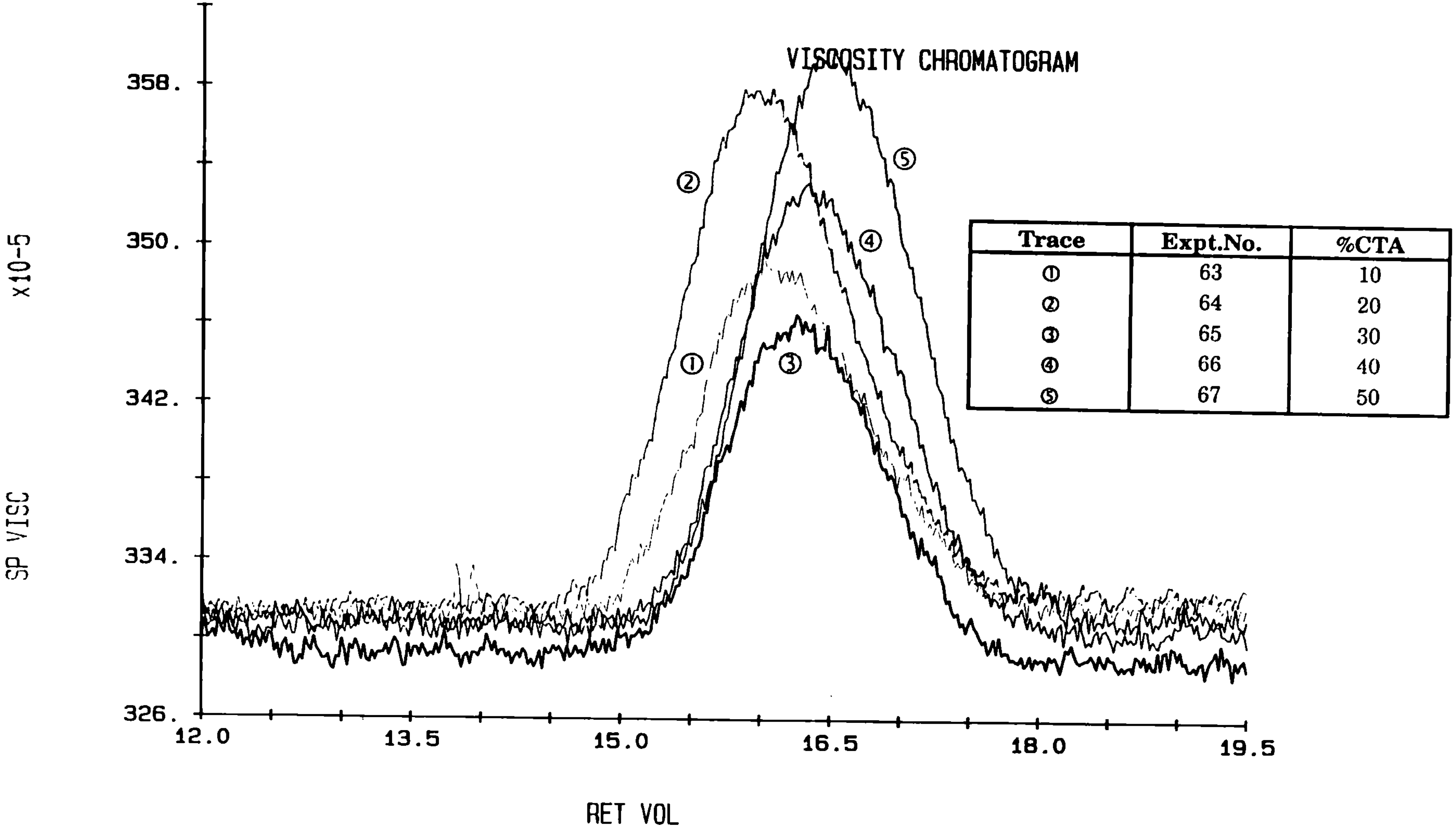
④	61	40
⑤	62	50

APPENDIX G7 GPC Traces for chain transfer studies on poly(5-hexylnorbornene)



