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SYNTHESIS AND RING OPENING METATHESIS POLYMERIZATION OF SOME SUBSTITUTED NORBORNENES

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A thesis submitted for the degree of Master of Science
by
Panagiotis Dounis
First degree in Petroleum Technology (Kavala, Greece)
(Graduate Society)

UNIVERSITY OF DURHAM
1990

21 MAR 1991

ABSTRACT

The work reported in this thesis is concerned with an investigation of the synthesis and ring-opening metathesis polymerization of some substituted norbornenes. The monomers investigated were 2-phenoxy-3-chloro-2,3-difluorobicyclo[2.2.1]hept-5-ene and 2-phenoxycarbonylbicyclo[2.2.1]hept-5-ene.

The attempted synthesis of 2-phenoxy-3-chloro-2,3-difluorobicyclo[2.2.1]hept-5-ene and the synthesis and characterisation of 2-phenoxycarbonylbicyclo[2.2.1]hept-5-ene (or 2-phenoxycarbonyl norbornene) are discussed in Chapter 2.

The ring-opening metathesis polymerization of 2-phenoxycarbonyl norbornene and the characterisation of the polymers obtained *via* classical and well-defined catalysis are described in Chapter 3. The final chapter is concerned with some of the physical properties of the polymers.

ACKNOWLEDGEMENTS

I would like to express my sincere thanks to Prof.W.J.Feast for his help, supervision and encouragement during the work and writing of this thesis. Thanks also go to Dr.V.C.Gibson for his supervision throughout the year.

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I would like to express my dearest thanks to my parents for their loving and financial support throughout the period of research for this degree.

Finally thanks go to Alexandra for her help, support and existence.

MEMORANDUM

The work of this thesis was carried out in the Chemistry Laboratories of the University of Durham between October 1989 and September 1990. This work has not been submitted for any other degree and is the original work of the author, except where acknowledged by reference.

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CHAPTER 2: SYNTHESIS AND CHARACTERISATION OF MONOMERS

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CHAPTER 4: PHYSICAL PROPERTIES OF THE POLYMERS. CONCLUSIONS AND PROPOSALS FOR FURTHER WORK.

CHAPTER 1: GENERAL INTRODUCTION AND BACKGROUND

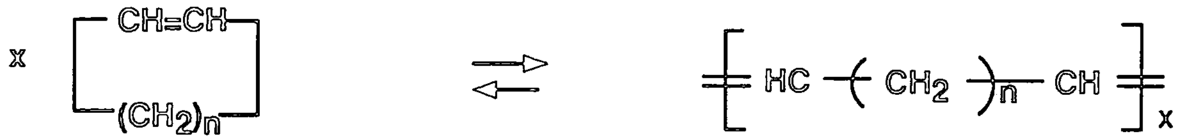
1.1 DEFINITION AND HISTORICAL BACKGROUND OF OLEFIN METATHESIS

The Olefin Metathesis reaction is a catalytically induced bond reorganization reaction, involving the breaking and making of carbon-carbon double bonds. It is characterized by the fact that the total number and the type of chemical bonds remain unchanged during the proccess.

In the presence of heterogeneous catalysts prepared from tungsten and molybdenum hexacarbonyls, the reaction, for acyclic olefins, leads to the exchange of alkylidene units. This was first reported by Banks and Bailey[1], in 1964, and was termed 'olefin disproportionation':

$$\begin{matrix} R_1CH{=}CHR_1 \\ + \\ R_2CH{=}CHR_2 \end{matrix} \rightleftharpoons \begin{matrix} R_1CH \\ \| \\ R_2CH \end{matrix} + \begin{matrix} HCR_1 \\ \| \\ HCR_2 \end{matrix}$$

For cyclic olefins the metathesis reaction leads to ring scission and the formation of linear polymers:



$$x\ \left[\begin{matrix} CH{=}CH \\ (CH_2)_n \end{matrix}\right] \rightleftharpoons \left[{=}HC{-}(CH_2)_n{-}CH{=} \right]_x$$

In 1967, Calderon *et al*[2] were the first to use the term 'olefin metathesis' for the overall result of these reactions, realizing that ring opening of alkenes to yield unsaturated polymers, and the olefin disproportionation reaction, were governed by the same mechanism.

Probably the first mention of an olefin metathesis reaction, catalysed by a transition metal, was reported by Anderson and Merckling[3], in 1955, when they successfully polymerized bicyclo [2.2.1] hept-2-ene, using a mixture of titanium tetrachloride and either ethylmagnesium bromide or lithium tetrabutylaluminium.

In 1960, Truett and coworkers[4,5] showed that the catalyst system used by Anderson and

Merkling worked by ring opening.

In 1957, Eleuterio[6] reported that a catalyst prepared from molybdenum oxide on alumina, activated by hydrogen reduction and further reacted with aluminium hydride, was able to ring-open polymerize a variety of monocyclic, bicyclic and tricyclic olefins. In the case of cyclopentene, *trans*-poly(1-pentenylene) was formed, but only in low yield.

In 1963, Dall'Asta and Natta[7], demonstrated the possibility of producing stereoregular polymers from cycloalkenes. In this work cyclobutene was polymerized to predominantly or exclusively *cis*- or *trans*-poly(1-butylene) by using different catalyst systems such as $TiCl_4$ / Et_3Al / n-heptane , $TiCl_4$ / R_3Al / toluene , $MoCl_5$ / Et_3Al / toluene , $RuCl_3$ / H_2O and $RuCl_3$ / EtOH and different reaction conditions.

The same authors[8], in 1964, investigated tungsten and molybdenum halides in combination with organoaluminium compounds as catalysts for the ring-opening polymerization of cyclopentene under mild conditions. They were able to obtain high *cis*- and *trans*-poly(1-pentenylene).

In 1967, Calderon *et al.*[9,10,11], converted 2-pentene into a mixture of 2-butene and 3-hexene, using a catalyst derived from tungsten hexachloride (or the product of the reaction of equimolar amounts of tungsten hexachloride and an alcohol), and an organoaluminium compound.

The contribution of this work to the evolution of the olefin metathesis concept was significant as it demonstrated that ring-opening reactions and olefin disproportionation belong to the same class of reaction and they are affected by similar transition metal-based catalyst systems.

The olefin metathesis reaction has been extensively reviewed and is the subject of relatively recent books[12-14].

1.2 CATALYST SYSTEMS

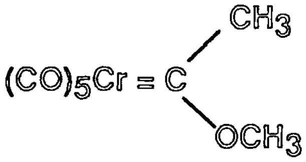
The most important catalyst systems are derived from compounds of the transition elements and the most effective are shown to be those based on W, Mo and Re[15].

A wide range of catalyst systems,including some based on Ti, V, Ru, Os and Ir can initiate the ring-opening metathesis polymerization of strained rings, such as norbornene, while more active catalyst systems are required for less strained rings, such as cyclopentene. Metathesis of acyclic olefins can be only achieved by the use of the most active W-, Mo- and Re-based catalyst systems.

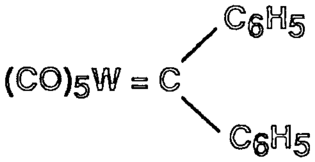
Ring opening metathesis polymerization (ROMP) has been well-studied in systems which employ these empirically derived ('classical') W, Mo and Re catalysts.

The classical catalyst systems can be divided into three main types:

1. Single component systems comprised of a metallocarbene such as:



Fischer type



Casey type

2. Two component systems containing a transition metal compound and an alkyl-, aryl- or allyl- containing species such as:

$MoCl_5$ / $Sn(CH_3)_4$

WCl_6 / $Sn(Ph)_4$

WCl_6 / $EtAlCl_2$

3. Compounds with neither a preformed metallocarbene nor an alkyl, aryl or allyl containing species. These systems usually consist of a transition metal halide such as:

WCl_6 , $ReCl_5$, $RuCl_3$, $IrCl_3$, $OsCl_3$

The ratio of *cis* and *trans* double bonds in a ring opened polymer is primarily dependant upon the catalyst system but other parameters such as concentration, temperature and the nature of the monomer can also have an influence.

These classical,ill-defined ROMP initiators have suffer from disadvantages which include:

-limited tolerance of functional groups

-lack of molecular weight control. Because of the high activity of most classical catalysts for the metathesis of ordinary olefins, the metal-carbon double bond at the end of the polymer chain reacts with carbon-carbon double bonds in the chain itself, either intramolecularly to give cyclic oligomers or intermolecularly to give linear oligomers (see 1.3).

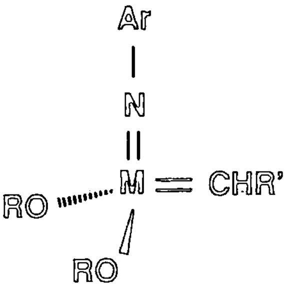
-an element of irreproducibility.

Furthermore, these catalysts only rarely produce stereoregular polymers[16].

It is also generally true in classical systems that alkylidene complexes are generated in low yield and decompose over the course of a typical polymerization reaction.

The key to the preparation of highly stereoregular polymers and well defined block copolymers is the careful design of isolable, well characterized catalysts. This has been demonstrated in the ring-opening metathesis polymerization of norbornene by a titanacyclobutane / titanium carbene complex[17] and by a related tantalum catalyst[18]. These living polymer systems produce monodispersed polymer.

Tungsten[19] and molybdanum[20] well defined ROMP initiators have been reported to be much more active than the titanium catalysts and show a greater tolerance of polar functional groups. These initiators are well defined, four coordinate, alkylidene complexes containing bulky ligands[21]. For Mo and W, a suitable combination is two alkoxides and an imido ligand[22]:

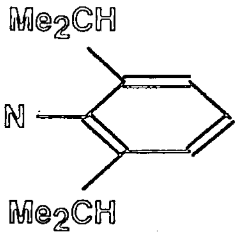


M ≡ Mo or W

R ≡ t - Bu

R' ≡ t - Bu

NAr ≡

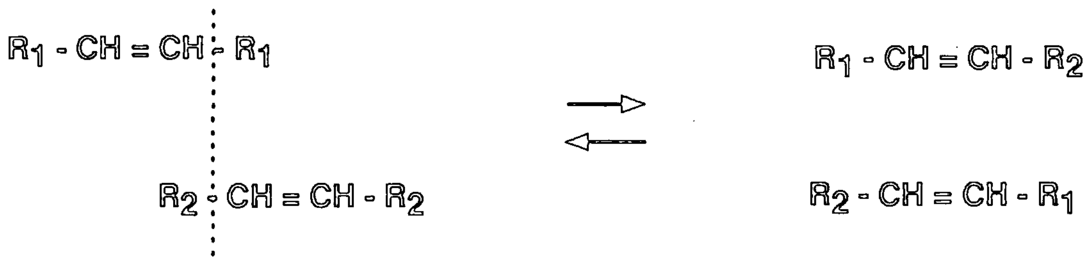


M(CH-t-Bu)(NAr)(O-t-Bu)$_2$ complexes do not react readily with ordinary olefines, however they do react rapidly with the strained double bond in norbornenes and norbornadienes to give essentially monodisperse polymers.

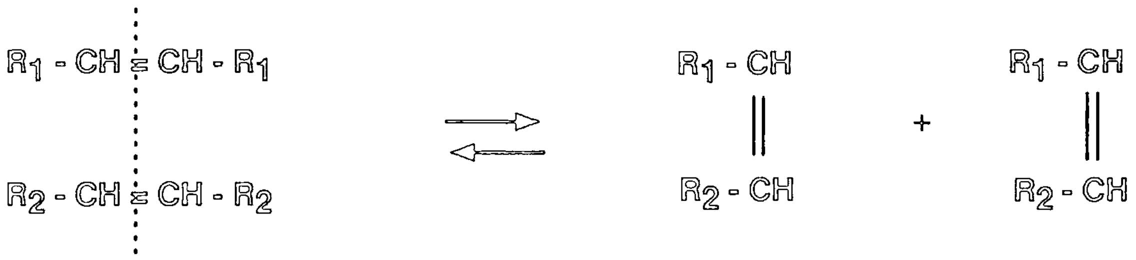
1.3 OLEFIN METATHESIS MECHANISM

The first problem to be solved was the indentification of the bonds which are broken and made during the reaction. Initially there were two possible reaction schemes:

(a) a transalkylation scheme:

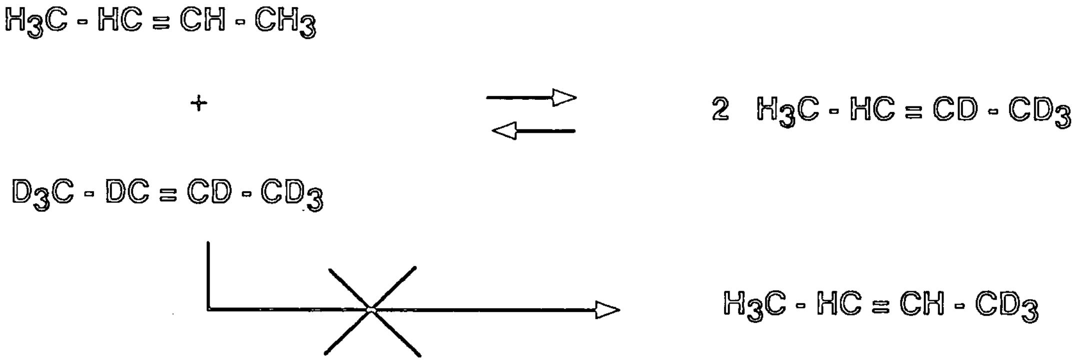


(b) a transalkylidenation scheme

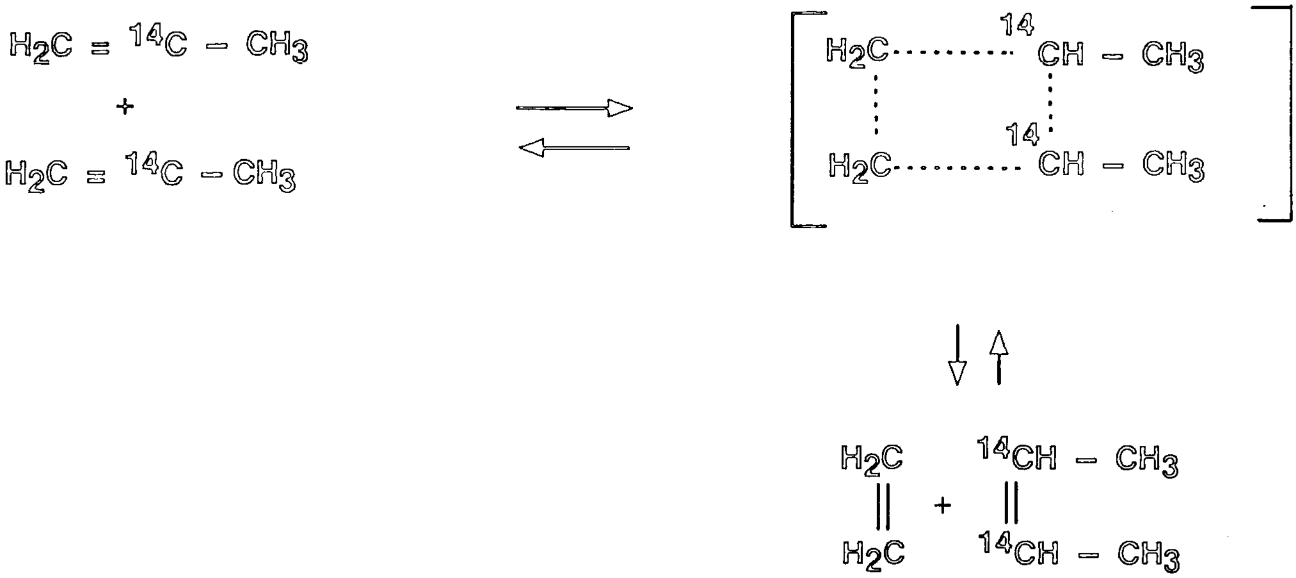


A transalkylidenation scheme was proved by ^{14}C and deuterium labelling experiments[23,24].

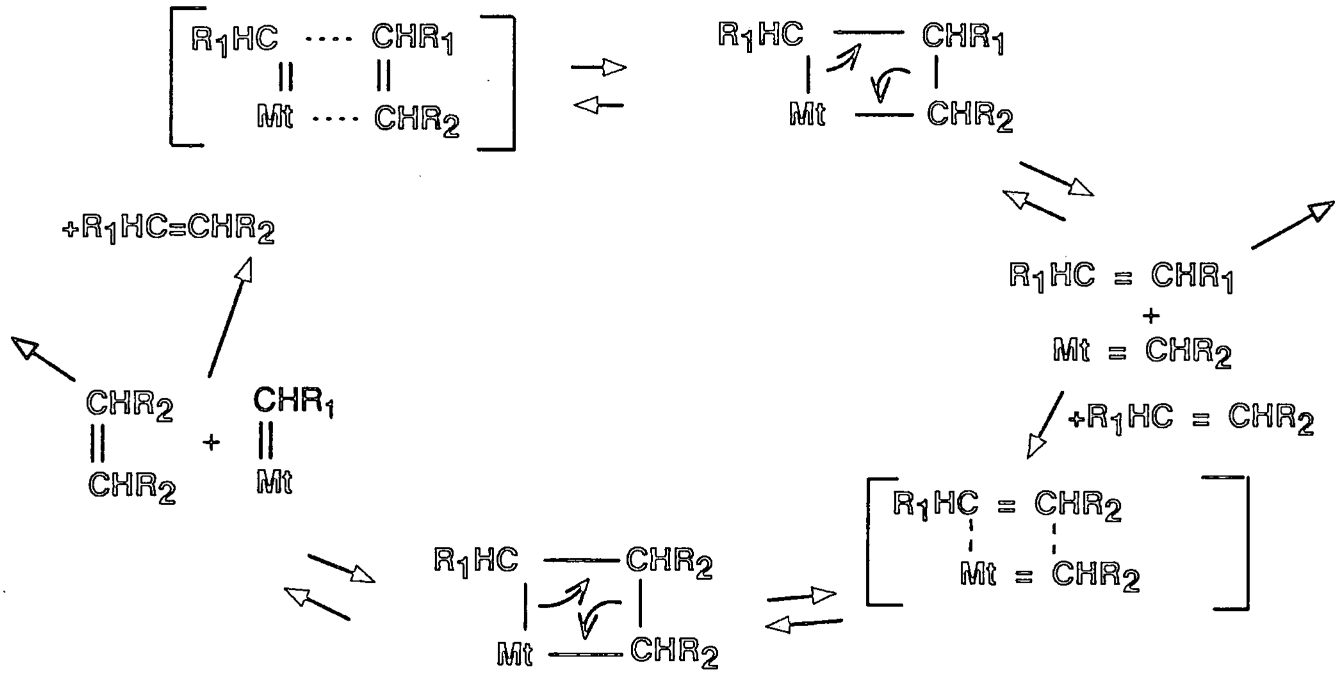
Calderon *et al*[25] showed that the reaction of 2-butene with 1-octadeuterio-2-butene, using the catalyst system WCl_6 / $EtAlCl_2$ /EtOH, gave 1,1,1,2 - tetradeuterio-2-butene and not 1,1,1-trideuterio-2-butene:



Describing another pairwise mechanism, Mol *et al* [26], proposed the existence of an intermediate quasi-cyclobutane in the reaction of ^{14}C isotopic labelled propene, catalysed by Re_2O_7 / Al_2O_3 :



The first evidence for a non pairwise mechanism was proposed by Herrison and Chauvin[27], involving a metallocarbene as a chain carrier:



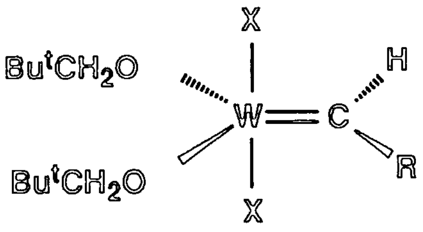
This mechanism is the currently accepted mechanism for the olefin metathesis reaction.

Polymerization of cycloolefins via olefin metathesis reaction, like other chain processes proceeds via initiation, propagation and termination. Some of the main evidence for the species involved in each step is given below:

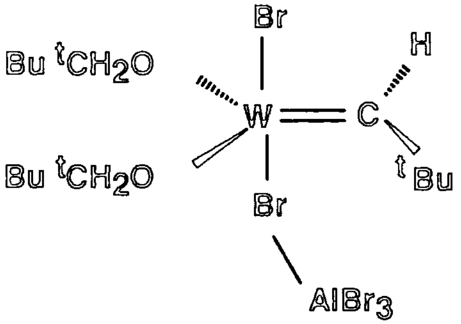
1.3.1 INITIATION:

The induction of olefin metathesis reactions by stable metallocarbenes, like the Casey[28,29] and Fischer[30,31] carbenes,is good evidence that these species are involved in the initiation step.