Trace	Expt.No.	%CTA
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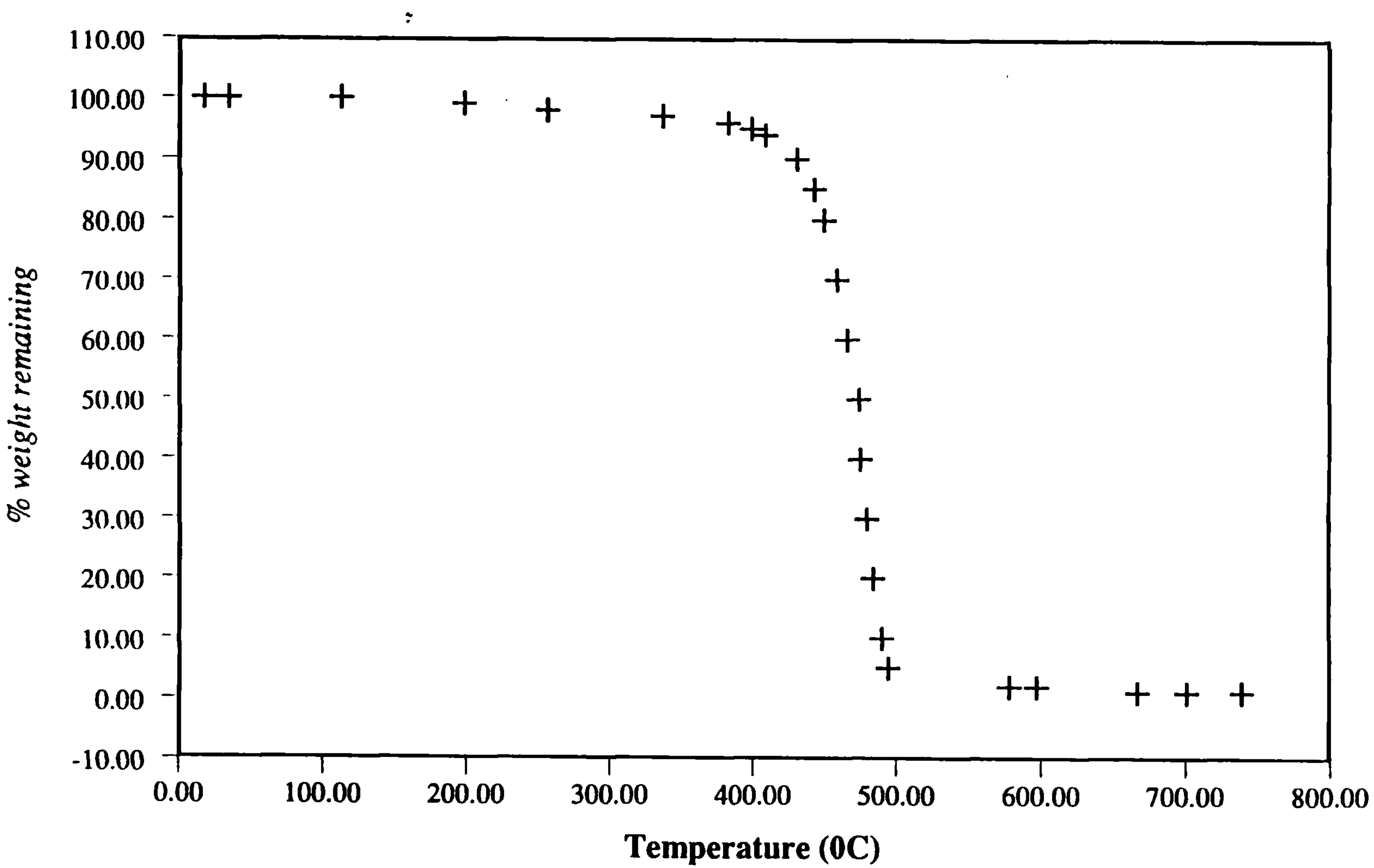
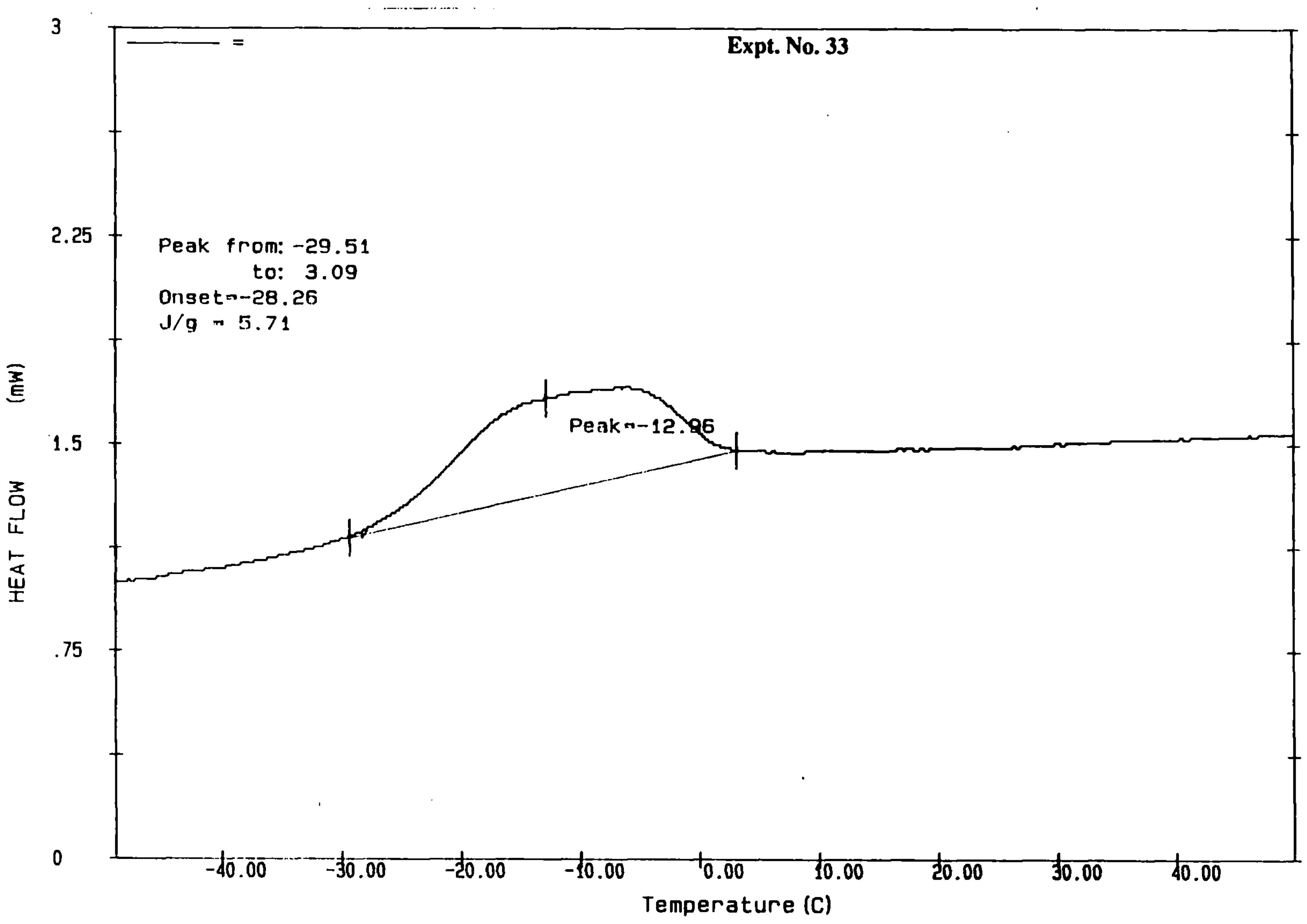
②	64	20
③	65	30
④	66	40
⑤	67	50