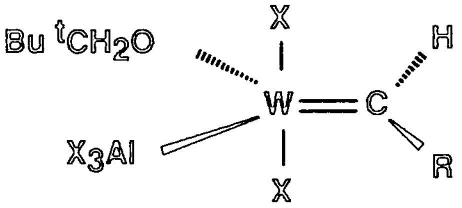
Stable metallocarbenes[32-34] which although inactive themselves, gave highly active catalyst systems in the presence of $AlCl_3$ or $AlBr_3$, like the tungsten (IV) carbene (a) synthesized by Kress and Osborn, for which the active species have been shown to be (b) and (c):



(a)



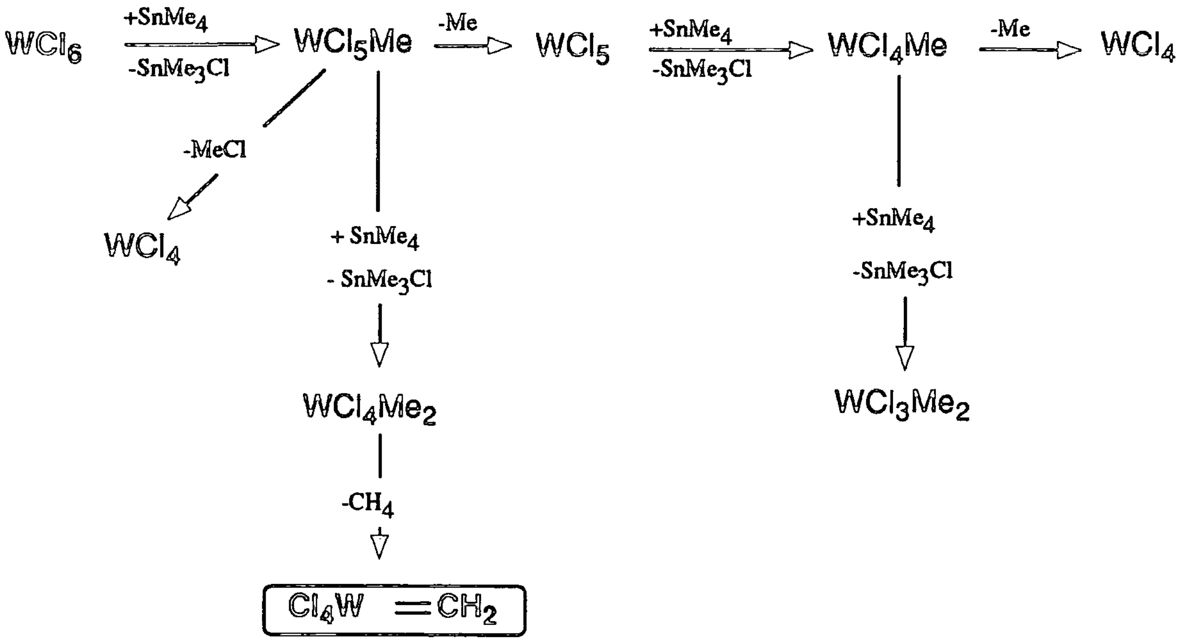
(b)



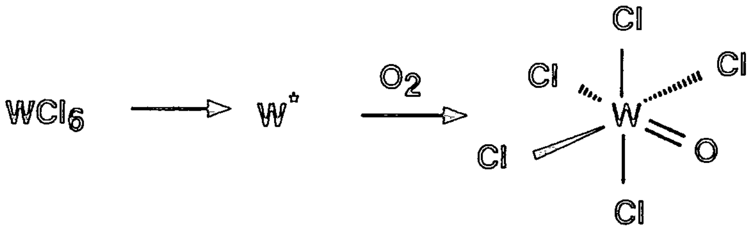
(c)

Catalyst systems consisting of transition metal halides, such as WCl_6, $MoCl_5$ and alkyl- or aryl-metal cocatalysts such as $(CH_3)_4Sn$, $(C_6H_5)_4Sn$, $(CH_3)_2Zn$, are believed to form the metallocarbene by reaction between the two components[35].

A study by Thorn-Csyani *et al*[36-38] of the WCl_6 / $(CH_3)_4Sn$ system, using UV spectroscopy lead them to propose a detailed scheme for the formation of the metallocarbene:



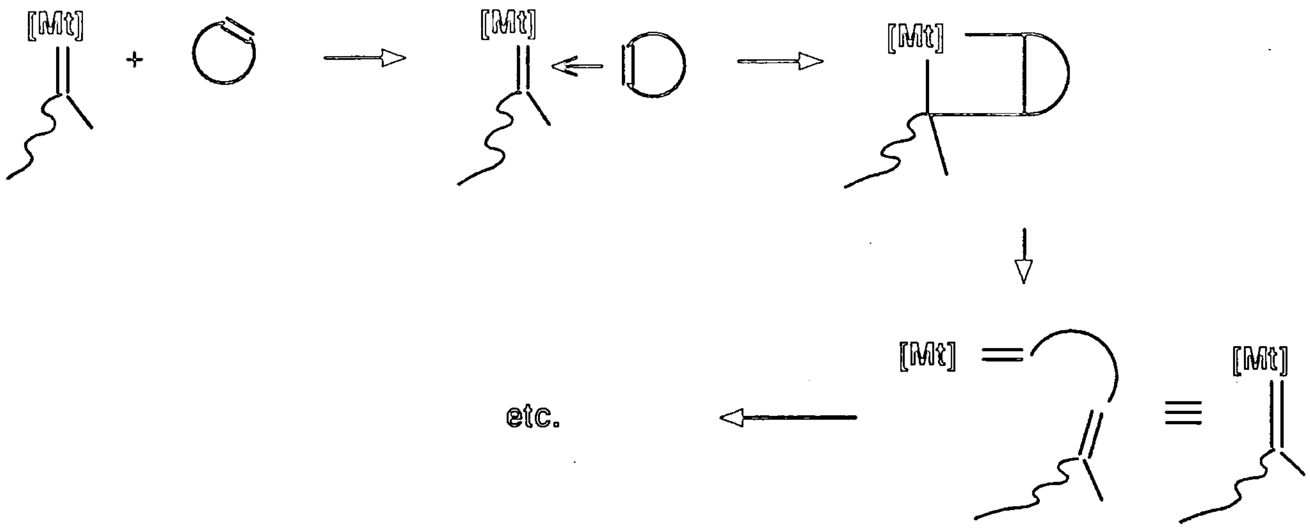
Their observations suggested that alkyl groups play an important role in generating metallocarbenes. However this leaves the problem of how catalysts which do not contain any of these groups, generate active species. Amass[39] reported that oxygen activated some catalyst systems and proposed the formation of a W=O site.



Another possibility is that the metallocarbene can be formed by interaction of the substrate olefin itself with the transition metal centre[12].

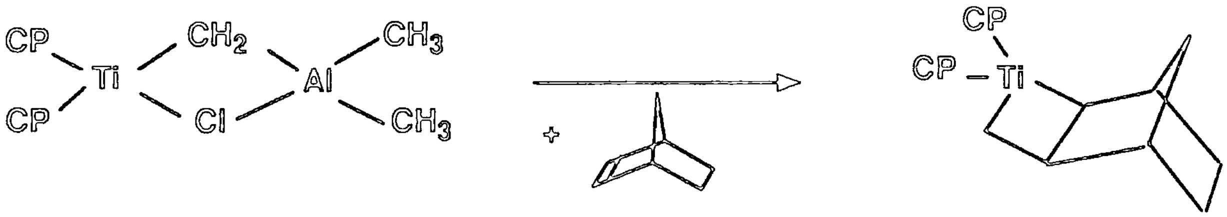
1.3.2 PROPAGATION:

Propagation in ROMP takes place via reaction of the initiating metallocarbene with the olefin in order to form an intermediate metallocyclobutane which cleaves as shown below, reproducing a metallocarbene at the end of the chain.

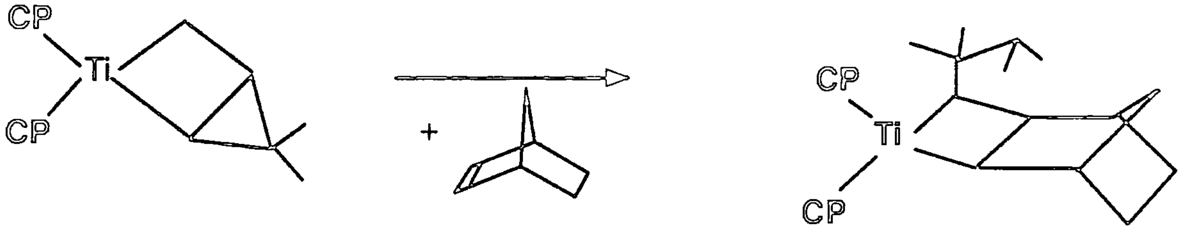


There is evidence to support the formation of a metallocyclobutene as an intermediate. Green *et al*[40] observed that the reaction of a stable metallocyclobutene by thermolysis or photolysis gave a metallocarbene plus an alkene.

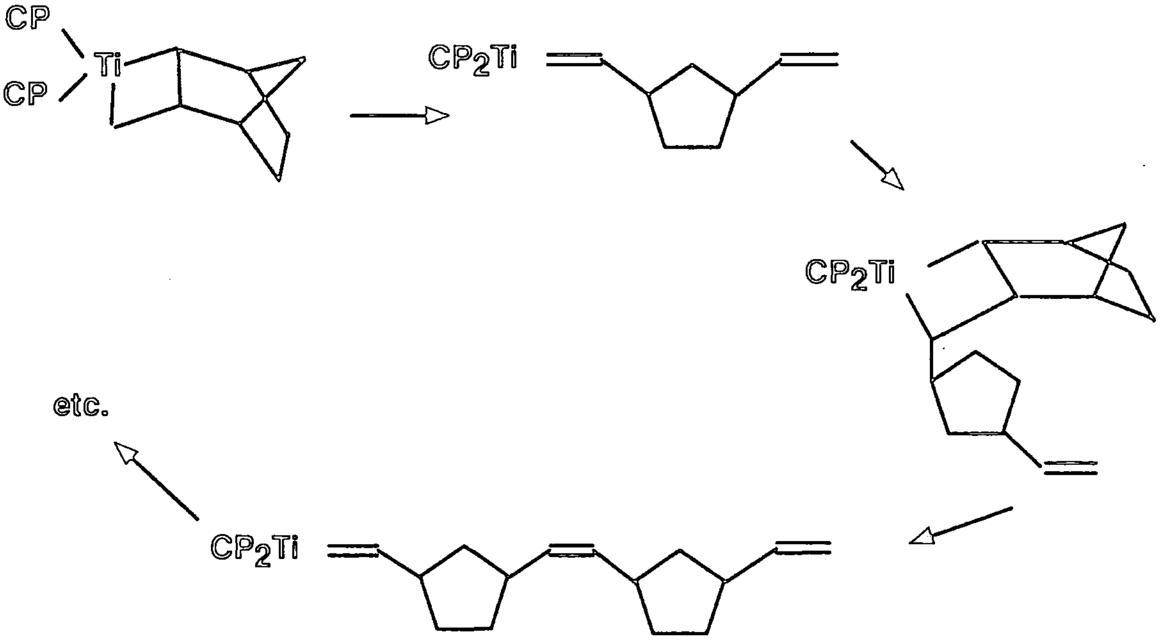
Further evidence comes from the work of Grubbs and Gillion[41] who have shown that titanocyclobutanes such as (a) and (b) can initiate the ROMP of norbornene,creating a 'living' chain end.



(a)



(b)

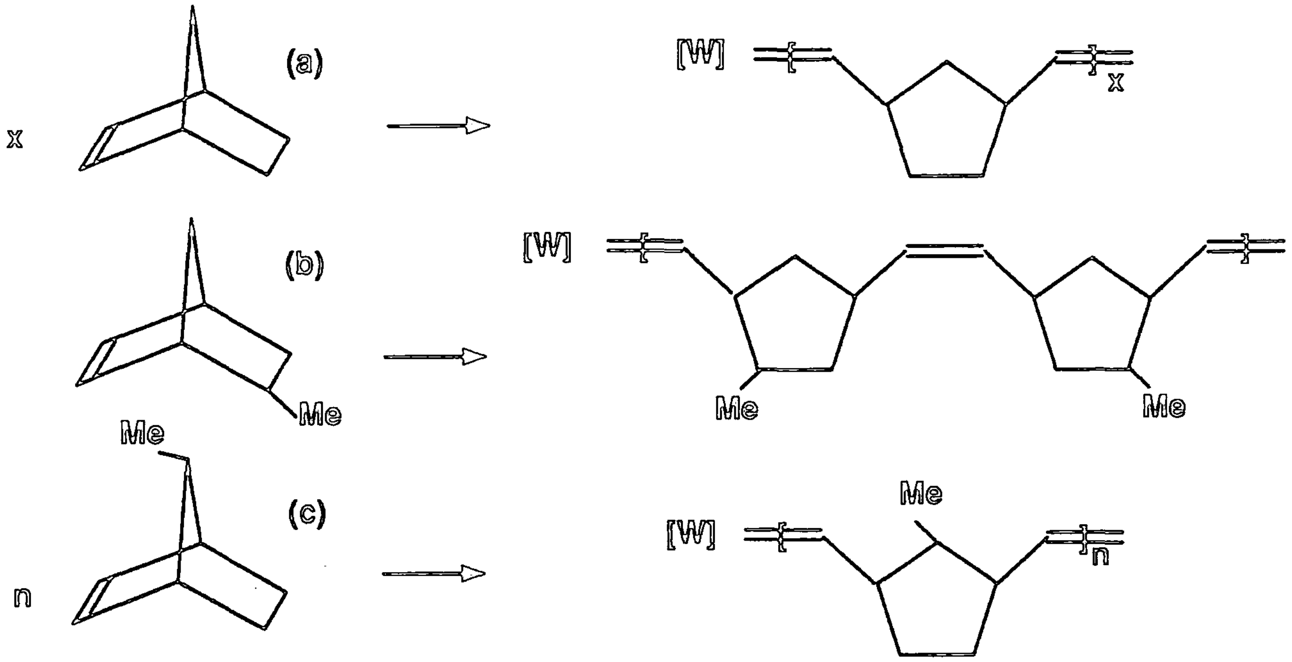


Such living catalyst systems allow the addition of a second monomer after the first is consumed to yield polymers that contain 'blocks' of homopolymers connected to one another.

Schrock *et al*[42] obtained the copolymer NBE /5,6-dicarbomethoxy -2-norbornene using the catalyst Mo(CH-tBu)(NAr)(O-tBu)$_2$ and Osborn *et al.*[43] prepared the block copolymer NBE-COOMe / NBE-CN using W(CHC(CH$_3$)$_2$)(OCH$_2$CMe$_3$)$_2$Br$_2$ as a catalyst.

Grubbs *et al.*[44] prepared a NBE-based three-block copolymer using the Ti-based catalyst system (CP$_2$Ti=CH$_2$).

Kress *et al.*[45] have shown that tungsten carbene complexes initiate the ROMP of some bicyclic alkenes such as (a), (b) and (c) using the catalyst system W(CH-tBu)(O-CH$_2$-tBu)$_2$Br$_2$ / GaBr$_3$.



The authors proved that these complexes lead to living polymers.

The propagation step is important in controlling the stereoselectivity of the polymer.

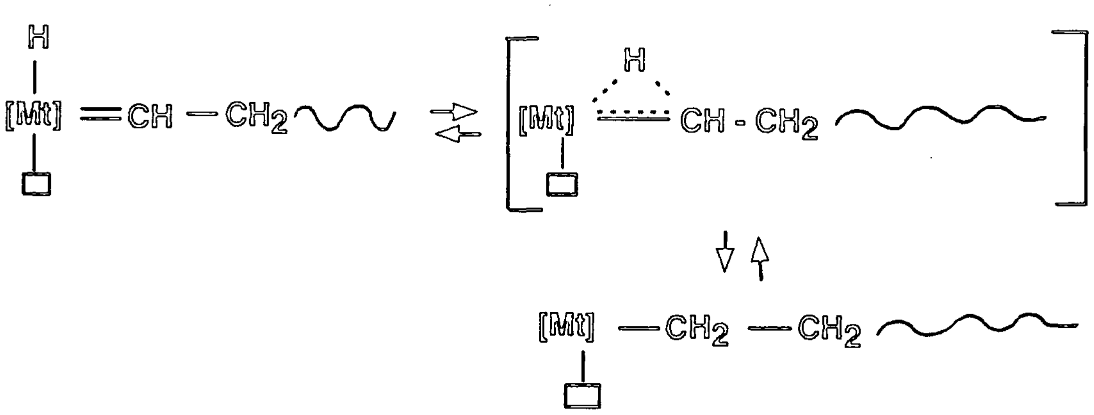
1.3.3 TERMINATION:

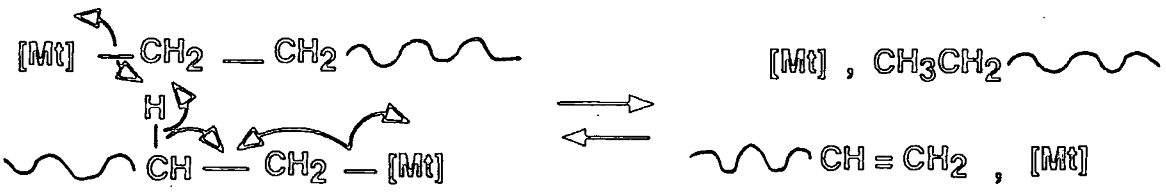
a) Reaction of the metallocarbene.

Compounds such as alcohol or water can destroy the active species by proton transfer. This type of reaction can usually be avoided by modification of the experimental procedures.

Another possible reaction of the metallocarbene is the formation of a cyclopropene:

Termination could also occur by β-hydrogen atom abstraction, followed by reaction between two metal-alkyl species, as shown below:

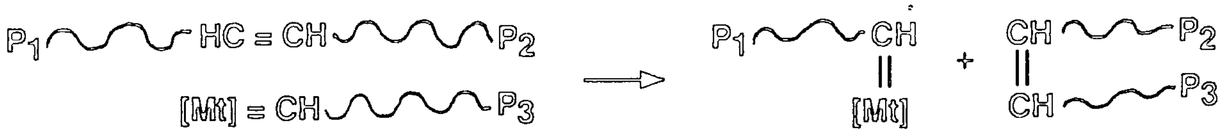




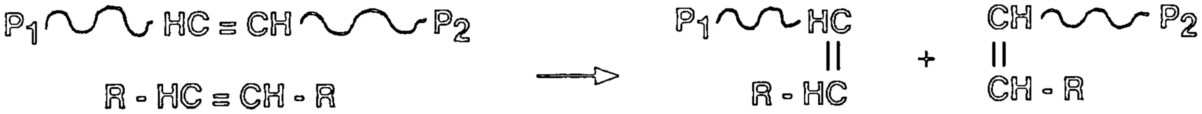
These kind of reactions have been proposed to occur as a termination in Ziegler - Natta polymerizations, and can be extended to the metathesis reaction assuming that the metallocarbene is in equilibrium with the simple transition metal alkyl

b) <u>Chain transfer.</u>

A chain transfer reaction can occur either between the propagating species and the polymer chains:



or between the polymer chain and an acyclic alkene

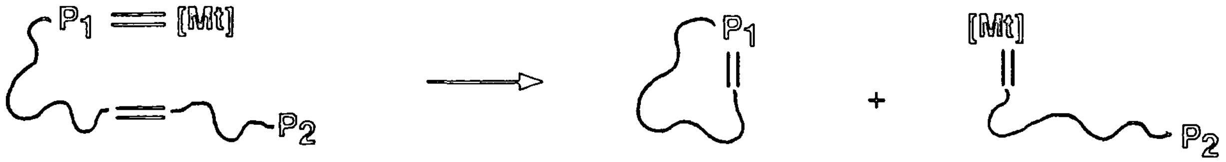


In the first case, a non-productive metathesis reaction occurs, which decreases the availability of the active catalyst for propagation.

In the second case, the cross-metathesis between the acyclic olefin and the polymer chain leads to a reduction in the molecular weight of the polymer due to the formation of linear oligomers.

c) Back biting.

Cyclic oligomers are formed via an intramolecular backbiting reaction, during which the metallocarbene at the end of the polymer chain reacts with a carbon-carbon double bond in the chain itself:



The occurrence of cyclic or linear oligomers contributes to the formation of relatively broad molecular weight distributions.

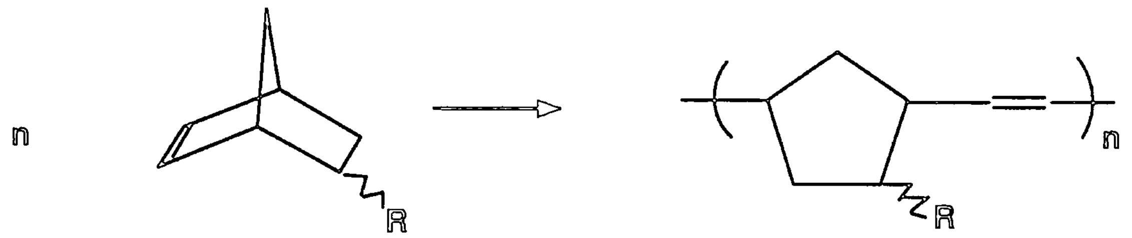
1.4 MICROSTRUCTURE OF POLYMER CHAINS AND STEREOREGULARITY

The physical properties of a polymer depend not only on the basic molecular structure, but also on differences in microstructure and morphology.

In some cases it is possible to obtain polymers with a desired microstructure, using proper catalyst systems and reaction conditions.

So it is possible to attempt to design polymers with the required physical behaviour. Furthermore microstructural control, extends the range of polymers that can be derived from a particular monomer.

The generalized case for the ring-opening metathesis polymerization of subtituted norbornenes is shown below:



For this generalized case there can be variations in the abundance and distribution of three features of microstructure of the polymer:

a) *cis* and *trans* double bonds

b) head-tail effects and

c) tacticity effects

a) *cis* and *trans* double bonds

The polymer derived from the POMP of norbornene is unsaturated and the carbon-carbon double bonds along the chain may have *cis* (c) or *trans* (t) geometry as shown on Fig. 1.4.a.The carbon-carbon bonds from the cyclopentane ring to the vinylene are 1,3-*cis* disposed on each ring.