APPENDIX G8 GPC Traces for chain transfer studies on poly(5-hexylnorbornene)

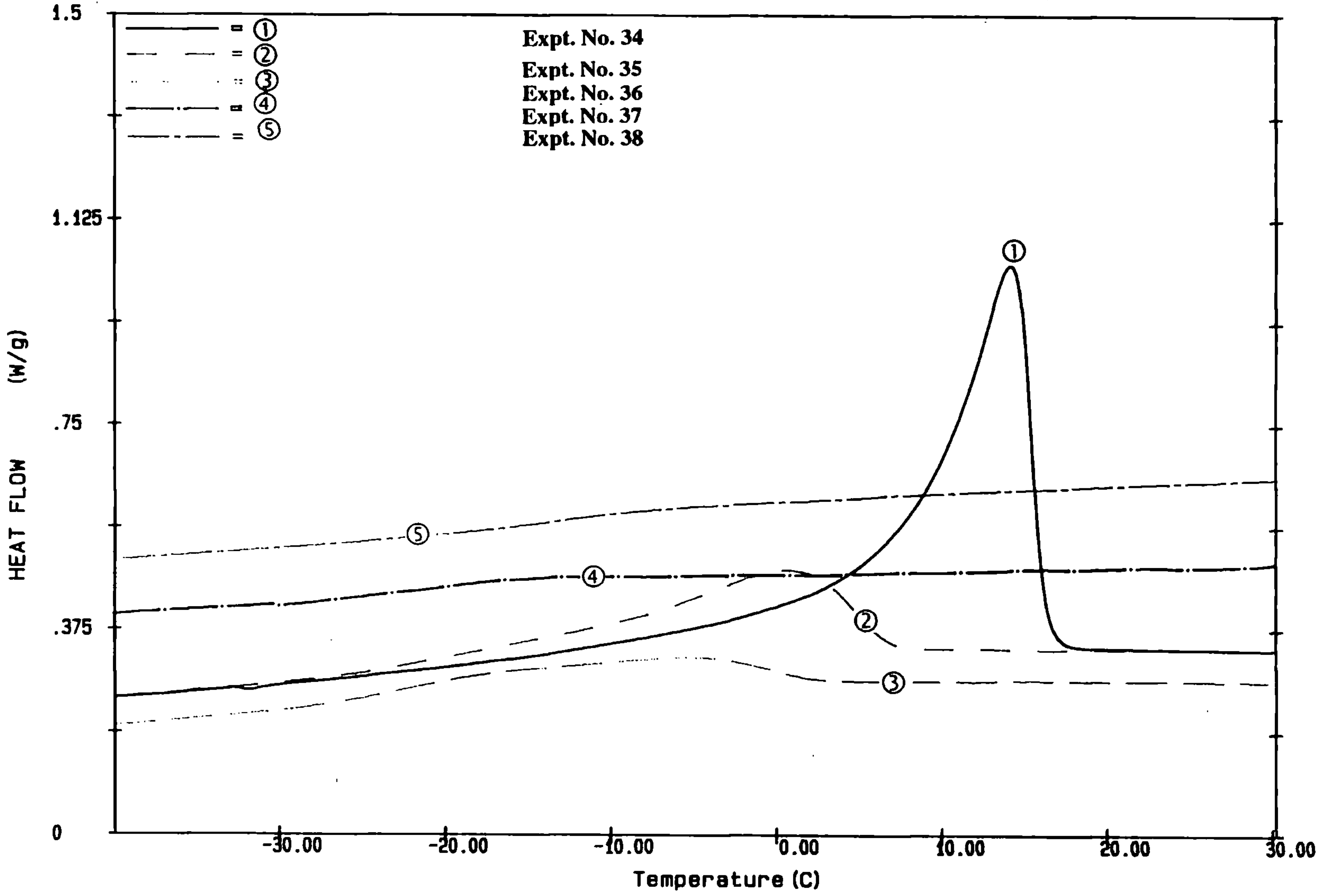