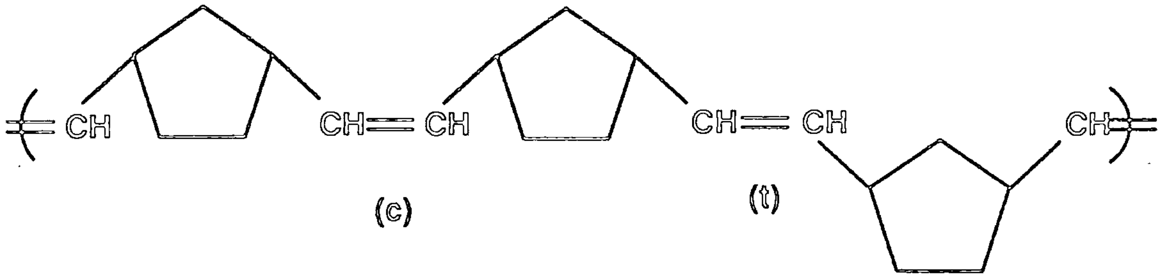


Figure 1.4.a: *cis* and *trans* double bonds in Poly-NBE

b) Head - tail effects

In the case of unsymmetrically substituted monomers, head - tail effects may occur in the polymer chain.

Consider for example the polymer of NBE-COOPh, for which the repeat unit and the numbering system is shown in Fig. 1.4.b.

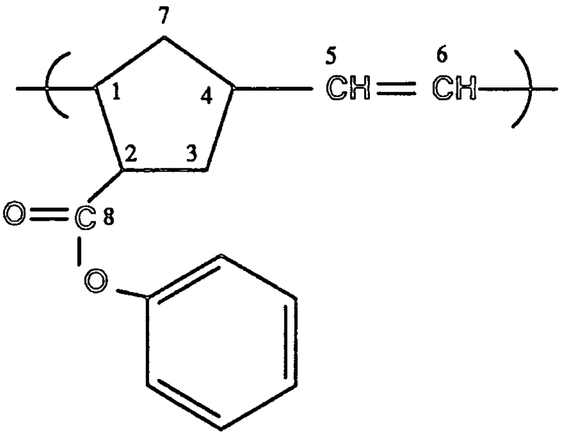


Figure 1.4.b: Repeat unit of polyNBE-COOPh

By definition the portion of the repeat unit substituted by the ester group (carbons 6,1,2 and 8) is called the head (H) fragment while the other portion (carbons 3,4 and 5) is defined as the tail (T).

So the environment of the head portion can be HT if the adjacent unit is a tail part or HH if the adjacent unit is a head part.

Similarly the tail fragment environment can be TT or TH.This effect is shown in Fig.1.4.c.

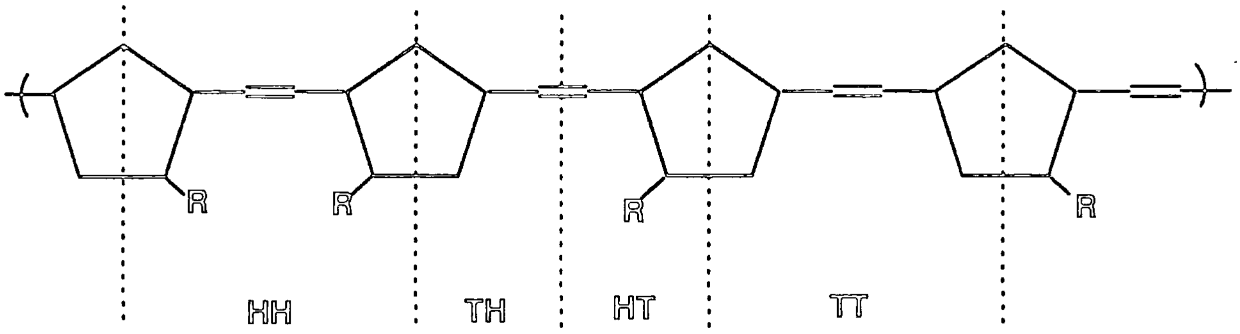


Figure 1.4.d: Head-tail effect

c) Tacticity effects

Additional stereochemistry in polynorbornenes arises from the fact that two tertiary carbon atoms in the polymer, C_1 and C_4 are chiral.

Therefore, there is a possibility of having centres on either side of the vinylene unit with the same or opposite chiralities.

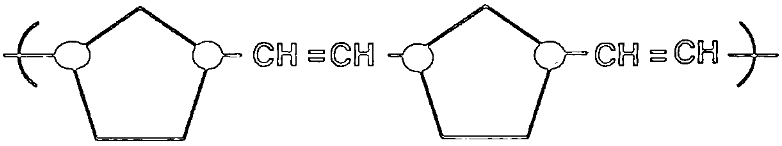
When the chiralities are the same we have a racemic (r) dyad and sequences of racemic dyads define a syndiotactic polymer.

When the chiralities are opposite, we have a meso (m) dyad and sequences of meso dyads define an isotactic polymer.

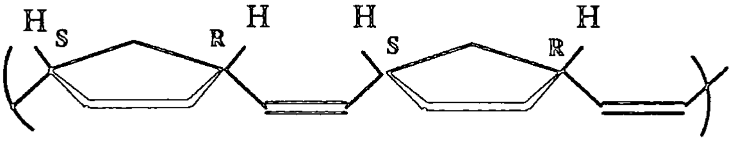
When the distribution of r and m dyads is random along the polymer chain, then an atactic polymer is derived.

These definitions are illustrated bellow for all *cis* and *trans* polymers of polynorbornene

(a)

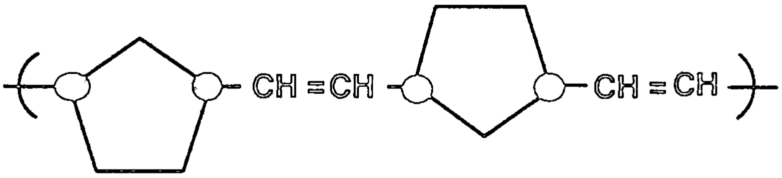


(b)

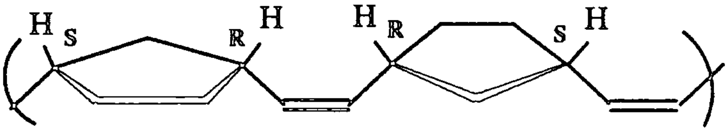


meso dyads cis isotactic polymer

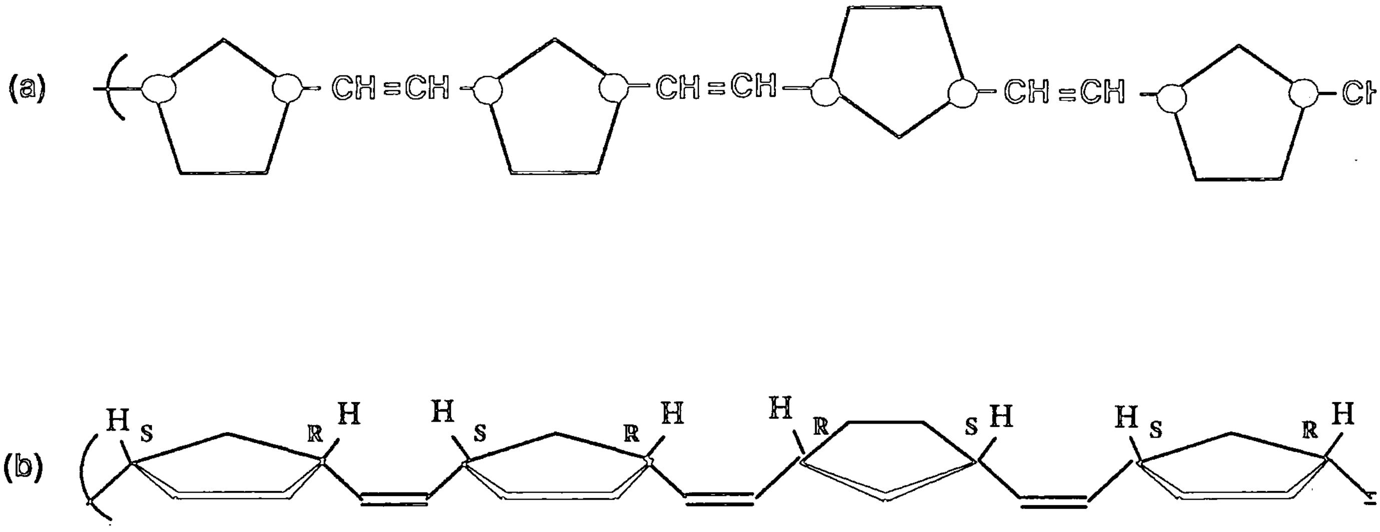
(a)



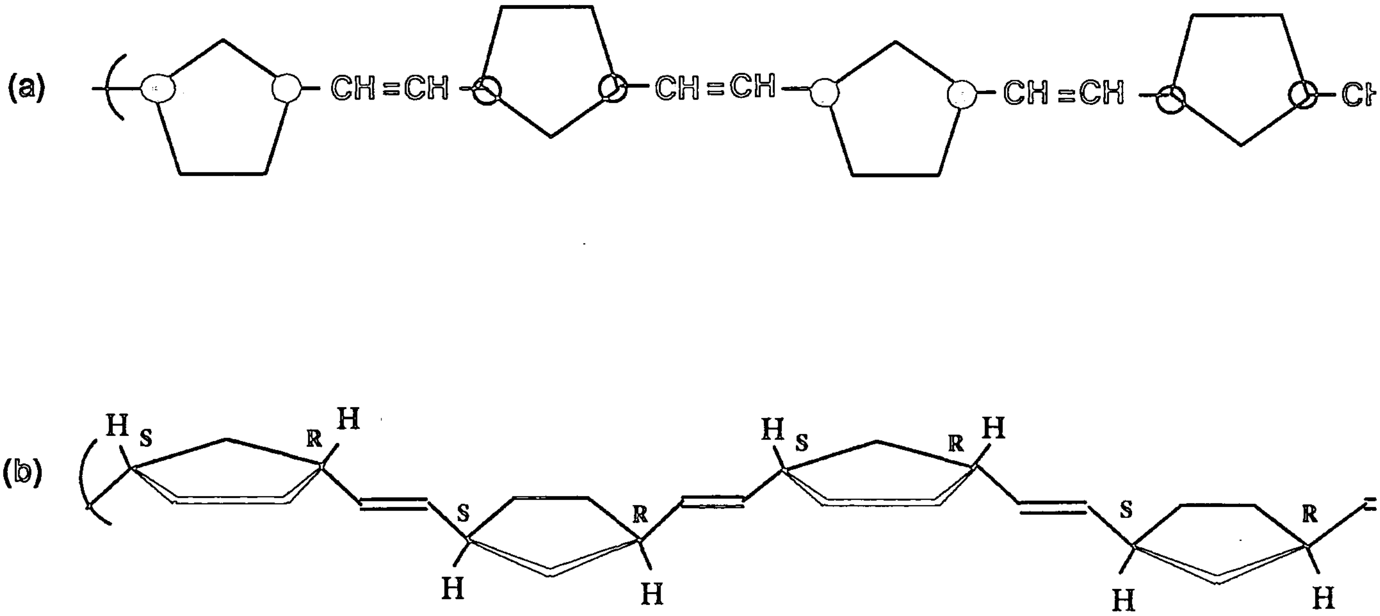
(b)



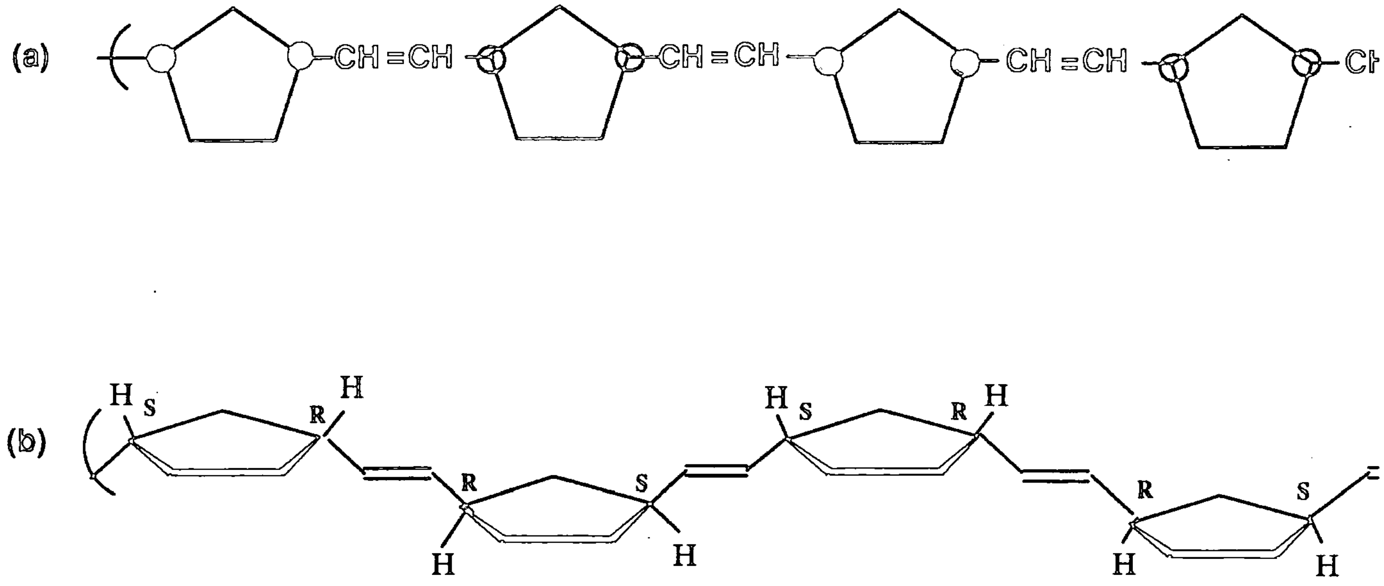
recemic dyads cis syndiotactic polymer



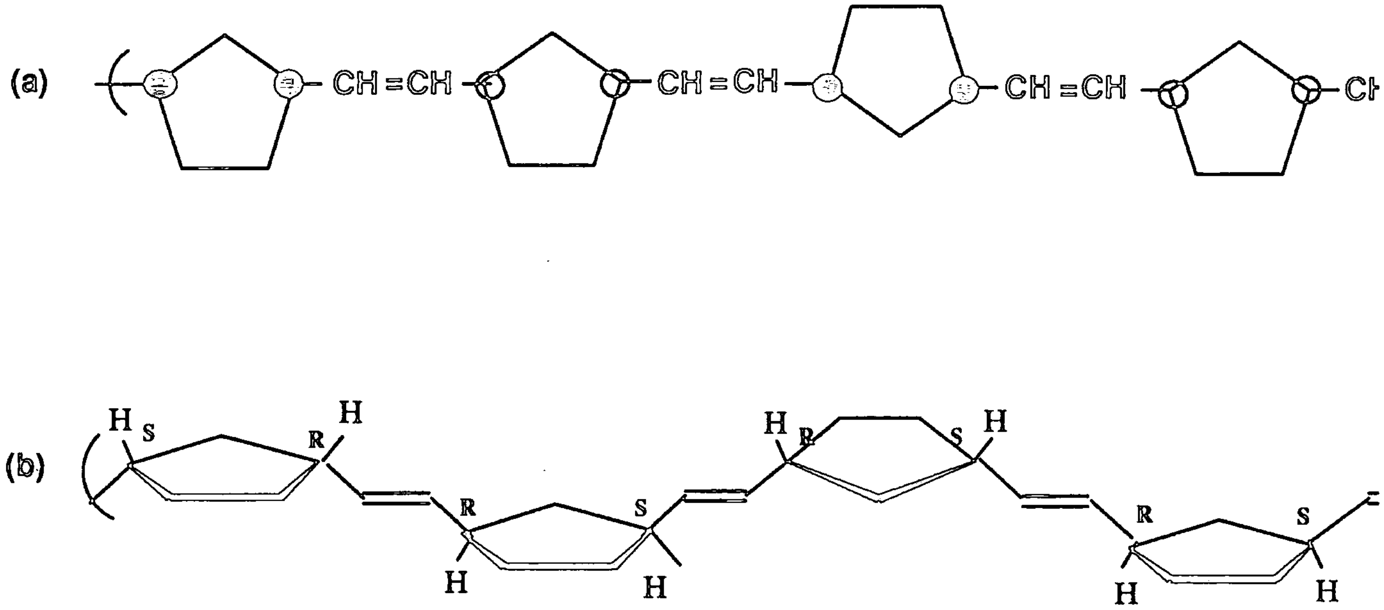
meso and racemic dyads cis atactic polymer



meso dyads trans isotactic polymer



racemic dyads   trans syndiotactic polymer



m and r dyads   trans atactic polymer

KEY: a: viewed from above

b: heavy lines project towards the viewer

o: indicates the CH bond at this point approaches the viewer

R,S: configuration prefixes (R-rectus, S-sinister)

1.5 OBJECTIVES OF THE WORK DESCRIBED IN THIS THESIS

Our objectives were to synthesise some new substituted polynorbornenes. Our approach was the attempted preparation of 2-phenoxy-3-chloro-2,3-difluorobicyclo[2.2.1]hept-5-ene as well as the preparation of 2-phenoxycarbonylbicyclo[2.2.1]hept-5-ene and its polymerization using classical and well defined catalyst systems.

An attempt was made to investigate the microstructure of the polymers using ^{13}C-NMR spectroscopy. The properties of the polymers are discussed in chapter four.

CHAPTER 2: SYNTHESIS AND CHARACTERISATION OF MONOMERS

2.1 THE DIELS-ALDER REACTION

The Diels-Alder Reaction[46-50] is a [4+2] cycloaddition, since it involves a system of four π electrons and a system of two π electrons, used to form two new σ bonds. A compound containing a double (or triple) bond, the dienophile, adds to a conjugated diene to form a cyclohexene (or a cyclohexadiene) as shown in figure 2.1.a.

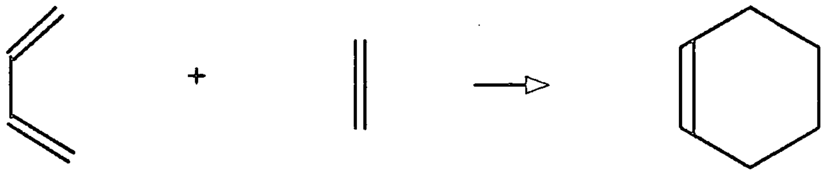
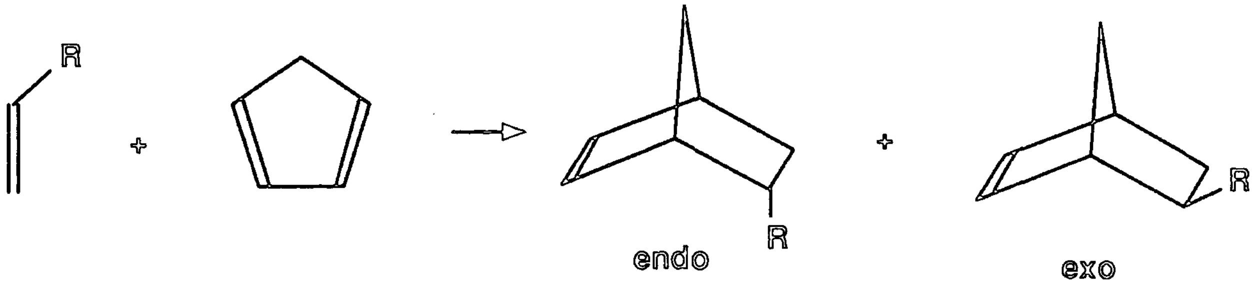


Fig 2.1.a The Diels - Alder Reaction

The diene must be in a *cis* conformation which permits the ends of the conjugated diene to 'reach' the multiply bonded carbons of the dienophile. Reaction of a *trans* diene would result in a product with a high degree of strain and this kind of reaction is not observed. Cyclopentadiene, in which the double bonds are locked in the *cis* configuration and in which the termini are in optimum separation, is highly active in Diels-Alder reactions.

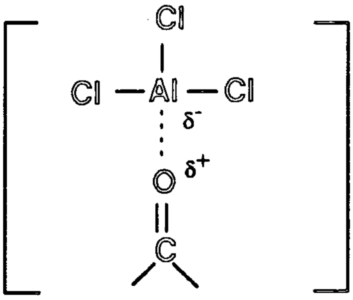
An unsymmetrically substituted dienophile may be added to cyclopentadiene in two possible ways, giving rise to exo and endo isomers.



The ratio of endo and exo isomers is dependent upon the conditions of the reaction, the endo being the product of kinetic control and the exo being the product of thermodynamic or equilibrium control.

The reaction is favoured by the presence of electron withdrawing substituents, such as -CN, >C=O and -NO_2 on the dienophile or electron donating groups on the diene. This is the 'normal' Diels-Alder reaction; Diels-Alder reaction with inverse electron demand (ie. donors in dienophiles, acceptors in diene) is also a favoured reaction.

The normal D-A reaction where the dienophile carries multiply bonded substituents can be catalysed by Lewis acids[51] such as $AlCl_3$ or $SnCl_4$ *via* the formation of intermediates of the type:



2.2 ATTEMPTED SYNTHESIS OF 2-PHENOXY-3-CHLORO-2,3-DIFLUORO BICYCLO[2.2.1]HEPT-5-ENE

A potential route for the synthesis of 2-phenoxy-3-chloro-2,3-difluorobicyclo[2.2.1]hept-5-ene is illustrated in Figure 2.2.a:

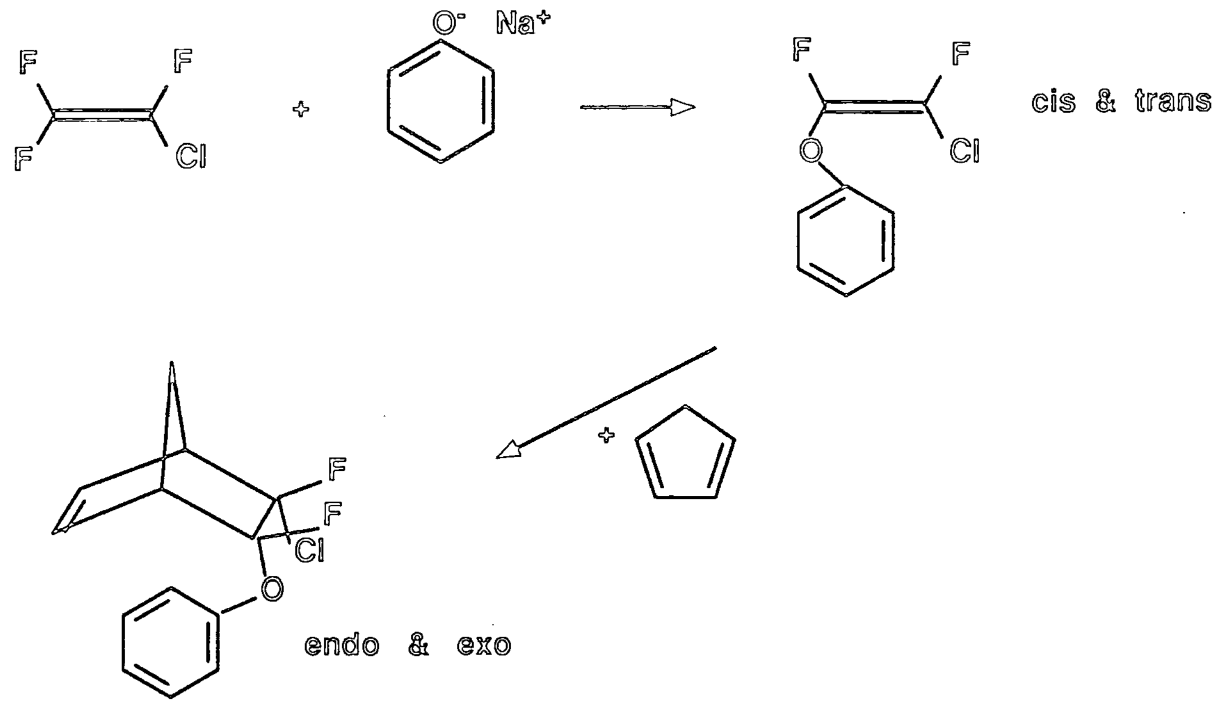
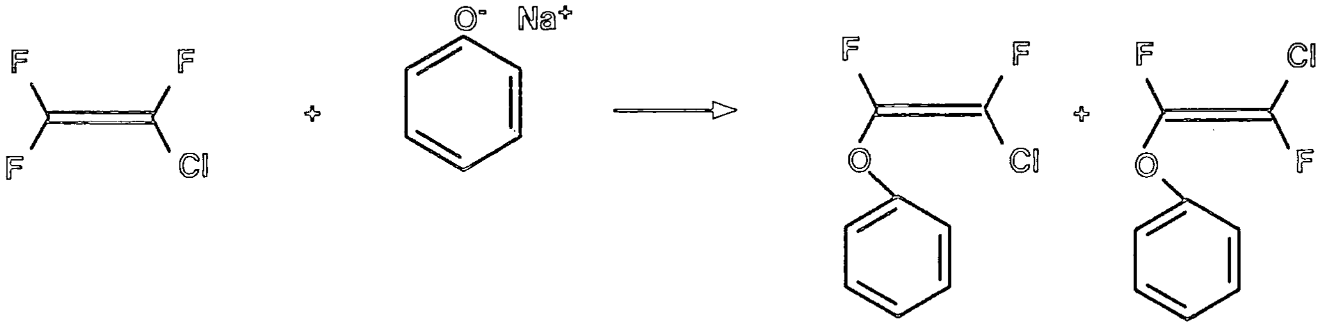


Fig.2.2.a Potential route for the synthesis of 2-phenoxy-3-chloro-2,3-difluoro bicyclo[2.2.1]hept-5-ene.

This route, if successful, will give *cis* and *trans* 1-chloro-1,2-difluorovinylphenyl ether isomers as the product of the first step. The Diels-Alder reaction[52,53] of this product with cyclopentadiene will give a mixture of four isomers, one endo and one exo isomer of 2-phenoxy-3-chloro-2,3-difluoro bicyclo[2.2.1]hept-5-ene for each of the *cis* and *trans* dienophiles.

2.2.1 Synthesis and characterisation of 1-chloro-1,2-difluorovinylphenyl ether.

The dienophile 1-chloro-1,2-difluorovinylphenyl ether was prepared using the Williamson synthesis, a nucleophilic substitution of phenoxide ion for halide ion.



Trifluorovinylphenyl ether was prepared by Pummer and Wall[54] using the same experimental method.

The reaction of chlorotrifluoroethylene with sodium phenoxide in an evacuated and degassed autoclave at 140°C, yielded 53% 1-chloro-1,2-difluorovinylphenyl ether and a small amount of 2-chloro-1,1,2-trifluoroethylphenyl ether as a by-product. The reaction was carried out under dry conditions, because the presence of moisture leads to the formation of 2-chloro-1,1,2-trifluoroethylphenyl ether as the main product.

The product was characterised by ^{19}F-NMR (Fig.2.2.a, Tab.2.2.a), the assignment was based on the FF coupling constant being bigger in the *trans* isomers than in the *cis* isomers[61]. The *cis* (60%) isomer predominated in the product mixture.

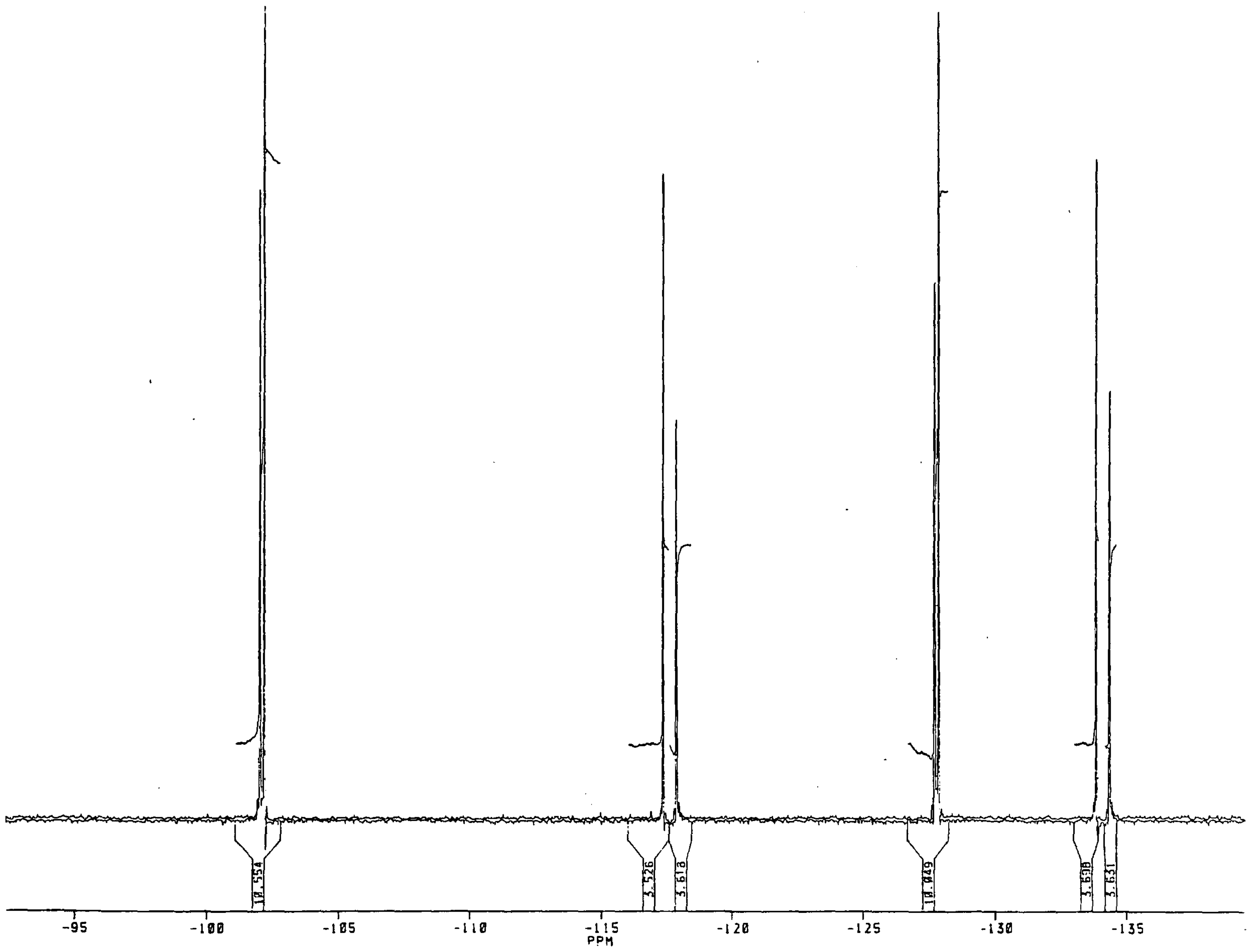


Fig.2.2.a ^{19}F-NMR spectrum of 2-chloro-1,2-difluorovinylphenyl ether

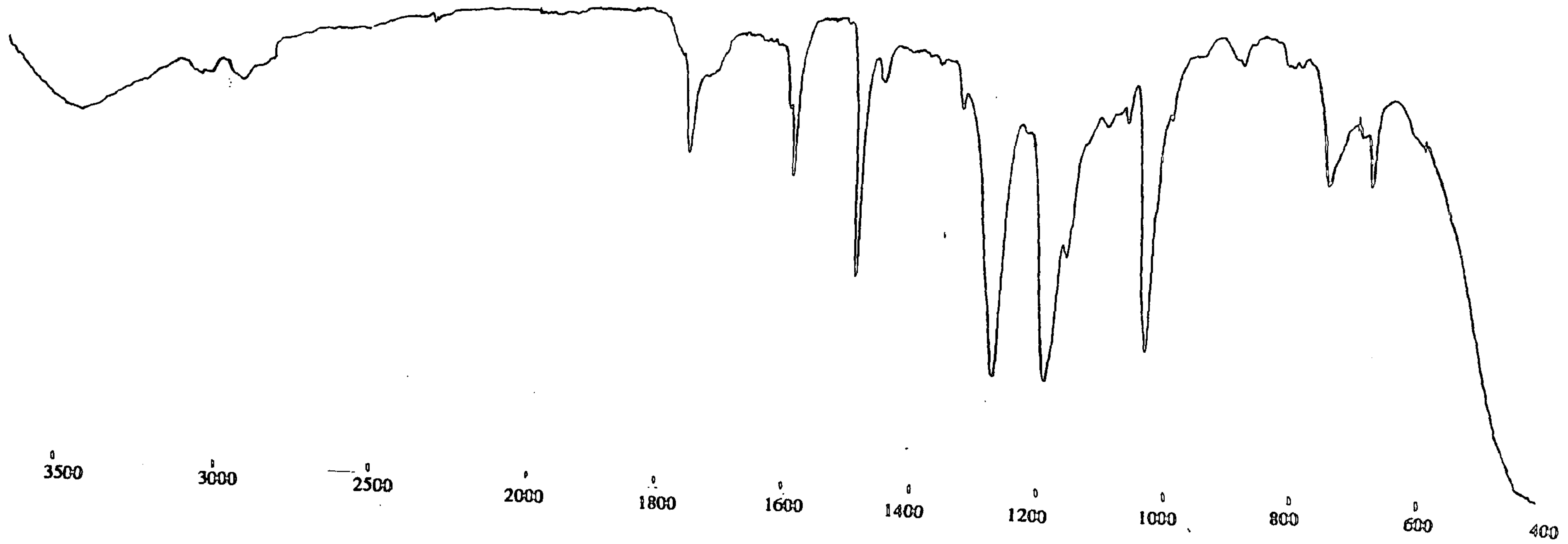


Fig.2.2.b Infrared spectrum of 2-chloro-1,2-difluorovinylphenyl ether

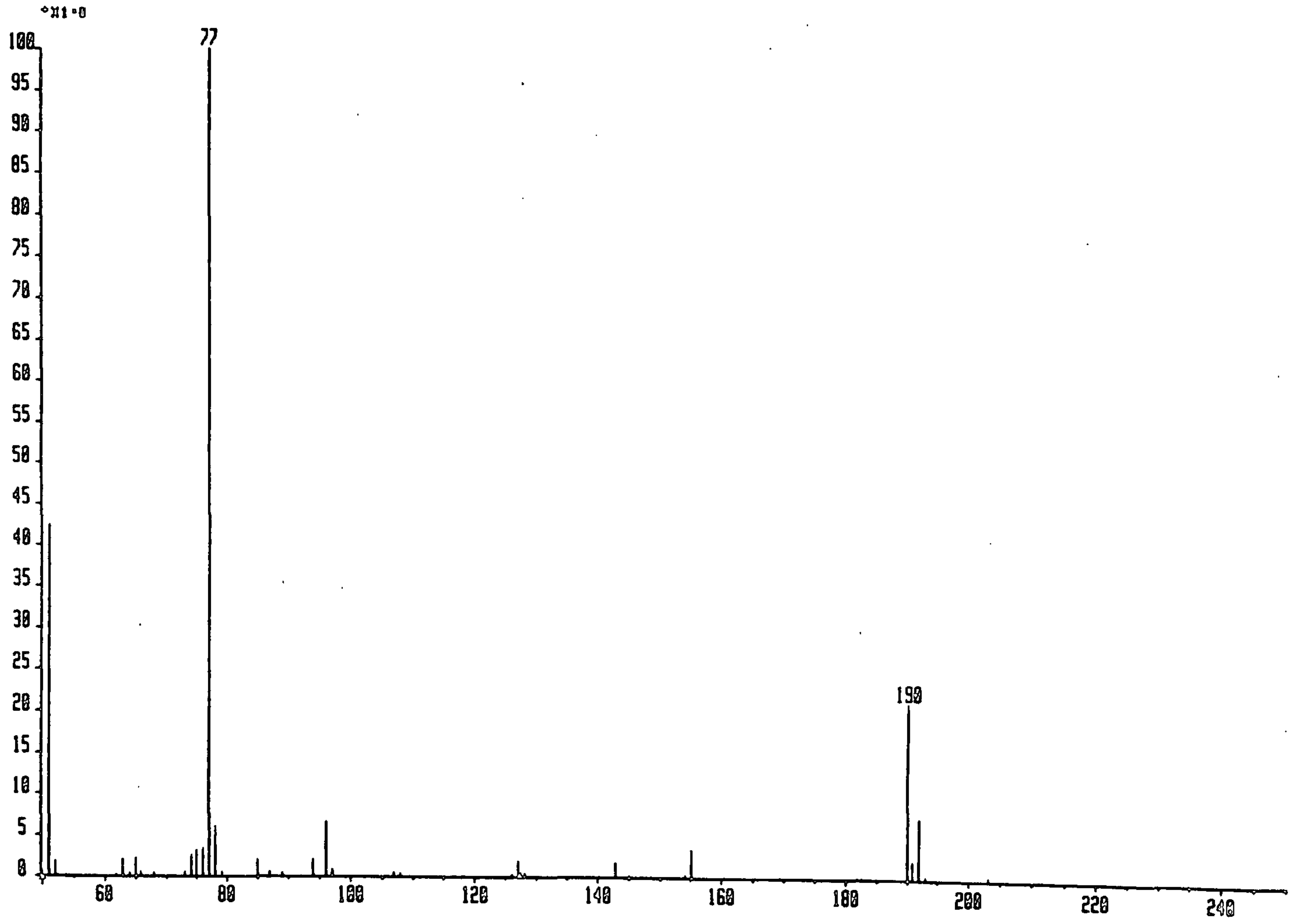
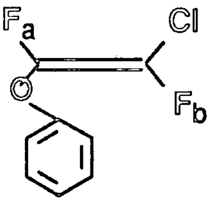
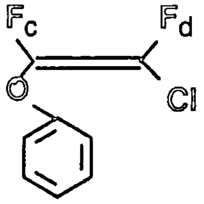


Fig.2.2.c Mass spectrum of 2-chloro-1,2-difluorovinylphenyl ether

Table 2.2.a ^{19}F-NMR shifts and assignments of 1-chloro-1,2-difluoro vinylphenyl ether, recorded at 235.36 MHz.

Compound	Shift (ppm)	Multiplicity	Integral	Assignment
	-117.6	doublet J_{FF}= 121.4 Hz	1	F_a
	-134.1	doublet J_{FF}= 121.4 Hz	1	F_b
	-102.1	doublet J_{FF}= 39.1 Hz	1	F_c
	-127.8	doublet J_{FF}= 39.1 Hz	1	F_d

The infrared spectrum (Fig 2.2.b) showed characteristic bands at 1760 cm^{-1} (-C=C- stretch), at 1600 and 1500 cm^{-1} (aromatic ring vibrations), at 1275 cm^{-1} (-C-O-C- asym.strech) and at 1040 cm^{-1} (-C=C-O-C- sym.strech).

The Mass Spectrum (Fig 2.2.c) showed the expected chlorine isotope pattern with signals of relative intensity 3:1 at 190 and 192 mass units (parent ion). The base peak was observed at 77 mass units [Parent ion - (CClF=CFO)]$^+$.

2.2.2 Attempted synthesis of 2-phenoxy-3-chloro-2,3-difluorobicyclo[2.2.1]hept-5-ene.

The reaction between 1-chloro-1,2-difluorovinylphenyl ether and freshly distilled dicyclopentadiene at low and moderate temperatures did not form any 2-phenoxy-3-chloro-2,3-difluorobicyclo[2.2.1]hept-5-ene. The reaction was carried out in a Carius tube from 100°C to 160°C in ca 20°C intervals; at lower temperatures starting materials were recovered and at highest temperatures 'coke' but at no temperature was there any evidence for a 1:1 adduct. This was a surprising and disappointing result for which we have no satisfactory explanation.

2.3 SYNTHESIS OF 2-PHENOXYCARBONYLBICYCLO[2.2.1]HEPT-5-ENE

The route followed for the synthesis of 2-phenoxycarbonylbicyclo[2.2.1]hept-5-ene is illustrated in figure 2.3.a.

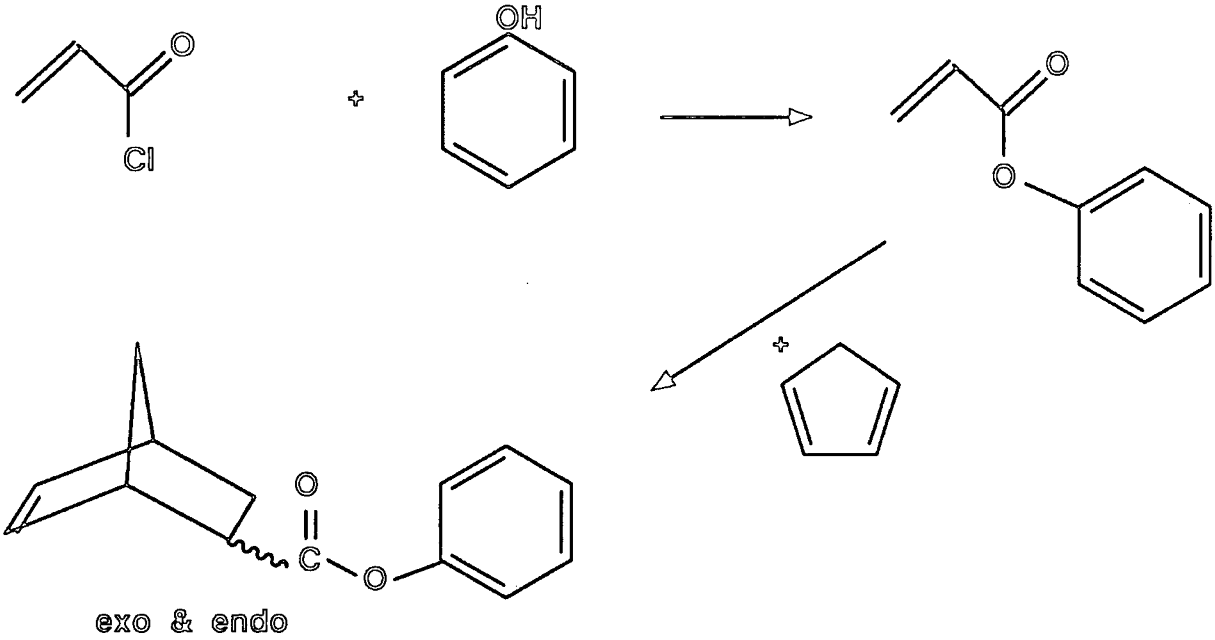


Fig.2.3.a Synthesis of 2-phenoxycarbonylbicyclo[2.2.1]hept-5-ene

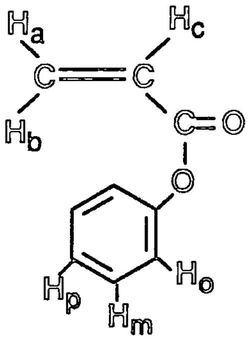
The first step is an esterification reaction involving an acid chloride (acryloyl chloride) and a phenol[55]. The second step is the Diels-Alder reaction between phenyl acrylate and cyclopentadiene. Carbomethoxynorbornene[56-58] has been prepared succesfully by this method. The Diels-Alder adduct is a mixture of the exo and endo isomers of 2-phenoxycarbonylbicyclo[2.2.1]hept-5-ene.