APPENDIX H



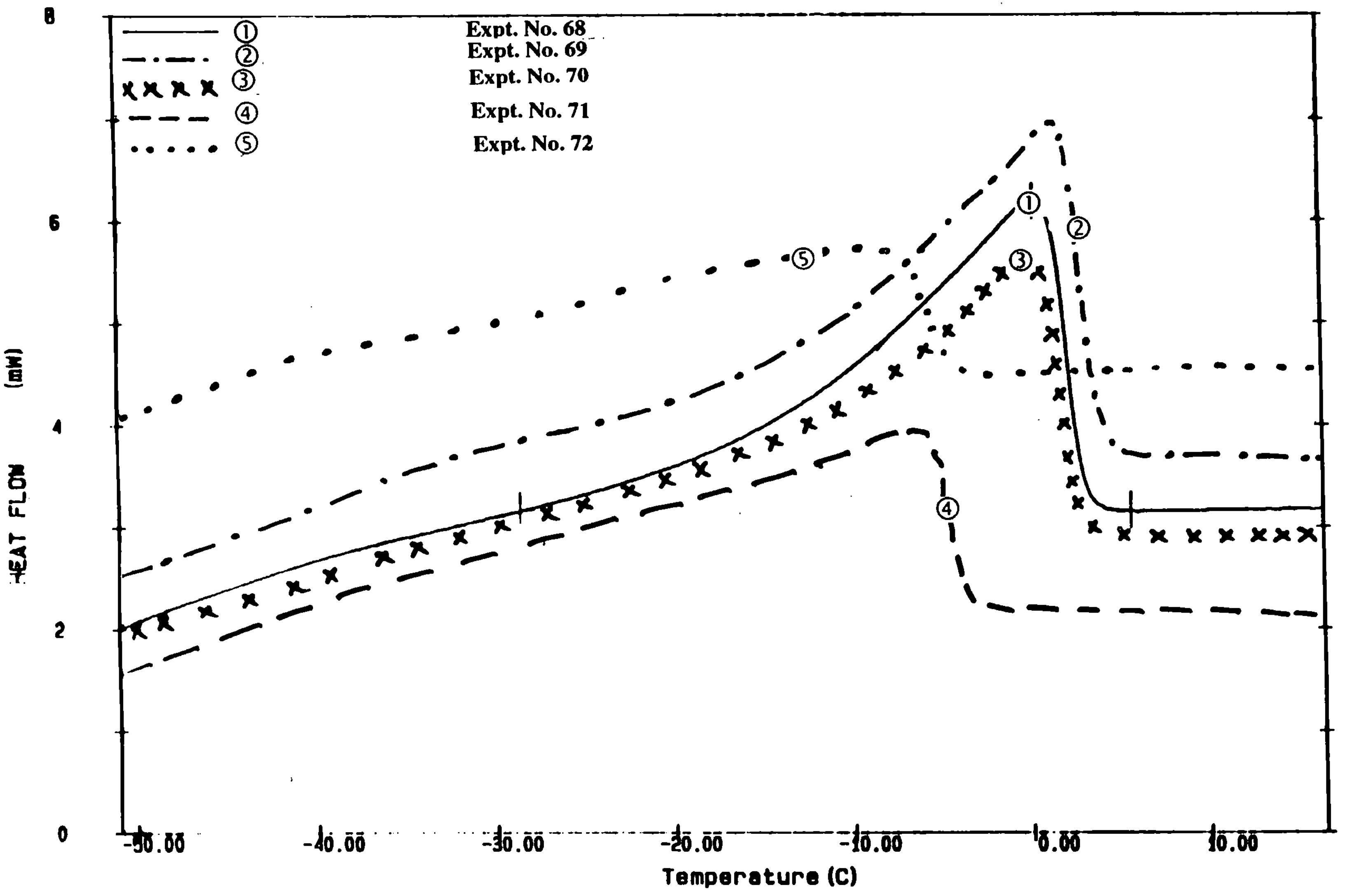
APPENDIX H1 TGA on hydrogenated poly(5-tetradecylnorbornene)($25^{h/d}$)



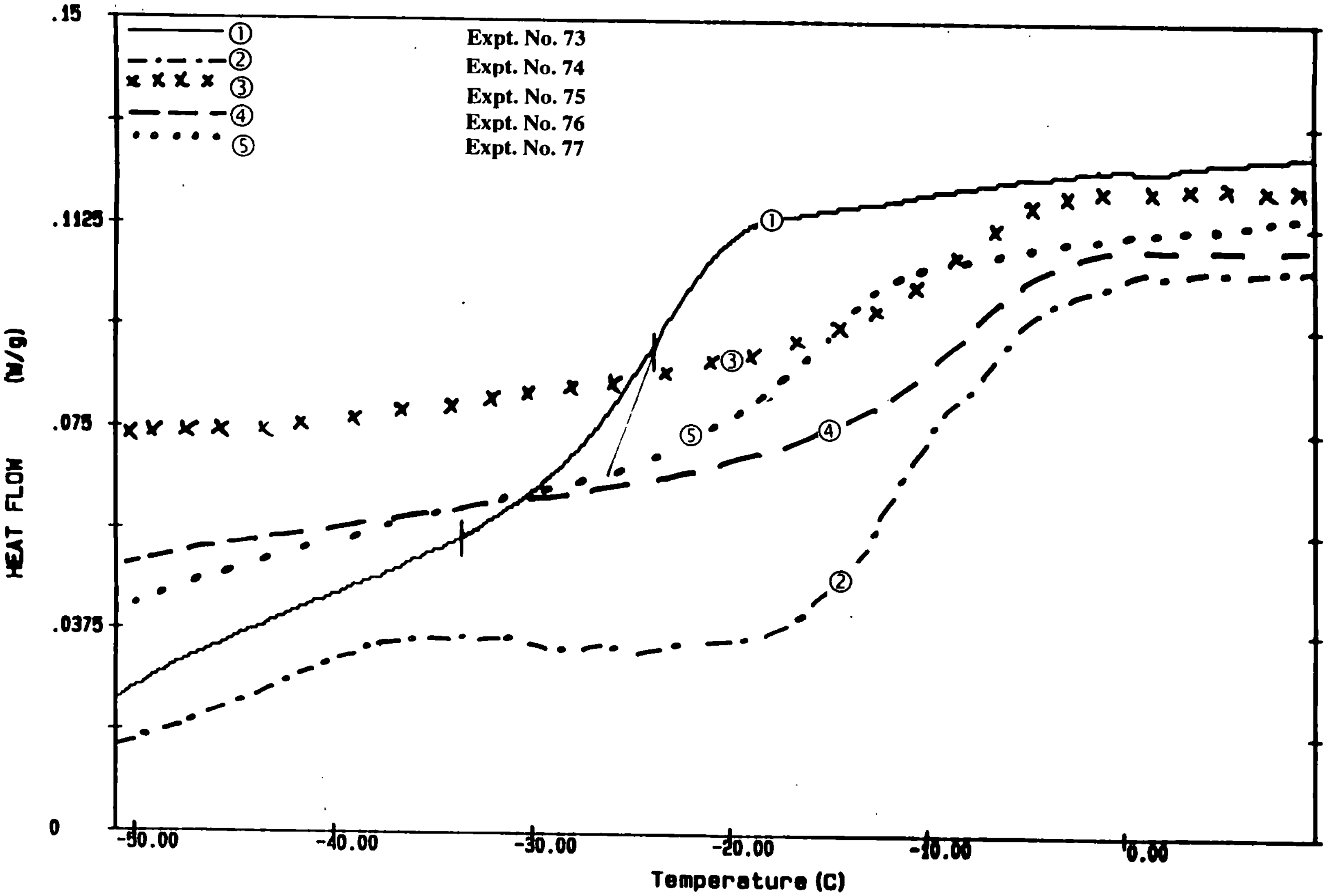
APPENDIX H2 DSC Trace of co-polymer poly(5-tetradecylnorbornene/norbornene)



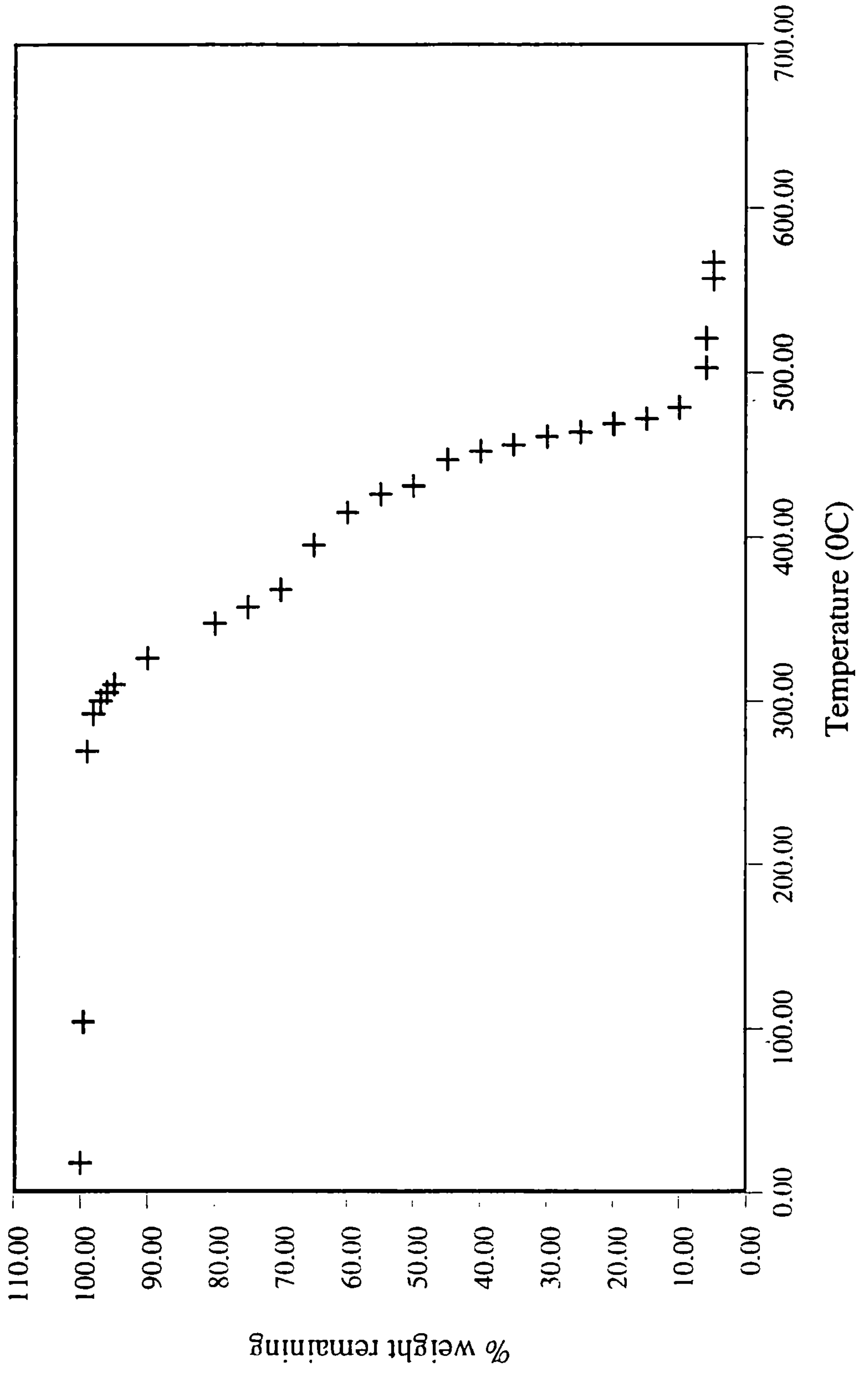
APPENDIX H3 DSC Traces of co-polymers of poly(5-tetradecylnorbornene/norbornene)