2.3.1 Synthesis and characterisation of phenyl acrylate.

The reaction between acryloyl chloride and phenol in toluene at 70°C gave phenyl acrylate in 49% yield. The reaction was also carried out at lower temperatures in the presence of K_2CO_3 or

$N(CH_2CH_3)_3$ but the yield did not improve. The product was characterised by ^{1}H-NMR (Tab.2.3.a) spectroscopy and Mass spectroscopy (Fig.2.3.a).

Table 2.3.a ^{1}H-NMR shifts and assignments of phenyl acrylate, recorded at 399.952 MHz.

Compound	Shift (ppm)	Multiplicity	Integral	Assignment
	6.53	d J_{bc}=18.2 Hz	1	H_b
	5.88	d J_{ac}=12.6 Hz	1	H_a
	6.26	q	1	H_c
	7.1	m	2	H_o
	7.15	m	1	H_p
	7.3	m	2	H_m

The Mass Spectrum showed a peak at 148 mass units (parent ion) while the base peak appeared at 55 mass units $(CH_2=CH-C=O)^+$.

2.3.2. Synthesis and characterisation of 2-phenoxycarbonylbicyclo[2.2.1]hept-5-ene.

The Diels-Alder reaction between phenyl acrylate and cyclopentadiene at 0°C gave a 1:4 mixture of the exo and endo isomers of 2-phenoxycarbonylbicyclo[2.2.1]hept-5-ene in 68% yield. The carboxylic group is an electron withdrawing group which makes phenyl acrylate a good dienophile. The endo and exo ratio was determined from the ^{1}H-NMR spectrum.

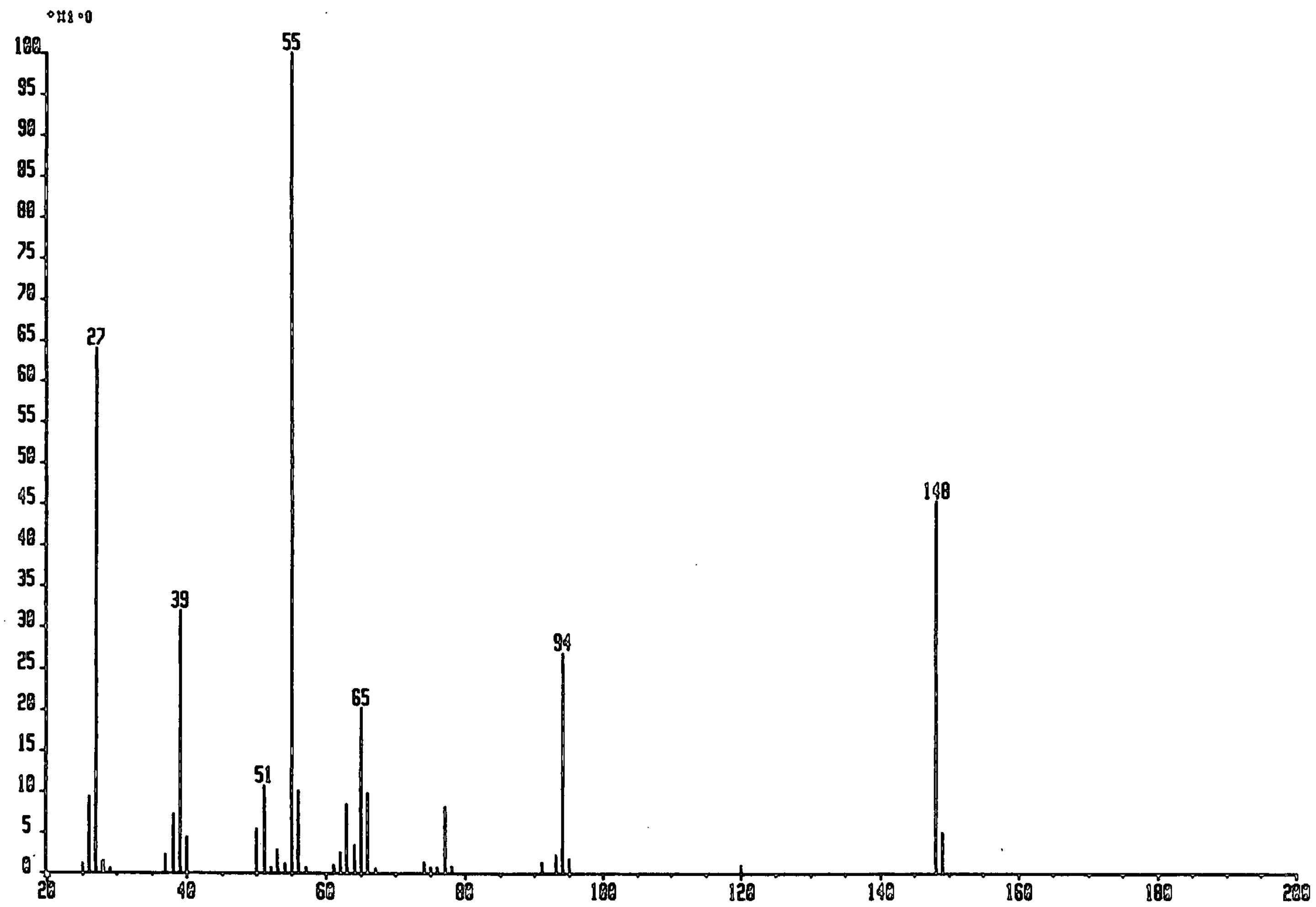


Fig.2.3.a Mass spectrum of phenyl acrylate

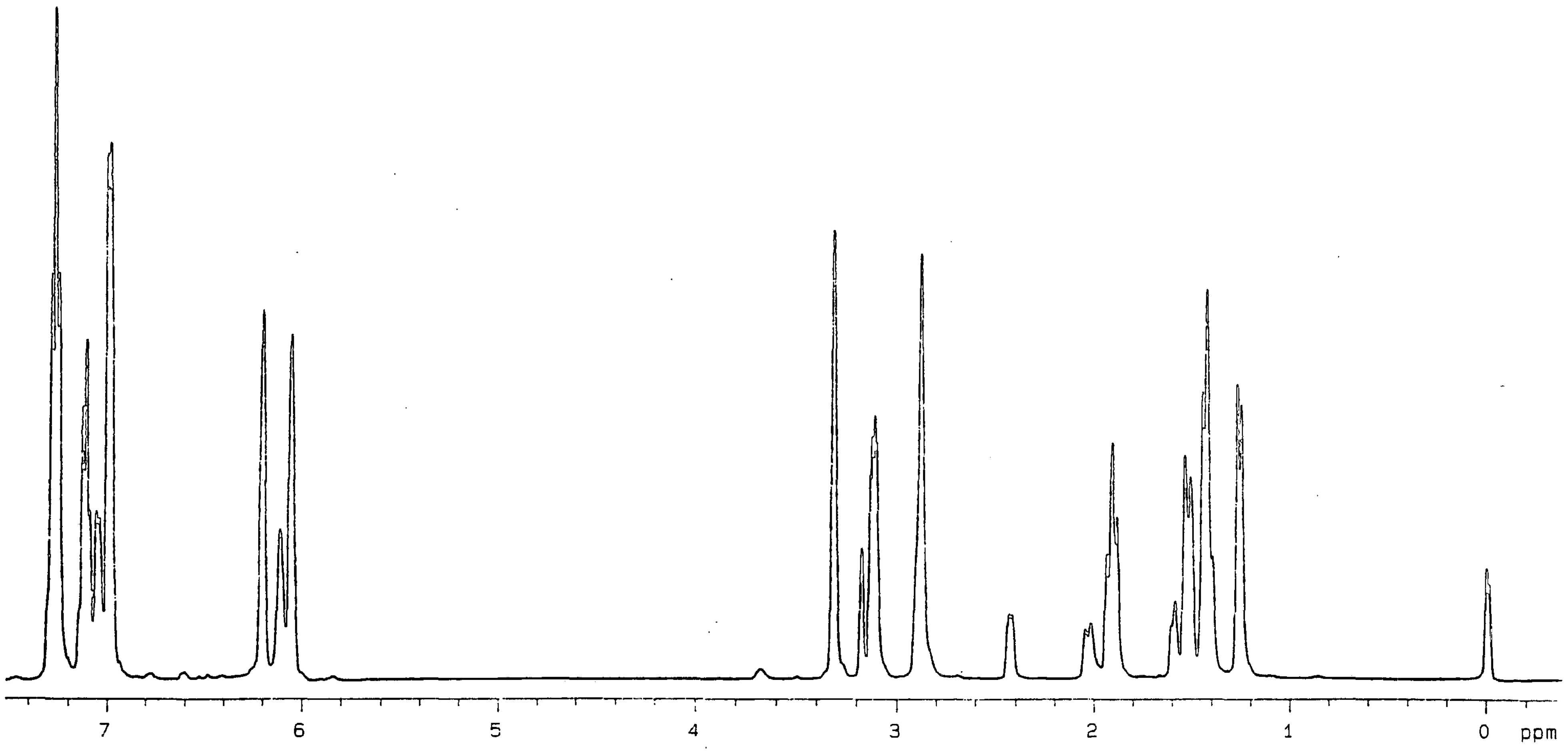
The reaction was also carried out using $AlCl_3$ as a Lewis acid catalyst which led to the formation of many side products detected by gas chromatography. The yield did not improve and the exo : endo ratio remained the same.

The product was purified by distillation using a Kugelrohr apparatus (80°C , 3mmHg) and has been characterised by ^{1}H-NMR (Tab.2.3.b), ^{13}C-NMR (Tab 2.3.c), Mass (Fig.2.3.b) and Infrared (Fig.2.3.c) spectroscopy.

The relative intesity of signals in the ^{13}C-NMR spectrum (Fig.2.3.e) allows resonances due to exo and endo monomers to be differentiated. In the vinyl region (138 - 131 ppm) carbons 5 and 6 (see Tables 2.3.b and 2.3.c for numbering system) were distinguished on the basis that the phenoxycarbonyl group is more likely to interact with carbon 6 shifting the absorption upfield. Furthermore, the signal for carbon 6 in the exo isomer is shifted downfield (+ 4.4ppm) from the signal for the same carbon in the endo isomer, while the signals for carbon 5 in the endo and exo isomers are very close to each other (exo +0.1ppm). The methylene and methine were distinguished with the aid of the heteronuclear correlation (HETCOR) spectrum (Fig.2.3.f) in which -CH- carbons appear as one contour corresponding to the proton attached, while $-CH_2-$ carbons appear as two contours. Carbons 3 and 7 as well as carbons 1 and 4 were assigned by analogy with monosubstituted norbornenes[59,60]. For carbon 7 the signal for the exo isomer appears 3.4ppm upfield from the signal for the endo isomer, while the signal for carbon 3 in the exo conformation is shifted 1.2ppm downfield from the signal for the endo. The endo or exo position of the carbophenoxy group affects the carbon 7 signal more than the carbon 3 signal. The chemical shifts due to ortho-, meta- and para- carbons were assigned with the aid of relative reference books[61].

The ^{1}H-NMR spectrum (Fig.2.3.d) was interpreted with the aid of the HETCOR spectrum, using the assignments for the ^{13}C-NMR spectrum.

Fig.2.3.d ^{1}H-NMR spectrum of 2-phenoxycarbonylbicyclo[2.2.1]hept-5-ene



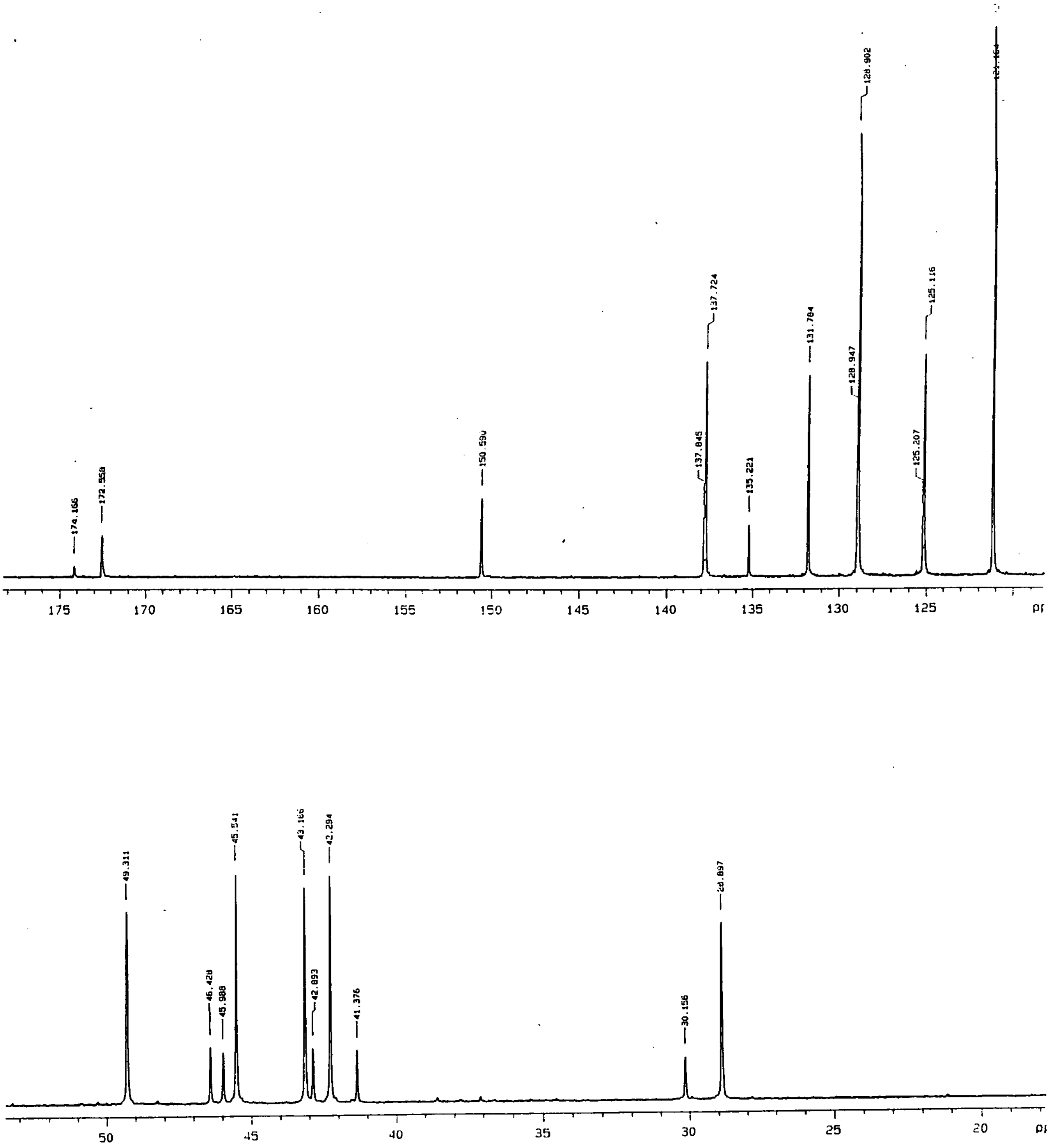


Fig.2.3.e ^{13}C-NMR spectrum of 2-phenoxycarbonylbicyclo[2.2.1]hept-5-ene

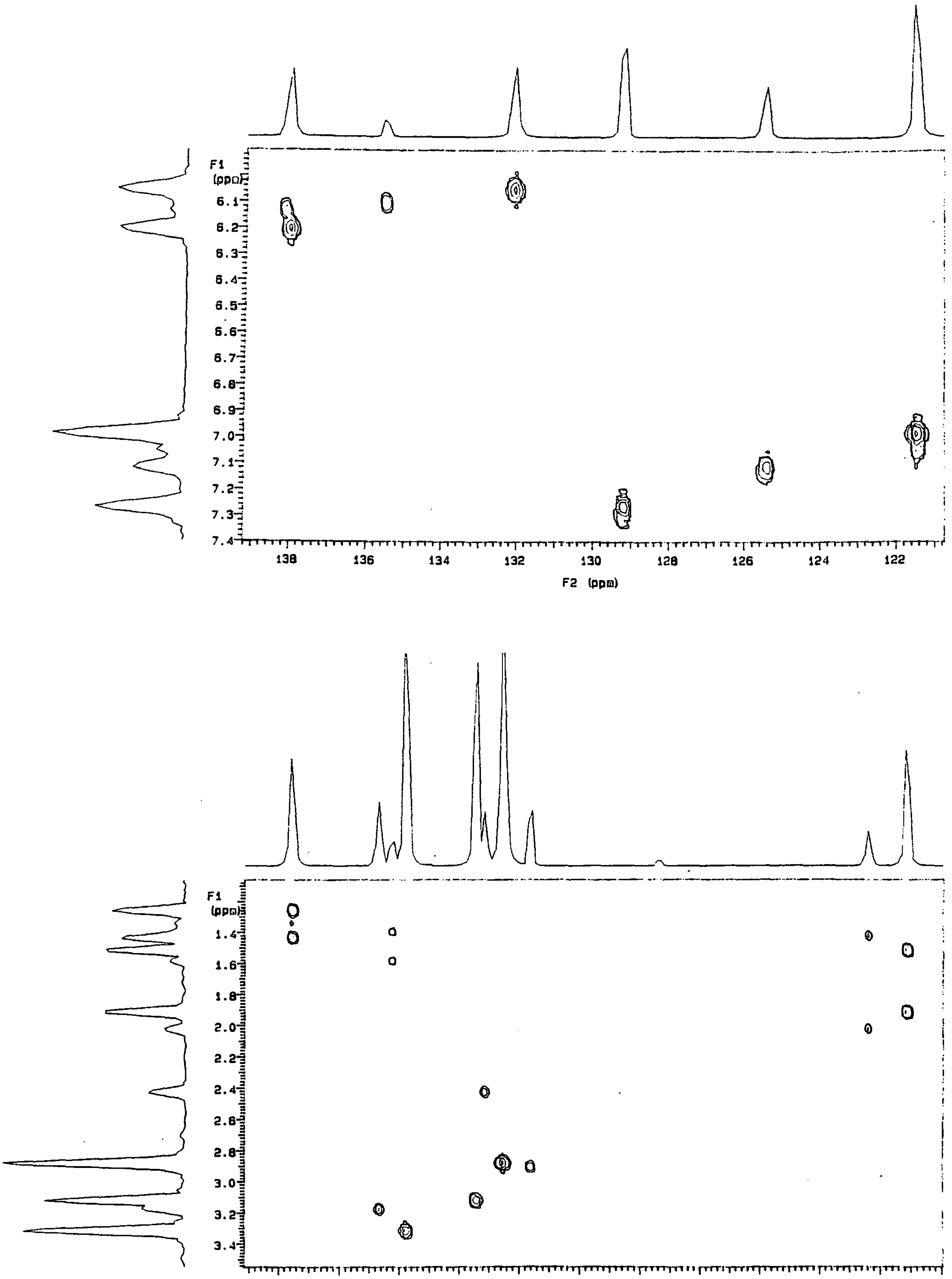


Fig.2.3.e HETCOR spectrum of 2-phenoxycarbonylbicyclo[2.2.1]hept-5-ene

Table 2.3.b ^1H NMR shifts and assignments of 2-phenoxycarbonyl bicyclo[2.2.1]hept-5-ene, recorded at 399.952 MHz.

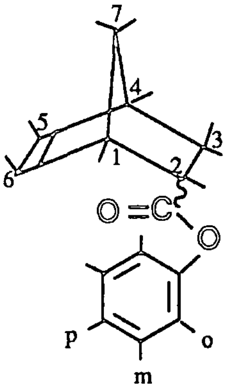
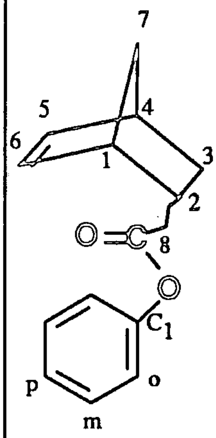
Compound	Shift (ppm)	Multiplicity	Integral	Assignment
	7.32	s		m exo
	7.27	s		m endo
	7.14	s		p exo
	7.12	s		p endo
	7.06	s		o exo
	7.00	s		o endo
	6.2	s		5 endo
	6.14	s		5 exo
	6.1	s		6 exo
	6.06	s		6 endo
	3.32	s		2 endo
	3.17	s		2 exo
	3.12	m		4 endo
	2.92	s		1 exo
	2.9	s		1 endo
	2.42	m		4 exo
	2.02	m		3 exo
	1.42	m		exo
	1.92	m		3 endo
	1.5	m		endo
	1.58	d		7 exo
	1.38	d		exo
	1.44	d		7 endo
	1.25	d		endo

Table 2.3.c ^{13}C-NMR shifts and assignments of 2-phenoxycarbonyl bicyclo[2.2.1]hept-5-ene, recorded at 100.5 MHz.