APPENDIX H4 DSC Traces of co-polymers of poly(5-tetradecylnorbornene/norbornene)



APPENDIX H5 DSC Traces of co-polymers of poly(5-hexylnorbornene/norbornene)



APPENDIX H6 TGA on poly(1-acetoxy-4,8-cyclododecadiene)

APPENDIX I

UNIVERSITY OF DURHAM
Board of Studies in Chemistry
Colloquia, Lectures and Seminars given by Invited Speakers

1990

October 11	Dr.W.A.MacDonald, (ICI, Wilton). Materials for the Space Age.
October 24	Dr.M.Bochmann, (University of East Anglia). Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls.
October 26	Prof.R.Soulen, (South Western University, Texas). Preparation and Reactions of Bicycloalkenes.
October 31	Dr.R.Jackson, (Newcastle University). New Synthetic Methods: α-Amino Acids and Small Rings.
November 1	Dr.N.Logan, (Nottingham University). Rocket Propellants.
November 6	Dr.P.Kocovsky, (Uppsala University) Stereo-Controlled Reactions Mediated by Transition and Non-Transition Metals.
November 7	Dr.D.Gerrard, (British Petroleum). Raman Spectroscopy for Industrial Analysis.
November 8	Dr.S.K.Scott, (Leeds University). Clocks, Oscillations and Chaos.
November 14	Prof.T.Bell, (SUNY, Stoney Brook, USA). Functional Molecular Architectures and Molecular Recognition.
November 21	Prof.J.Pritchard, (Queen Mary & Westfield College, London University). Copper Surfaces and Catalysts.
November 28	Dr.B.J.Whitaker, (Leeds University). Two-Dimensonal Velocity Imaging of State-Selected Reaction Products.
November 29	Prof.D.Crout, (Warwick University). Enzymes in Organic Synthesis.
December 5	Dr.P.G.Pringle, (Bristol University). Metal Complexes with Functionalised Phosphines.
December 13	Prof.A.H.Cowley, (University of Texas). New Organometallic Routes to Electronic Materials.

1991

January 15	Dr.B.J.Alder, (Lawerence Livermore Labs. California). Hydrogen in all its Glory.
January 17	Dr.P.Sarre, (Nottingham University). Comet Chemistry.

January 24	Dr.P.J.Sadler, (Birkbeck College London). Design of Inorganic Drugs: Precious Metals, Hypertension and HIV.
January 30	Prof.E.Sinn, (Hull University). Coupling of Little Electrons in Big Molecules. Implications for the Active Site of (Metalloproteins and other) Macromolecules.
January 31	Dr.D.Lacey, (Hull University). Liquid Crystals.
February 6	D.R.Bushby, (Leeds University). Biradicals and Organic Magnets.
February 14	Dr.M.C.Petty, (Durham University). Molecular Electronics.
February 20	Prof.B.L.Shaw, (Leeds University). Syntheses with Coordinated, Unsaturated Phosphine Ligands.
February 28	Dr.J.Brown, (Oxford University). Can Chemistry Provide Catalysts Superior to Enzymes?
March 6	Dr.C.M.Dobson, (Oxford University). NMR Studies of Dynamics in Molecular Crystals.
March 7	Dr.J.Markam, (ICI Pharmaceticals). DNA Fingerprinting.
April 24	Prof.R.R.Schrock, (Massachusettes Institute of Technology). Metal-Ligand Multiple Bonds and Metathesis Initiators.
April 25	Prof.T.Hudlicky, (Virginia Polytechnic Institute). Biocatalysts and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products.
June 20	Prof.M.S.Brookhart, (University of N.Carolina). Olefin Polymerisations, Oligomerisations and Dimerisations using Electrophilic Late Transition Metal Catalysts.
July 29	Dr.M.A.Brimble, (Massey University, New Zealand). Synthetic Studies Towards the Antibiotic Griseusin-A.
October 17	Dr.J.A.Salthouse, (University of Manchester). Son et Lumiere-A Demonstration Lecture.
October 31	Dr.Keeley, (Metropolitan Police Forensic Science). Modern Forensic Science.
November 6	Prof.B.F.G.Johnson, (Edinburgh University). Cluster-surface Analogies.
November 7	Dr.A.R.Butler, (St.Andrews University). Traditional Chinese Herbal Drugs: A Different Way of Treating Disease.
November 13	Prof.D.Gani, (St.Andrews University). The Chemistry of PLP Dependent Enzymes.

November 20	Dr.R.More O'Ferrall, (University College, Dublin). Some Acid-Catalysed Rearrangements in Organic Chemistry.
November 28 **SCI Lecture**	Prof.I.M.Ward, (IRC in Polymer Science, Leeds University). The Science and Technology of Orientated Polymers.
December 4	Prof.R.Grigg, (Leeds University). Palladium-Catalysed Cyclisation and Ion-Capture Processes.
December 5	Prof.A.L.Smith, (Ex. Unilever). Soap, Detergents and Black Puddings.
December 11	Dr.W.D.Cooper, (Shell Research). Colloid Science: Theory and Practice.

1992

January 22	Dr.K.D.M.Harris, (St.Andrews University). Understanding the Properties of Solid Inclusion Compounds.
January 29	Dr.A.Holmes, (Cambridge University). Cycloaddition Reactions in the Service of the Synthesis of Piperidine and Indolizine Natural Products.
January 30	Dr.M.Anderson, (Sittingbourne, Shell Research). Recent Advances in the Safe and Selective Chemical Control of Insect Pests.
February 12	Prof.D.E.Fenton, (Sheffield University). Polynuclear Complexes of Molecular Clefts as Models for Copper Biosites.
February 13	Dr.J.Saunders, (Glaxo Group Research Limited). Molecular Modelling in Drug Discovery.
February 19	Prof.E.J.Thomas, (University of Manchester). Applications of Organostannanes to Organic Synthesis.
February 20 **Musgrave Lecture**	Prof.E.Vogel, (University of Cologne). Porphyrins: Molecules of Interdisciplinary Interest.
February 25 **Tilden Lecture:**	Prof.J.F.Nixon, (University of Sussex). Phosphaalkynes: New Building Blocks in Organic and Organometallic Chemistry.
February 26	Prof.M.L.Hitchman, (Strathcylde University). Chemical Vapour Deposition.
March 5	Dr.N.C.Billingham, (University of Sussex). Degradable Plastics-Myth or Magic.
March 11	Dr.S.E.Thomas, (Imperial College). Recent Advances in Organoiron Chemistry.
March 12	Dr.R.A.Hann, (ICI Imagedata). Electronic Photography-An Image of the Future.

March 18	Dr.H.Maskill, (Newcastle University). Concerted or Stepwise Fragmentation in a Deamination-type Reaction.
April 7	Prof.D.M.Knight, (University of Durham). Interpreting Experiments: The Beginning of Electrochemistry.
May 13	Dr.J-C.Gehret, (Ciba Geigy, Basel). Some Aspects of Industrial Agrochemical Research.
October 15	Dr.M.Glazer and Dr.S.Tarling, (Oxford University and Birbeck College). It Pays to be British!-The Chemist's Role as an Expert Witness in Patent Litigation.
October 20	Dr.H.E.Bryndza, (Du Pont Central Research). Synthesis, Reactions and Thermochemistry of Metal(alkyl)cyanide Complexes and Their Impact on Olefin Hydrocyanation Catalysts.
October 22 **Ingold-Albert Lecture**	Prof. A.G.Davies, (University College, London). The Behaviour of Hydrogen as a Pseudometal.
October 28	Dr.J.K.Cockroft, (Durham University). Recent Developments in Powder Diffraction.
October 29	Dr.J.Emsley, (Imperial College, London). The Shocking History of Phosphorus.
November 4	Dr.T.Kee, (University of Leeds). Synthesis and Coordination Chemistry of Silylated Phosphites.
November 5	Dr.C.J.Ludman, (University of Durham). Explosions, A Demonstration Lecture.
November 11	Prof.D.Robins, (Glasgow University). Pyrrolizidene Alkaloids: Biological Activity, Biosynthesis and Benefits.
November 12	Prof.M.R.Truter, (University College, London). Luck and Logic in Host-Guest Chemistry.
November 18	Dr.R.Nix, (Queen Mary College, London). Characterisation of Heterogeneous Catalysts.
November 25	Prof.Y.Vallee, (University of Caen). Reactive Thiocarbonyl Compounds.
November 25	Prof.L.D.Quin, (University of Massachusetts, Amherst) Fragmentation of Phosphorus Heterocycles as a Route to Phosphoryl Species with Uncommon Bonding.
November 26	Dr.D.Humber, (Glaxo, Greenford). AIDS - The Development of a Novel Series of Inhibitors of HIV.
December 2	Prof.A.F.Hegarty, (University College, Dublin). Highly Reactive Enols Stabilised by Steric Protection.
December 2	Dr.R.A.Aitkin, (University of St.Andrews). The Versatile Cycloaddition Chemistry of $Bu_3P.CS_2$.

December 3 **SCI Lecture**	Prof.P.Edwards, (Birmingham University). What is a Metal?
December 9	Dr.A.N.Burgess, (ICI Runcorn). The Structure of Perfluorinated Ionomer Membranes.