Compound	Shift (ppm)	Multiplicity	Assignment
	174.2	s	8 exo
	172.6	s	8 endo
	150.6	s	C_1 exo & endo
	137.8	s	5 exo
	137.7	s	5 endo
	135.2	s	6 exo
	131.8	s	6 endo
	128.95	s	m exo
	128.9	s	m endo
	125.3	s	p exo
	125.1	s	p endo
	121.2	s	o exo & endo
	49.3	s	7 endo
	46.4	s	2 exo
	46.0	s	7 exo
	45.5	s	2 endo
	43.2	s	4 endo
	42.9	s	4 exo
	42.3	s	1 endo
	41.4	s	1 exo
	30.2	s	3 exo
	28.9	s	3 endo

The infrared spectrum showed characteristic bands due to aromatic C-H (3070 cm^{-1}), saturated C-H (2890 cm^{-1}), olefinic C-H (2990 cm^{-1}), carbonyl (1760 cm^{-1}), CH=CH (1630 cm^{-1}(w)) and aromatic ring vibration (1600 and 1500 cm^{-1})

The mass spectrum showed a peak at 214 (parent ion) and peaks of high intensity at 55 mass units (CH_2=CHC=O)$^+$ and at 66 mass units as a result of the retro Diels-Alder reaction, while the base peak appeared at 121 mass units (parent ion - phenoxy ion)

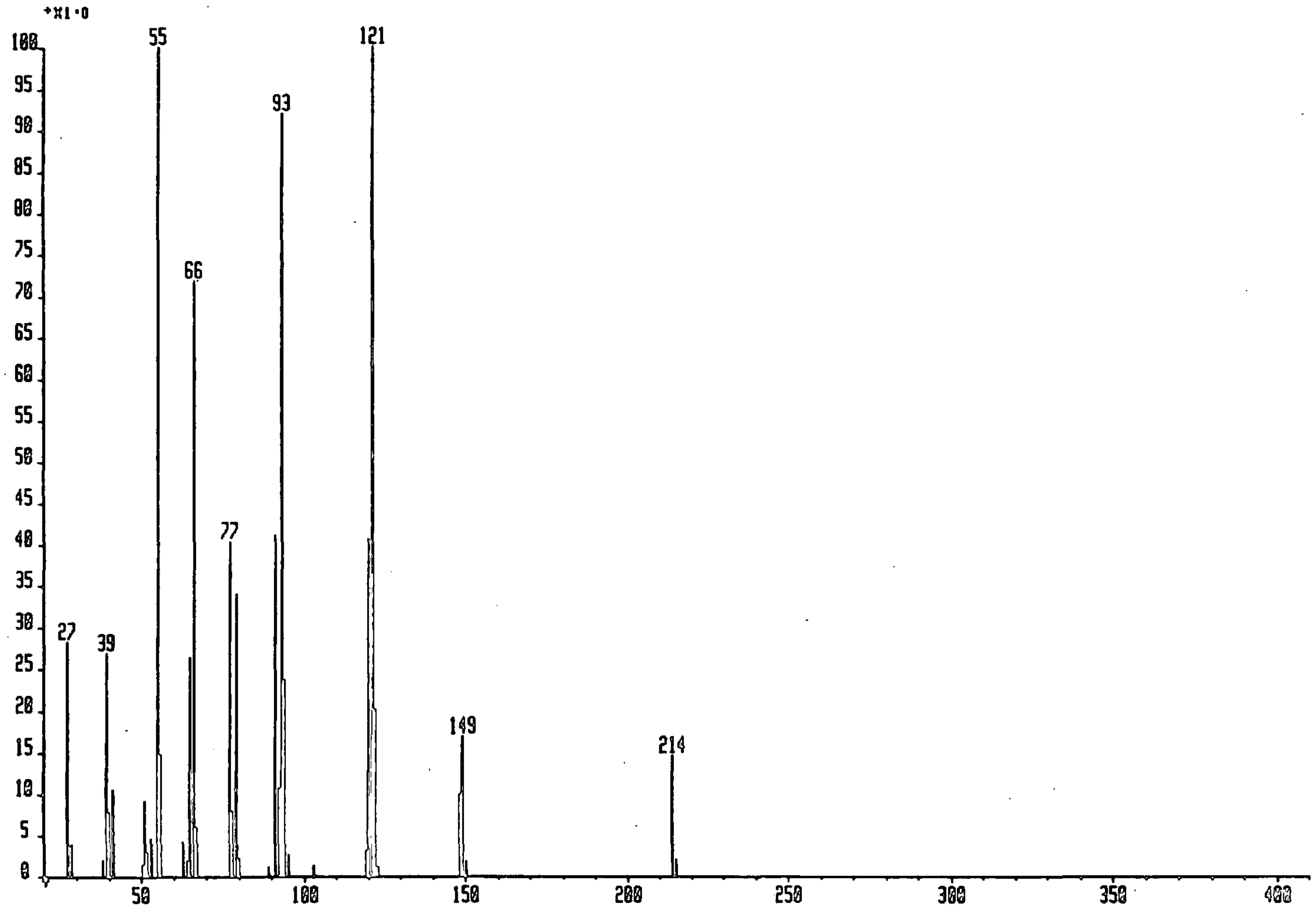


Fig.2.3.b Mass spectrum of 2-phenoxycarbonylbicyclo[2.2.1]hept-5-ene

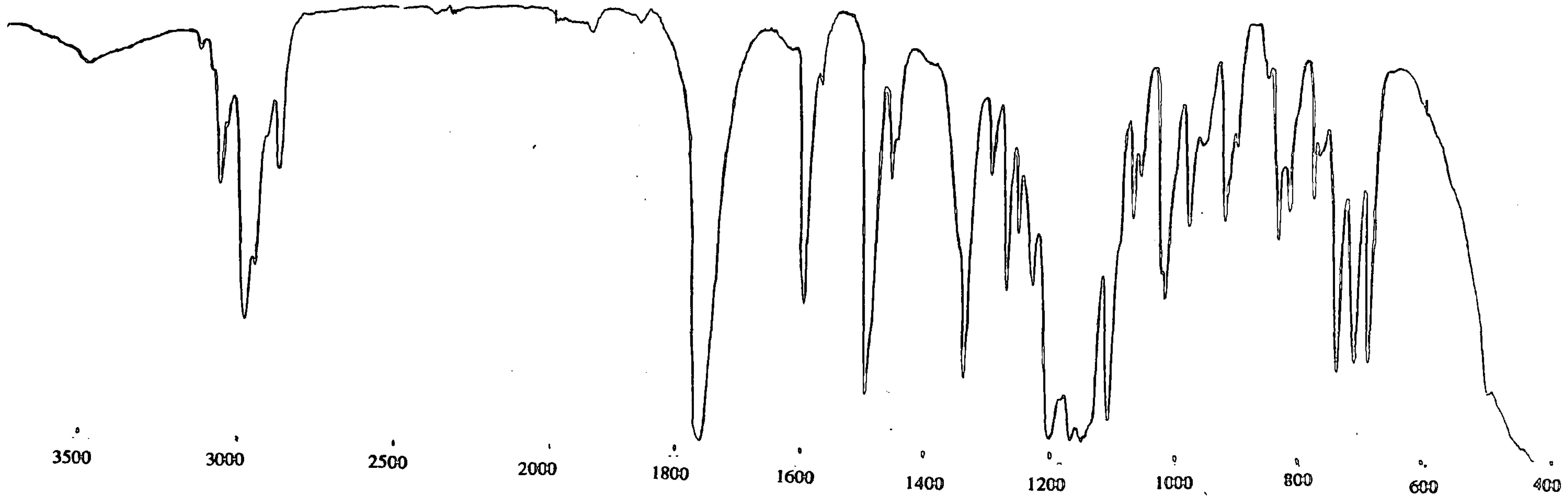


Fig.2.3.c Infrared spectrum of 2-phenoxycarbonylbicyclo[2.2.1]hept-5-ene

2.4 EXPERIMENTAL:

2.4.1 Reagents:

1-Chloro-1,2,2-trifluoroethylene used as supplied from Bristol Organics Ltd (stabilized with 0.1% dipentene)

Hydroquinone used as supplied from BDH.

Phenol used as supplied from Koch Light Ltd

Sodium hydroxide used as supplied from BDH.

Sodium phenoxide[62] was prepared by reaction of sodium hydroxide (27% w/v aq.solution) with phenol (130% w/v in methylated spirits methanol:ethanol 1:9) at room temperature for 1hr. The solvents were removed using a rotary evaporator and the sodium phenoxide dried under vacuum and further dried by azeotropic distillation with toluene using Dean-Stark apparatus.

Acryloyl chloride 98%,was purchased from Aldrich and vacuum transferred before use.

Cyclopentadiene was freshly prepared by thermal cracking of dicyclopentadiene[63] which was purchased from Aldrich.

2.4.2 Preparation of 1-chloro-1,2-difluorovinylphenyl ether.

Solvents: Tetrahydrofuran was refluxed over $LiAlH_4$ for 24 hours, then distilled again over sodium/benzophenone and collected over sodium/benzophenone. Benzene was dried over Na wire.

Apparatus: Parr-bomb (0.165 l autoclave), copper gasket.

Procedure: Sodium phenoxide (0.043 mol,5.07 g) together with tetrahydrofuran (5 ml)and benzene (20 ml) were placed in the bomb. The bomb was cooled in liquid air and then evacuated. 5.2g (0.043mol) Chlorotrifluoroethylene (5.2 g, 0.043 mol) were then condensed into the bomb, which was sealed and placed in the rocker mechanism(140°C for 30hrs). After the completion of the reaction there was no excess gas when the bomb was vented. The product and the solvents (green-grey colour) were removed from the precipitated salts by filtration. The salts were washed with benzene and the washings combined with the main solution.

The solvents were removed from the products by distillation under N_2 (bath temperature

100°C , 1atm) to give 1-chloro-1,2-difluorovinylphenyl ether (4.4 g, 53%)

2.4.3 Attempted preparation of 2-phenoxy 3-chloro 2,3-difluoro bicyclo[2.2.1]hept-5-ene.

Apparatus: Carius tube

Procedure: 1-phenoxy-2-chloro-1,2-difluorovinylphenyl ether (4.39g, 0.023mol) (together with a small amount of benzene and 2-chloro-1,1,2-trifluoroethylphenyl ether) was placed in a Carius tube. 0.05g hydroquinone was added as a polymerization inhibitor. The Carius tube was cooled in liquid air. Freshly distilled cyclopentadiene (1.897ml, 1.518g, 0.023mol) was added into the evacuated tube by vacuum transfer. The tube was then sealed with a glassblowers torch. The tube was placed in a protective metal sleeve and heated at 100°C for 60hrs. The Carius tube was opened (hot spot technique) and the product flame distilled from the tube.

The mass spectrum of the product did not show any trace of 2-phenoxy-3-chloro-2,3-difluorobicyclo[2.2.1]hept-5-ene.

The same procedure at 160°C gave a black solid after 70hrs of reaction. The product was extracted with dichloromethane and then filtered and treated with decolorizing charcoal. The solvent was removed in a rotary evaporator and crystals appeared. The mass spectrum of this solid did not show any trace of 2-phenoxy-3-chloro-2,3-difluorobicyclo[2.2.1]hept-5-ene.

The reaction was repeated at 110 °C and 130°C; in no case did the mass spectra revealed the presence of the expected 1:1 adduct. This attempted synthesis was abandoned at this stage

2.4.4 Preparation of phenyl acrylate.

Solvents: Toluene (Na dried)

Apparatus: 2-neck round bottomed flask, dropping funnel, water condenser, separating funnel.

Procedure: To a continuously stirred solution of phenol(8.46g, 0.09mol) in toluene(50ml) at 70°C under N_2, acryloyl chloride (8.1g, 0.09mol) was added within 5min. The HCl formed was led through a tube into an aq.solution of NaOH. The mixture was kept for 4hrs at 70°C and then after cooling ether (50ml)was added to the solution and the mixture poured into a separating funnel, together with 100ml aq. solution of K_2CO_3 and washed. The organic layer was then washed several times with distilled water, then separated and dried over $MgSO_4$. The solvents were removed using a rotary evaporator (60°C) and the crude product vacuum transferred to give phenyl acrylate (6.48g, 49%).

2.4.5 Preparation of 2-phenoxycarbonylbicyclo[2.2.1]hept-5-ene

Solvent: Anhydrous ether

Apparatus:3-neck round bottomed flask,water condenser, dropping funnel, ice bath, silica-gel drying tube.

Procedure:To a continuously stirred ice-cooled solution of phenyl acrylate (11.07g, 0.075mol) in anhydrous ether(100ml), freshly distilled cyclopentadiene (6.1ml, 4.95g, 0.075mol) was added dropwise.

The ice-bath was removed and the mixture left to react overnight at room temperature. The solvent was removed using a rotary evaporator (30°C). The product was a clear viscous liquid. The main impurity was the phenyl acrylate which was removed by distillation using a Kugelrohr apparatus (90°C, 4mmHg).The residue was an exo and endo mixture of 2-phenoxycarbonylbicyclo[2.2.1]hept-5-ene (10.89g, 68%).

CHAPTER 3: SYNTHESIS AND CHARACTERIZATION OF POLY(2-PHENOXYCARBONYLBICYCLO[2.2.1]HEPT-5-ENE) USING CLASSICAL AND WELL-DEFINED CATALYST SYSTEMS.

This chapter describes the polymerization of an endo/exo mixture of 2-phenoxycarbonyl norbornene, using WCl_6 / $SnMe_4$, $MoCl_5$ / $SnMe_4$ and Mo(CH-t-Bu)(NAr)(O-t-Bu)$_2$, and the characterization of the polymeric products of these reactions.

3.1 ANALYTICAL METHODS

a) NMR spectroscopy:

High field nuclear magnetic resonance is the most powerful analytical technique for studying the microstructure of polymers. ^{13}C spectra are the most useful since the overlap of signals in the ^{1}H-NMR spectra of polymers makes their detailed interpretation difficult.

In ^{13}C-NMR the spectra are often sufficiently well resolved to allow detailed assignment of the microstructure because the chemical shift range is larger, spin-spin interactions between adjacent nuclei are very infrequent and ^{1}H -^{13}C interactions can be eliminated by broad band decoupling. However, the interpretation of ^{13}C-NMR spectra can be very complicated since chemical shifts are affected by small changes in the microstructure of the polymer. For example in the case of a monosubstituted norbornene of interest in this work we would expect to see signals for the allylic carbons (C_1 and C_4, see Fig.3.2.a) corresponding to carbons adjacent to *cis* (c) or *trans* (t) vinylenes. In the event it is often found that these shifts are sensitive to nearest, next nearest neighbour effects and to tacticity effects. Consequently for a simple symmetric polynorbornene we see at least four signals cc, ct, tc and tt; and possibly further multiplicity due to tacticity effects. When these are well resolved this allows both *cis* / *trans* content and distribution (ie. statistical or blocky) to be elucidated. It is universally observed that *cis* occurs ca. 5 ppm upfield from *trans* allylic carbon signals. In the case we have to consider, the polar substituent at position 2 may also increase the multiplicity of these signals both through Head-Head, Tail-Tail and Head-Tail placements and because the monomer used was a mixture of endo and exo isomers. Thus we expect very complex spectra from our polymers if both endo and exo isomers are incorporated in a cis / trans atactic microstructure. If simple spectra were to be observed it would point to initiation and propagation procedures which were highly selective. Similar considerations apply to all the nuclei in the repeat unit.

b) Gel permeation chromatography (GPC)

Gel permeation chromatography (also termed as exclusion chromatography)[64] is a packed column technique used to determine the molecular weight of polymers[65,66]. Molecular size separation is achieved by injecting a solution of the polymer at one end of a column packed with either crosslinked polystyrene gel or porous glass beads. Molecules which are larger than the pore size (10-250nm for polymers in the 10^3 to 10^7 molecular weight range) pass through, whereas smaller molecules enter the pores. Hence, small molecules have longer retention times.

The molecular weight distribution of a new sample can be estimated from the relative concentration of polymer as a fraction of retention volume using a calibration curve.

c) Infrared spectroscopy

Infrared active groups along the chain generally absorb as if each were a localised group in a single molecule. The principle characteristic bands for this polymer are the aromatic C-H (>3000 cm^{-1}), the vinyl C-H (2940 cm^{-1}), the saturated C-H (2870 cm^{-1}), the CH=CH stretch (1660 cm^{-1}), the >C=O stretch (1760 cm^{-1}) and the aromatic ring vibration (1600 and 1500 cm^{-1}).

The infrared spectra of the polymers were recorded from free standing films cast from $CHCl_3$.

3.2 POLYMERIZATION OF 2-PHENOXYCARBONYL NORBORNENE

The process involved is represented schematically in Fig.3.2.a.

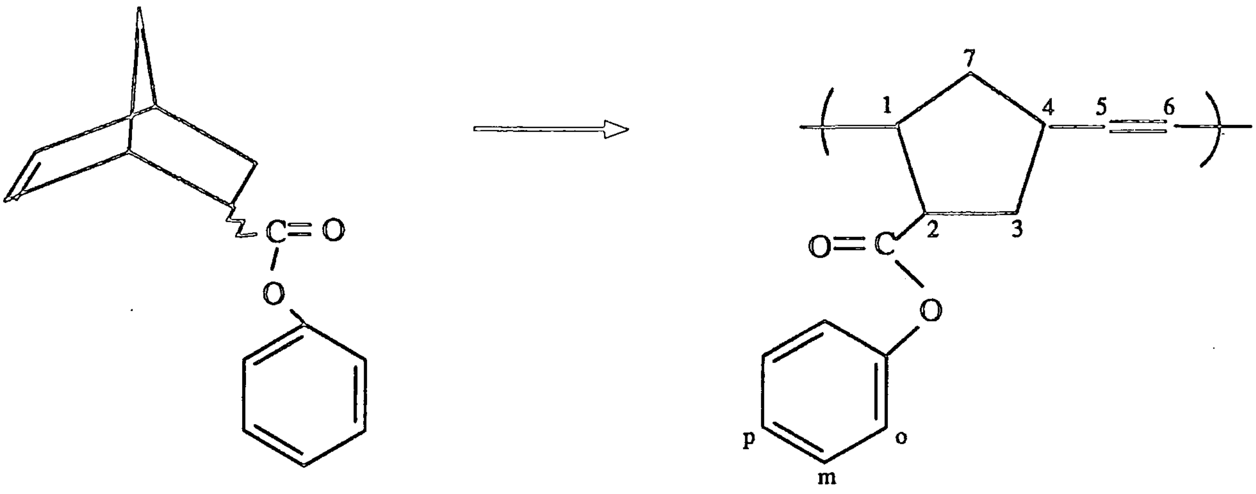


Fig 3.2.a Polymerization of 2-phenoxycarbonyl norbornene

3.2.1 Polymerization of 2-phenoxycarbonyl norbornene using WCl_6 / $SnMe_4$

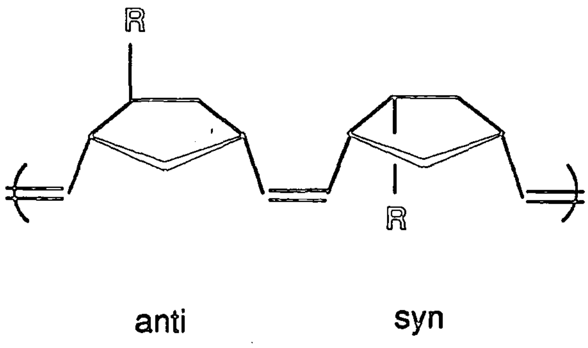
The polymerization of 2-phenoxycarbonyl norbornene with the classical catalyst system WCl_6 / $SnMe_4$ yielded 90% poly(2-phenoxycarbonyl norbornene). The reaction was carried out under nitrogen to protect the catalyst from decomposition caused by air exposure. The polymer was purified by precipitation from toluene into methanol.

The ^{1}H-NMR spectrum (Fig.3.2.1.a) showed very broad peaks due to overlapping of the signals and as a result a detailed interpretation was not possible. The broad peaks from 6.9 to 7.4 ppm correspond to the aromatic hydrogens, the broad peak from 5 to 6 ppm corresponds to the vinylic protons, while the peaks from 1.2 to 3.6 are the shifts of protons at carbons 1,2,3,4 and 7. The integration of the aromatic and vinylic proton signals is in agreement with expectation, but the aliphatic region indicates the presence of some impurity (probably solvent).

The ^{13}C-NMR spectrum (Fig.3.2.1.b) was recorded at 100.577 MHz and the total acquisition time was 7.1 hrs. The solvent used was $CDCl_3$ because the peak due to the solvent (triplet at 77 ppm) does not overlap any of the peaks of the polymer.

The signal for the carbonyl carbons appeared at 173.0 and 174.4 ppm respectively for the syn repeat unit (arising from the endo monomer) and the anti repeat unit (arising from the exo monomer) see Fig.3.2.1.c.

Fig3.2.1.c



Integration of these two peaks gives syn : anti ratio in the polymer chain of 2:1; since the endo:exo ratio in the monomer was 4:1 and since the yield of polymer was high (90% recovered) it is possible to say that this initiator polymerizes the exo isomer more readily than the endo isomer.

Two peaks for the quarternary aromatic carbon appeared at 150.8 ppm and 150.7 ppm and although in a qualitative similar intensity ratio were not well enough resolved for integration.

The signals for the vinylic carbons C_5 and C_6 appeared from 134.8 ppm to 129.6 ppm as a series of broad partially resolved bands and they have not been assigned in detail. There are six broad peaks observed due to *cis* and *trans* double bonds, tacticity effects and head-tail interactions, giving evidence for a cis-trans atactic polymer. One of these peaks, at 129.6 is overlapped by the peak associated with the meta carbons at 129.4. The signal for the para carbon appeared at 125.7ppm, while the signals for the ortho carbons appeared at 121.7 and 121.6 ppm, again in a similar intensity to the carbonyl and quaternary carbons but not well enough resolved for integration.

At high field the methylene and methine carbon signals were distinguished with the aid of a DEPT spectrum. The signal associated with C_2 was identified at 48.0 ppm (lowest field).The signals due to C_1 at 37.7 ppm and C_4 at 40.5 ppm are assigned on the basis of the expected upfield signal for C_1. The signals for the methylene carbons C_3 at 36 ppm and C_7 at 41.1 ppm are assigned by analogy

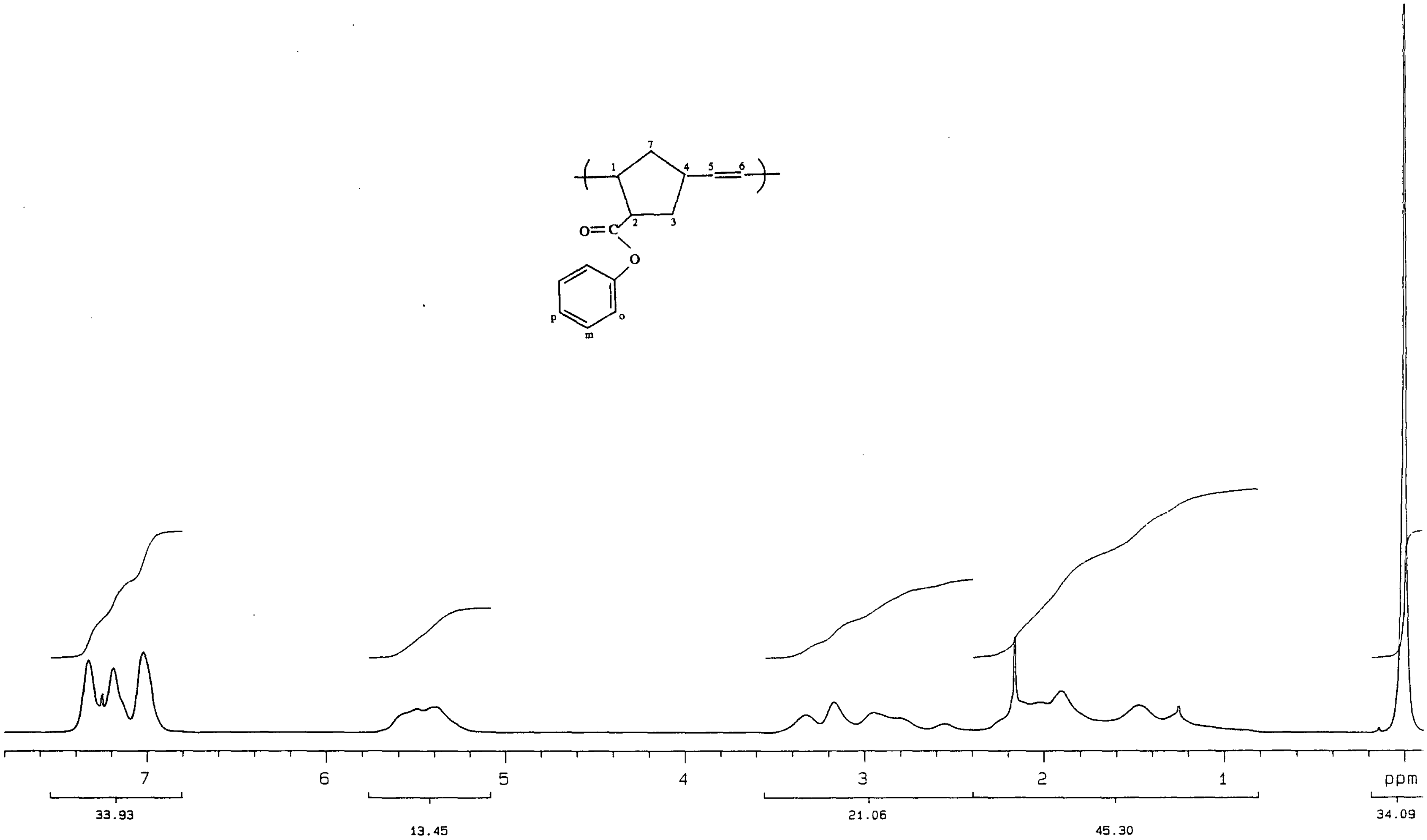
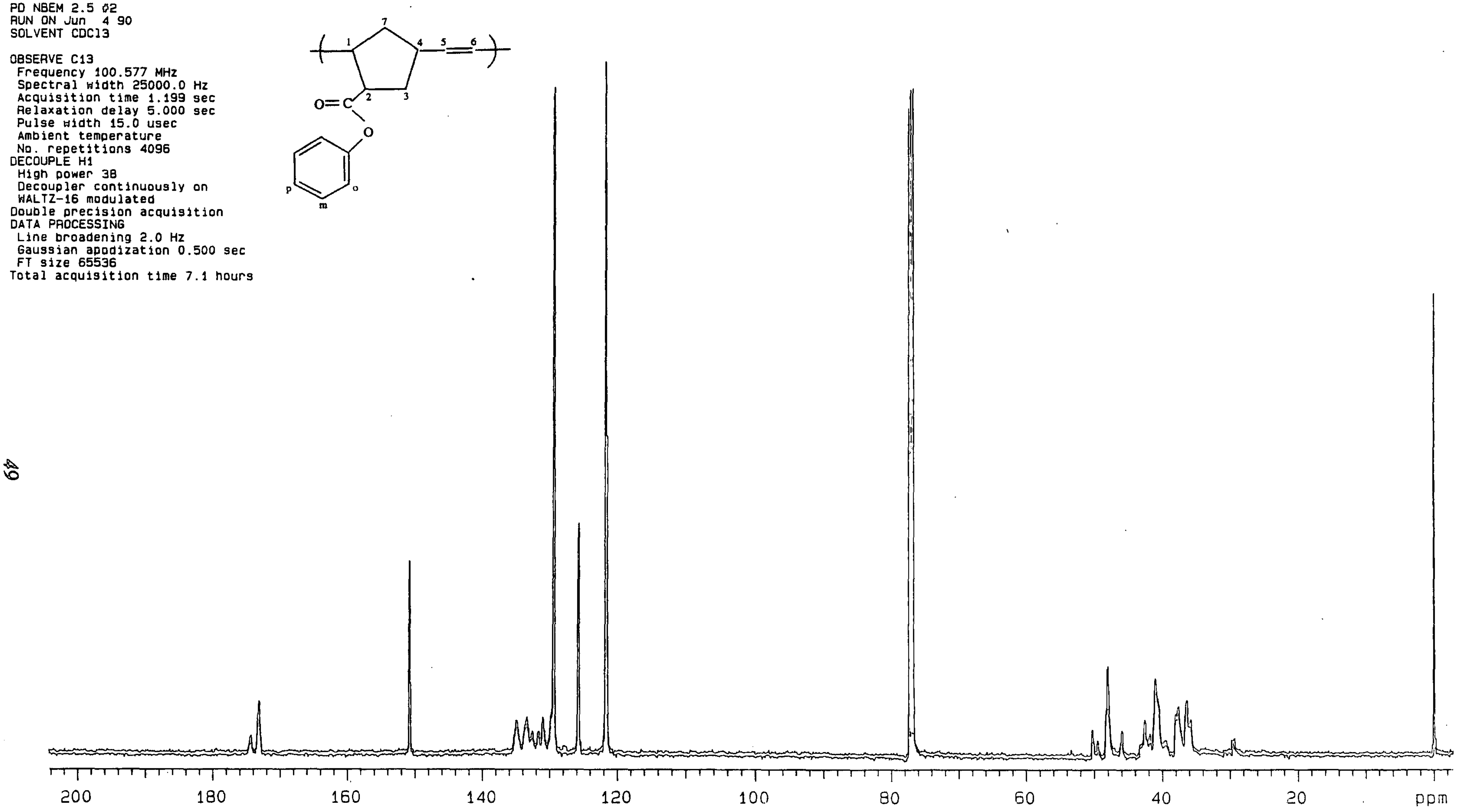


Fig.3.2.1.a ^{1}H-NMR spectrum of poly(2-phenoxycarbonyl norbornene) prepared *via* $WCl_6/SnMe_4$ catalysis



```
PD NBEM 2.5 02
RUN ON Jun  4 90
SOLVENT CDC13

OBSERVE C13
 Frequency 100.577 MHz
 Spectral width 25000.0 Hz
 Acquisition time 1.199 sec
 Relaxation delay 5.000 sec
 Pulse width 15.0 usec
 Ambient temperature
 No. repetitions 4096
DECOUPLE H1
 High power 38
 Decoupler continuously on
 WALTZ-16 modulated
Double precision acquisition
DATA PROCESSING
 Line broadening 2.0 Hz
 Gaussian apodization 0.500 sec
 FT size 65536
Total acquisition time 7.1 hours
```

Fig.3.2.1.b ^{13}C-NMR spectrum of poly(2-phenoxycarbonyl norbornene) prepared *via* $WCl_6/SnMe_4$ catalysis

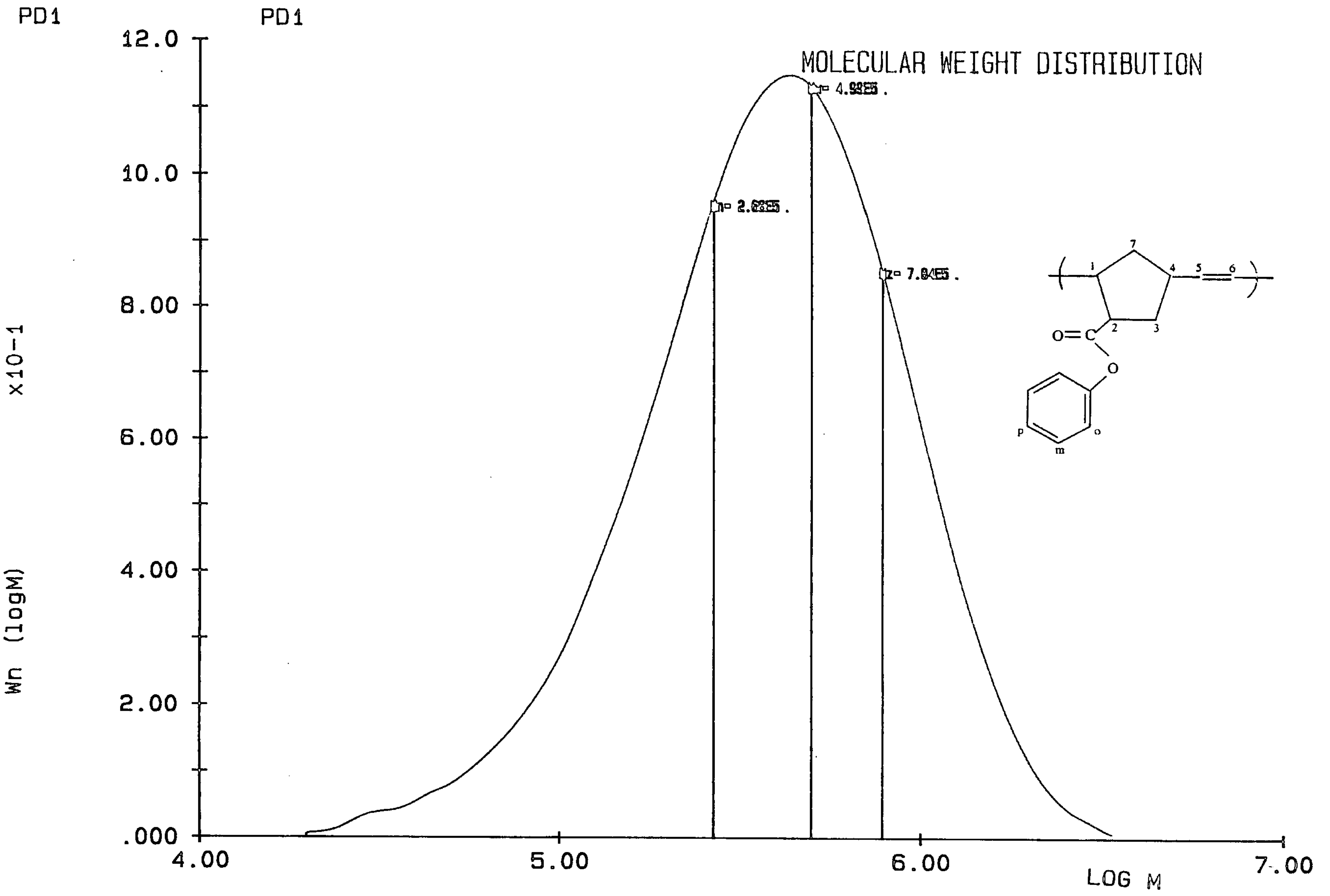


Fig.3.2.1.d Molecular weight distribution curve of poly(2-phenoxycarbonyl norbornene) prepared *via* WCl$_6$/SnMe$_4$ catalysis

```
==============================================================================
PD1      ENDED:  04/25/90  16:16:      PD1
==============================================================================
PARAMETERS                                  MOLECULAR WEIGHT VALUES
CONCENTRATION (mg/ml)              1.662     Mn (avg) =            2.677E   5
INJECTION VOLUME (ml)               .100     Mw (avg) =            4.992E   5
DPT SENSITIVITY (mv/Pa)            1.000     Mz (avg) =            7.836E   5
INLET PRESSURE (KPa)              22.406     Mp       =            4.363E   5
FLOW RATE (ml/min)                 1.000     Mv (avg) =            4.588E   5
VISCOMETER OFFSET (ml)             -.130
ACQ. START TIME (min)             10.000     POLYDISPERSITY RATIOS
ACQ. STOP TIME (min)              20.000     Mw/Mn =                1.865
DATA INTERVAL (sec)                1.200     Mz/Mn =                2.927
SIGMA (ml)                          .178
TAU (V)                             .143     SKEWNESS OF DISTRIBUTION
TAU (C)                             .076     SKEW(n) =              2.318
THRESHOLD                           .020     SKEW(w) =              1.736

METHOD:   UCAL-NARROW      INTEGRATED DETECTOR SIGNALS    BASELINE   X      Y
CAL FILE  PS(3490)         CONC (mv-ml) =        29.61    L. VISC   83     2.63
                           VISC (mv-ml) =        33.52    R. VISC  291     -.74
MARK-HOUWINK CONSTANTS
ALPHA      .652            IV  (dl/gm)            .361    L. CONC   92    39.86
LOG K    -4.137            VISCOTEK MODEL£     200        R. CONC  299    48.30
```

Tab.3.2.1 **GPC results of poly(2-phenoxycarbonyl norbornene) prepared *via* WCl$_6$/SnMe$_4$ catalysis**

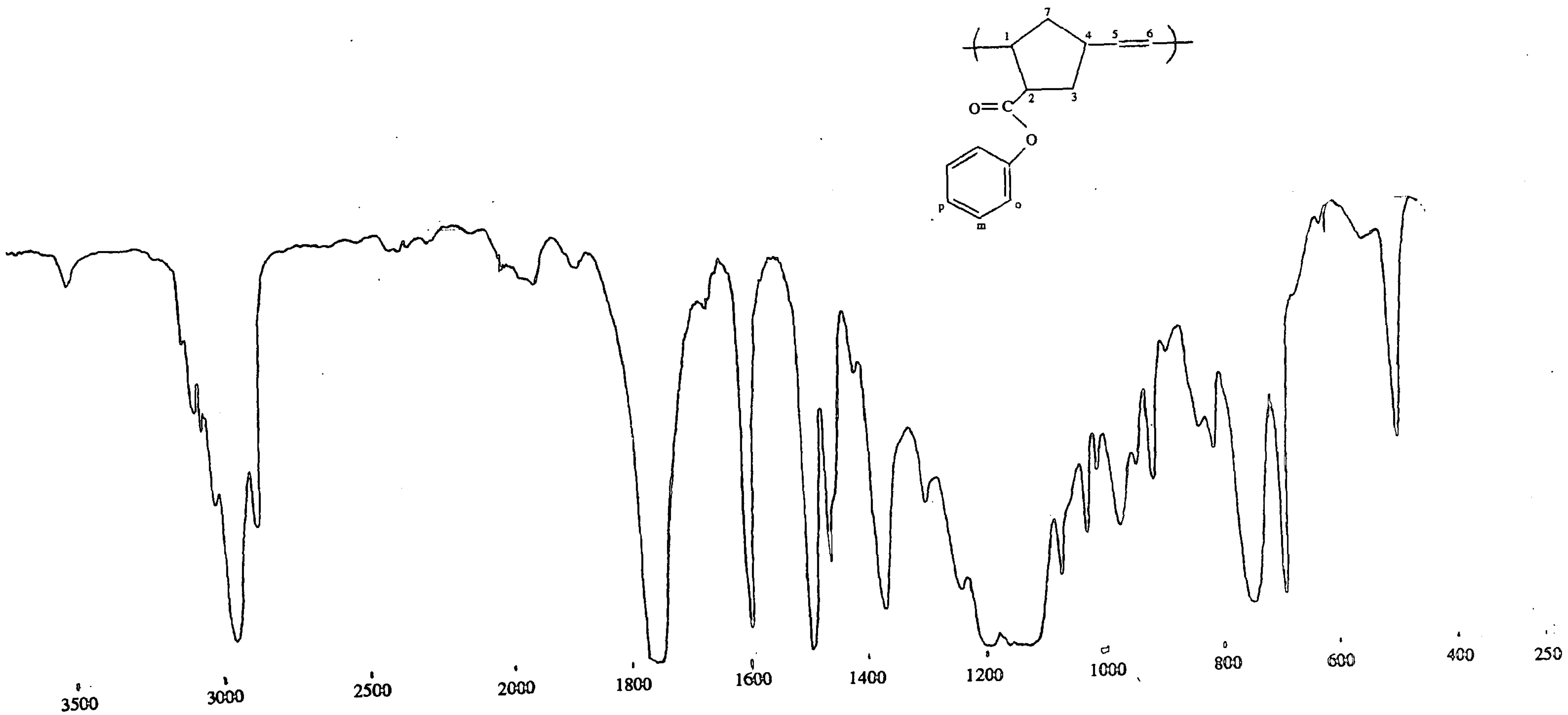


Fig.3.2.1.e Infrared spectrum of poly(2-phenoxycarbonyl norbornene) prepared *via* $WCl_6/SnMe_4$ catalysis

with the spectra of polynorbornene and the expected substituent shift effect. The complexity of the spectra are consistent with an c/t atactic polymer.

Gel permeation chromatography showed the number-average molecular weight (M_n) to be 268,000 and the weight-average molecular weight (M_w) to be 499,000. The polydispersity M_w / M_n of the polymer is 1.86. The molecular weight of the repeating unit in the polymer is 214, so the number average DP (degree of polymerization) is $M_n / 214$, ca.1250. The results from GPC are shown in Table 3.2.1. The molecular weight distribution curve is shown in Fig.3.2.1.d.

The infrared spectrum of the polymer (Fig 3.2.1.e) showed all the characteristic bands, the aromatic C-H (>3000 cm^{-1}), the vinyl C-H (2940 cm^{-1}), the saturated C-H (2870 cm^{-1}), the CH=CH stretch (1660 cm^{-1}), the >C=O stretch (1760 cm^{-1}) and the aromatic ring vibration (1600 and 1500 cm^{-1}), and is consistent with the assigned structure.

EXPERIMENTAL:

Reagents: Chlorobenzene as purchased from Aldrich, was refluxed over P_2O_5 under a dry nitrogen atmosphere and distilled when required. Tetramethyltin and WCl_6 were purchased from Aldrich and used as supplied.

Polymerization procedure: A dry nitrogen / vacuum line was used in order to carry out all manipulations of catalysts under a dry nitrogen atmosphere. The front manifold was connected to the vacuum pump and the back manifold to a dry nitrogen supply. The nitrogen was passed through a concentrated sulphuric acid bubbler into the line and out through a heavy white oil bubbler. Teflon taps and greaseless joints were used throughout, in order to avoid contamination of the reagents, the monomer and the polymer with grease. All glassware was dried in an oven before use, evacuated whilst still hot and let down to dry nitrogen.