1993

January 20	Dr.D.C.Clary, (University of Cambridge). Energy Flow in Chemical Reactions
January 21	Prof.L.Hall, (University of Cambridge). NMR - A Window to the Human Body.
January 27	Dr.W.Kerr, (University of Strathclyde). Development of the Pauson-Khand Annulation Reaction. Organocobalt Mediated Synthesis of Natural and Unnatural Products.
February 3	Prof.S.M.Roberts, (University of Exeter). Enzymes in Organic Synthesis.
February 10	Dr.D.Gillies, (University of Surrey). NMR and Molecular Motion in Solution.
February 11 **Tilden Lecture**	Prof.S.A.R.Knox, (Bristol University). Organic Chemistry at Polynuclear Metal Centres.
February 17	Dr.R.D.W.Kemmitt, (University of Leicester). Oxatrimethylenemethane Metal Complexes.
February 18	Dr.I.Fraser, (ICI, Wilton). Reactive Processing of Composite Materials.
February 22	Prof.D.M.Grant, (University of Utah). Single Crystals, Molecular Structure and Chemical-Shift Anisotropy
February 24	Prof.C.J.M.Stirling, (University of Sheffield). Chemistry on the Flat-Reactivity of Ordered Systems.
March 3	Dr.K.J.P.Williams, (BP). Raman Spectroscopy for Industrial Analysis.
March 10	Dr.P.K.Baker, (University College of North Wales, Bangor). An Investigation of the Chemistry of the Highly Versatile 7-Coordinate Complexes [MI$_2$(CO)$_3$(NCMe)$_2$] (M=Mo,W).
March 11	Dr.R.A.Jones, (University of East Anglia). The Chemistry of Wine Making
March 17	Dr.R.J.K.Taylor, (University of East Anglia).] Adventures in Natural Product Synthesis.
March 24	Prof.I.O.Sutherland, (University of Liverpool). Chromogenic Reagents for Chiral Amine Sensors.
May 13 **Boys-Rahman Lecture**	Prof.J.A.Pople, (Carnegie-Mellon University Pittsburgh). Applications of Molecular Orbital Theory.

May 21	Prof.L.Weber, (University of Biefield). Metallo-phospha Alkenes as Synthons in Organometallic Chemistry
June 1	Prof.J.P.Konopelski, (University of California, Santa Cruz). Synthetic Adventures with Enantiomerically Pure Acetals.
June 7	Prof.R.S.Stein, (University of Massachusetts). Scattering Studies of Crystalline and Liquid Crystalline Polymers.
June 16	Prof.A.K.Covington, (University of Newcastle). Use of Ion Selective Electrodes as Detectors in Ion Chromatography.
June 17	Prof.O.F.Nielsen, (H.C.Ørsted Institute, University of Copenhagen). Low-Frequency IR - and Raman Studies of Hydrogen Bonded Liquids.

The author has also attended the following lectures in the IRC in Polymer Science and Technology International Seminar Series.

1991

March 18	Prof.G.Wegner,(Max-Planck-Institut for Polymerforschung, Mainz), at Leeds University. New Developments in Main Chain Liquid Crystal Polymers
May 9	Prof.P.G.de Gennes, (Laboratoire de Physique de la Matiere Condensee, College de France, Paris), at Leeds University. Polymer-Polymer Interfaces
September 16	Dr.A.Griffin, (Melville Laboratory, University of Cambridge), at Leeds University. Photoactive Liquid Crystalline Polyacrylcinnamates.

1992

March 17	Prof.Sir S.Edwards, (Cavendish Laboratory, University of Cambridge), at Leeds University. Phase Dynamics and Phase Changes in Polymer Liquid Crystals
March 25	Prof.H.Chedron, (Hoechst AG, Frankfurt am Main), at Durham University. Structural Concepts and Synthetic Methods in Industrial Polymer Science.
May 11	Prof.W.Burchard, (University of Freiburg),at Durham University. Recent Developments in the Understanding of Reversible and Irreversible Network Formation.
September 21	Prof.E.L.Thomas, (MIT, Cambridge, Massachusetts),at Leeds University. Interface Structures in Copolymer-HomopolymerBlends.

1993

April 1	Prof. H.W.Speiss, (Max-Planck Institut for Polymerforschung, Mainz), at Durham University. Multidimensional NMR Studies of Structure and Dynamics of Polymers.
June 2	Prof.F.Ciardelli, (University of Pisa), at Durham University. Chiral Discrimination in the Stereospecific Polymerisation of α-olefins.
June 8	Prof.B.E.Eichinger, (BIOSYM Technologies Inc. San Diego), at Leeds University. Recent Polymer Modelling Results and a Look into the Future.
July 6	Prof.C.W.Macosko, (University of Minnesota, Minneapolis), at Bradford University. Morphology Development in Immiscible Polymer Polymer Blending.

CONFERENCES/MEETINGS ATTENDED BY THE AUTHOR

October 1990-March 1991
The Basics of Polymer Science and Technology-An Introductory Course in the Physics, Chemistry and Engineering of Polymers (15 days) Hugh Ripley Hall Ripon.

March 26-28 1991
Macro Group (UK) Polymer Conference, Lancaster University.

June 25 1991
Macro Group (UK) Transition Metal Mediated Polymerisations Conference, SCI London.

July 22-26 1992
Polymer Surfaces and Interfaces (II), Durham University,

March 26-28 1992
Macro Group (UK) Polymer Conference Durham University.

September 27-October 2 1992
European Polymer Federation: 4th Symposium on Polymeric Materials, Baden-Baden, Germany.

April 6-8 1993
Macro Group (UK) Polymer Conference, Lancaster University.

June 27-July 2 1993
Tenth International Symposium on Olefin Metathesis, Tihany-University of Vesprem, Hungary.

APPENDIX J

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"Would you tell me please, which way I ought to go from here?"
"That depends a good deal on where you want to get to," said the Cat.
"I don't much care where----------------," said Alice.
"Then it doesn't matter which way you go, " said the Cat.
"----------so long as I get somewhere," Alice added.
"Oh you're sure to do that," said the Cat.
"if only you walk long enough!"

Lewis Carroll *"Alice in Wonderland"*

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