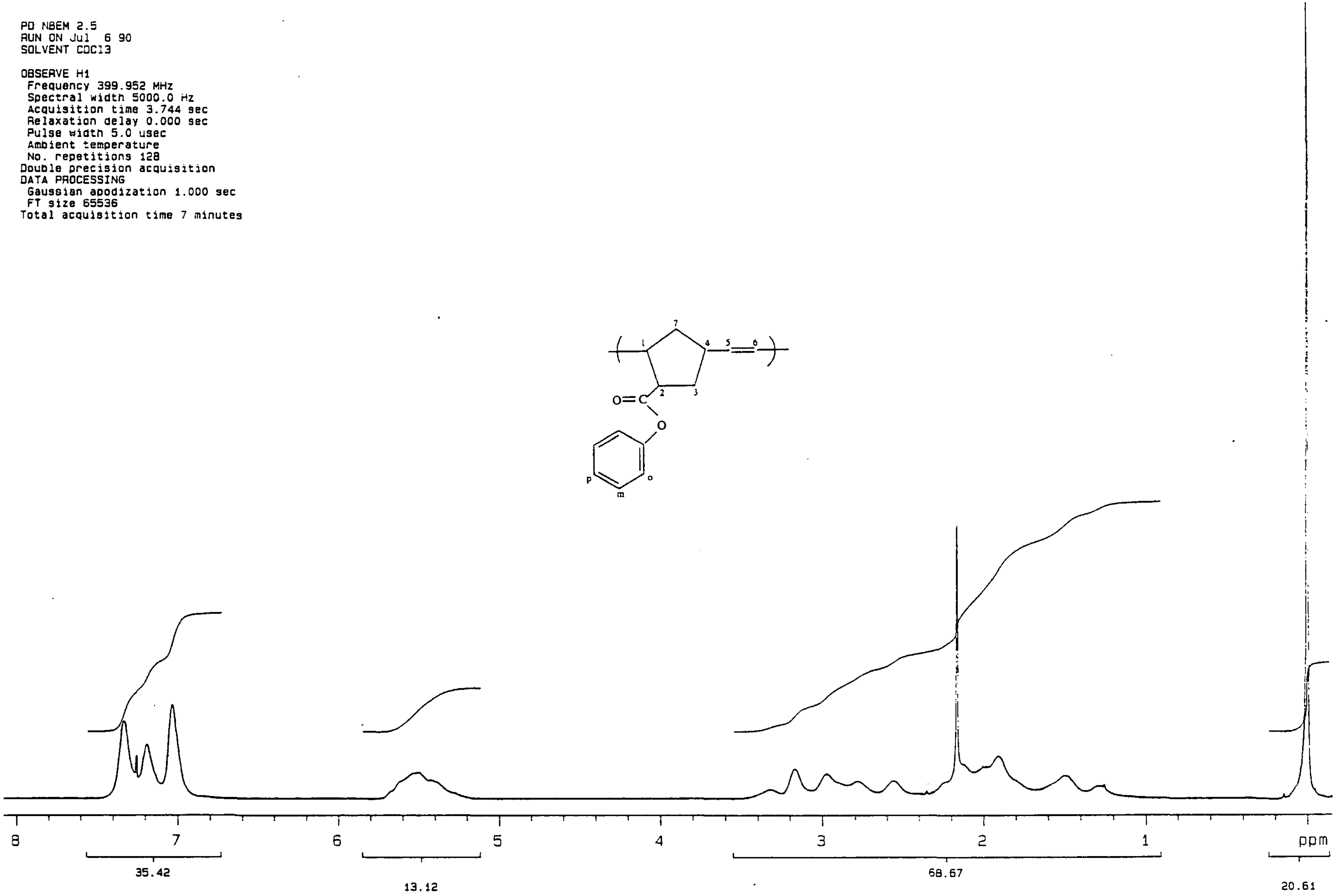
The ratio of monomer : catalyst : co-catalyst used was 100:1:2. The monomer and the solvent were degassed from O_2 by purging with nitrogen. The monomer was then placed in a Glove Box, passed through alumina, weighed (0.0050 mol, 1.0776 g) and transferred into the reaction ampoule.

A dry teflon coated magnetic follower placed into the reaction ampoule which then sealed with septum seals, removed from the Glove Box and connected to the line. Chlorobenzene (1 ml) was added with an airtight syringe. An empty ampoule was connected to the vacuum line, evacuated and let down to nitrogen. The tap could then be removed and replaced by a septum seal. A magnetic follower was inserted and the ampoule sealed. The catalyst WCl_6 was in a stock solution 0.066 g / ml in chlorobenzene in an ampoule under nitrogen. The co-catalyst $SnMe_4$ was also in a stock solution 0.01 g / ml in chlorobenzene in an ampoule under nitrogen. The two ampoules were connected to the line and the region from the socket to the teflon tap was evacuated and let down to nitrogen. The tap was removed and replaced by a septum seal. The catalyst (0.00005 mol, 0.0198 g) was transferred with an airtight syringe into the empty ampoule and then the co-catalyst (0.0001 mol, 0.0173 g). The mixture was stirred for 10 minutes until the appearance was reddish brown(activated catalyst) and then transferred by cannula into the reaction ampoule. The mixture was stirred and the colour was observed to change gradually to a greyish green after thirty minutes. After stirring overnight the septum seal was opened and 1 ml of acetone added. The mixture was then added to a large excess of non-solvent (methanol) causing the polymer to precipitate. The polymer was recovered, dried under vacuum and dissolved in 4 ml of toluene to give a viscous solution. The solution was added dropwise to stirred methanol, the polymer recovered and then dried. The reaction gave poly(2-phenoxycarbonyl norbornene) in 90 % yield (0.970 g).

3.2.2 Polymerization of 2-phenoxycarbonyl norborne using $MoCl_5$ / $SnMe_4$

The classical catalyst system $MoCl_5$ / $SnMe_4$ also polymerized 2-phenoxycarbonyl norbornene, but in a very poor yield 12.2 %.

Because the catalyst is very sensitive to air the polymerization reaction was carried out in a dry nitrogen atmosphere Glove Box. The polymer was purified by reprecipitating several times in methanol, but otherwise the procedures were similar to those described above.



```
PD NBEM 2.5
RUN ON Jul  6 90
SOLVENT CDCl3

OBSERVE H1
 Frequency 399.952 MHz
 Spectral width 5000.0 Hz
 Acquisition time 3.744 sec
 Relaxation delay 0.000 sec
 Pulse width 5.0 usec
 Ambient temperature
 No. repetitions 128
Double precision acquisition
DATA PROCESSING
 Gaussian apodization 1.000 sec
 FT size 65536
Total acquisition time 7 minutes
```

Fig.3.2.2.a ^{1}H-NMR spectrum of poly(2-phenoxycarbonyl norbornene) prepared *via* MoCl$_5$/SnMe$_4$ catalysis

```
SOLVENT CDCl3

OBSERVE C13
 Frequency 100.577 MHz
 Spectral width 25000.0 Hz
 Acquisition time 1.199 sec
 Relaxation delay 3.000 sec
 Pulse width 8.4 usec
 Ambient temperature
 No. repetitions 10000
DECOUPLE H1
 High power 40
 Decoupler continuously on
 WALTZ-16 modulated
Double precision acquisition
DATA PROCESSING
 Line broadening 0.5 Hz
 Gaussian apodization 0.600 sec
 FT size 65536
Total acquisition time 11.7 hours
```

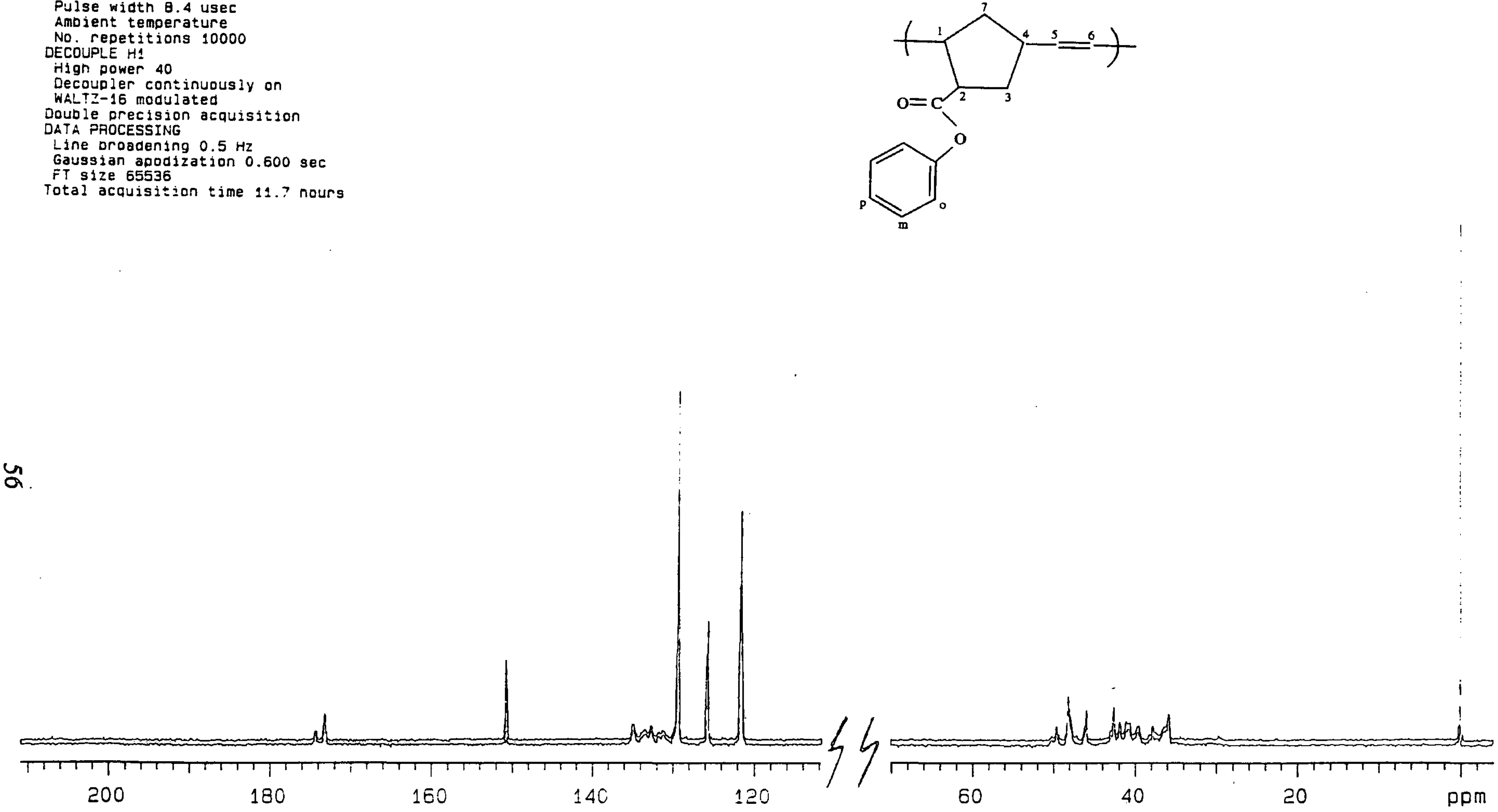


Fig.3.2.2.b ^{13}C-NMR spectrum of poly(2-phenoxycarbonyl norbornene) prepared *via* MoCl$_5$/SnMe$_4$ catalysis

The ^{1}H-NMR spectrum (Fig.3.2.2.a) showed only broad peaks which could not be assigned in detail. The signals for the aromatic protons appeared from 6.9 to 7.4 ppm and the signals for the vinylic protons from 5.2 to 5.8 ppm. The integration of these two groups of peaks was 5:2. The signals for carbons 1,2,3,4 and 7 appeared from 1.2 to 3.4 ppm; as previously there was indication of slight solvent contamination.

The ^{13}C-NMR (Fig 3.2.2.b) was also complicated in this case and the peaks were broad due to the effect of the microstructure on the chemical shift. The spectrum was recorded at 100.577 MHz and the total acquisition time was 11.7 hrs. The signal for the carbonyl carbon on the anti conformation appeared at 174.2 ppm and the signal for the syn conformation at 173.1 ppm. In view of the low yield the integration of these two peaks (1:2.7) can not be used as a basis of deducing relative monomer reactivity. The peaks for the vinylic carbons from 129.5 to 135 ppm, were broad and not very well resolved due to the low signal / noise ratio. Furthermore, as in the previous case there is one peak overlapped by the peak associated with the meta carbon at 129.3 ppm. The peak for the para carbon appeared at 121.6, for the ortho at 121.7 and for the quaternary at 150.8 ppm. At high field the signals for the methylene and methine carbons were distinguished with the aid of the DEPT spectrum and assigned by analogy with the spectrum of the polymer obtained from the WCl_6 / $SnMe_4$ catalyst system. Although the spectrum was relatively poor in terms of S/N it can be concluted that the microstructure is similar to the earlier sample and has a distribution of atactic *cis* / *trans* vinylene repeat units.

The gel permeation chromatography showed the number-average molecular weight (Mn) to be 76,000, while the weight-average molecular weight (Mw) was 145,000. The number average DP was Mn/214, ca. 350. The polydispersity Mw / Mn was 1.84. The parameters and the results of the gel permeation chromatography are displayed on Tab.3.2.2. The molecular weight distribution curve is shown on Fig.3.2.2.c.

The infrared spectrum (Fig.3.2.2.d) showed all the characteristic bands of the polymer, as previously discussed.

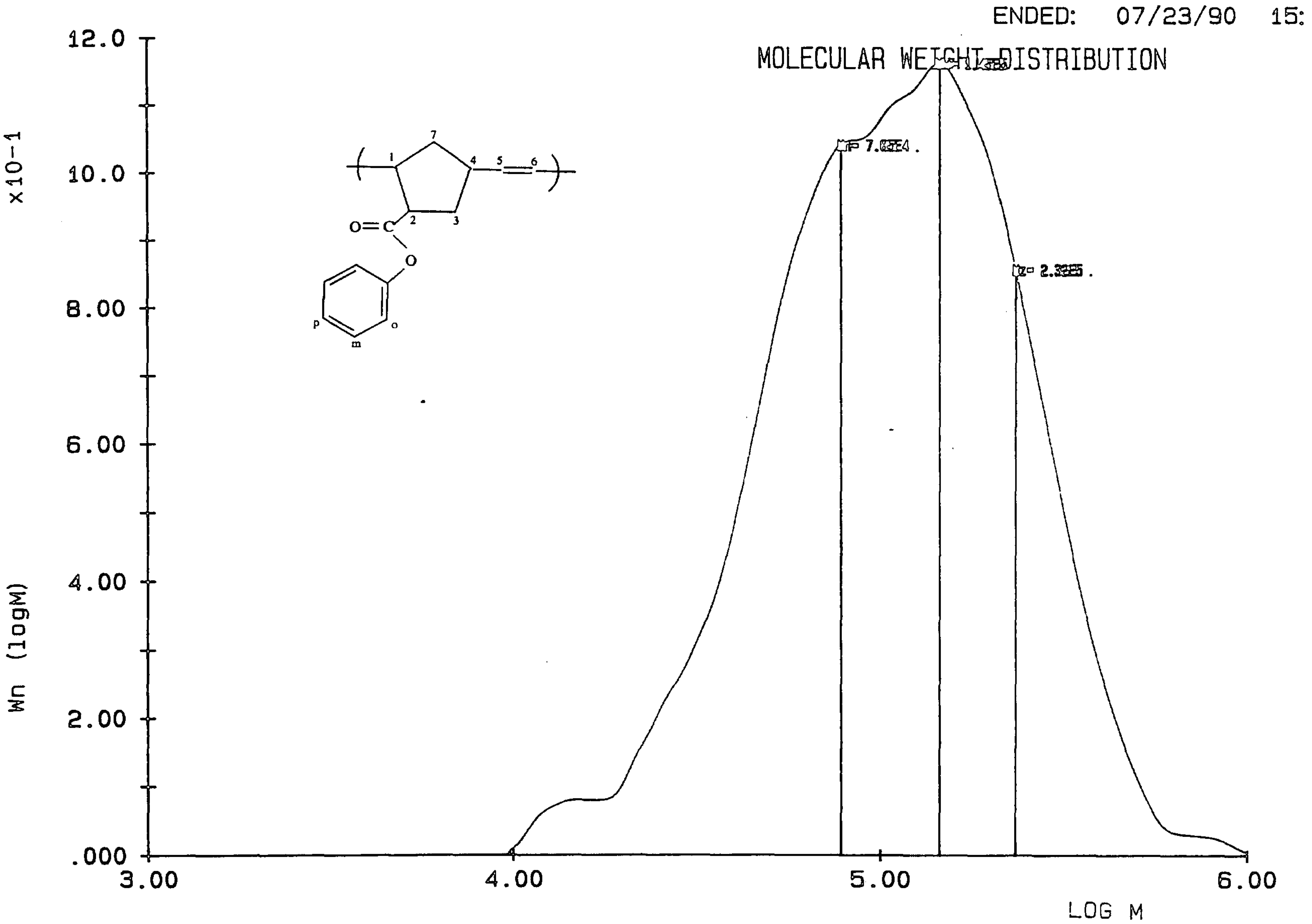


Fig.3.2.2.c Molecular weight distribution curve of poly(2-phenoxycarbonyl norbornene) prepared *via* $MoCl_5/SnMe_4$ catalysis

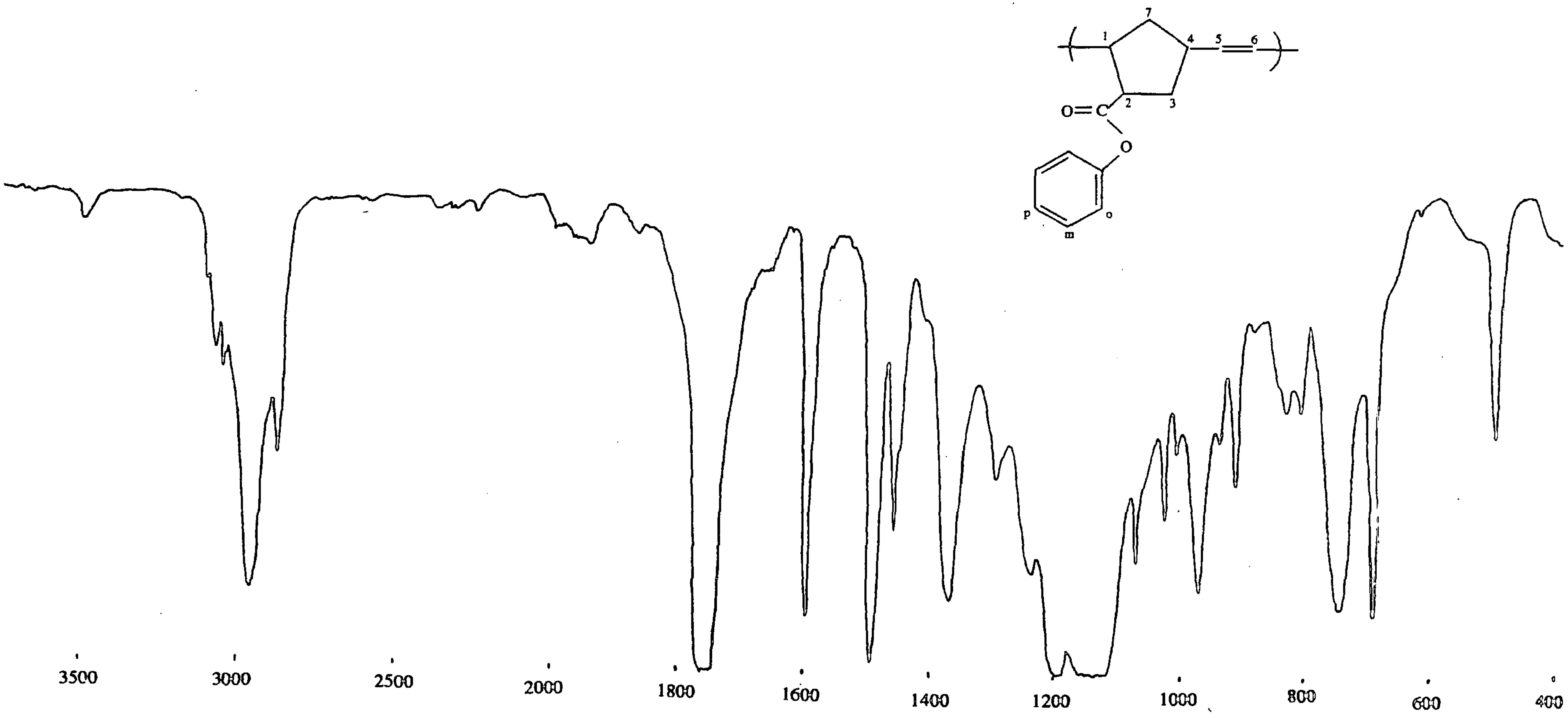


Fig.3.2.2.d Infrared spectrum of poly(2-phenoxycarbonyl norbornene) prepared *via* $MoCl_5/SnMe_4$ catalysis

```
================================================================================
PD2B     ENDED:  07/23/90   15:18:      PD2B
================================================================================
PARAMETERS                                  MOLECULAR WEIGHT VALUES
CONCENTRATION (mg/ml)           2.120       Mn (avg) =          7.850E   4
INJECTION VOLUME (ml)            .100       Mw (avg) =          1.445E   5
DPT SENSITIVITY (mv/Pa)          .250       Mz (avg) =          2.324E   5
INLET PRESSURE (KPa)           20.819       Mp       =          1.529E   5
FLOW RATE (ml/min)              1.000       Mv (avg) =          1.319E   5
VISCOMETER OFFSET (ml)          -.110
ACQ. START TIME (min)          10.000       POLYDISPERSITY RATIOS
ACQ. STOP TIME (min)           20.000       Mw/Mn =                  1.841
DATA INTERVAL (sec)             1.200       Mz/Mn =                  2.961
SIGMA (ml)                       .154
TAU (V)                          .100       SKEWNESS OF DISTRIBUTION
TAU (C)                          .044       SKEW(n) =                2.499
THRESHOLD                        .020       SKEW(w) =                2.165

METHOD:    UCAL-BROAD    INTEGRATED DETECTOR SIGNALS   BASELINE   X       Y
CAL FILE   PC180790      CONC (mv-ml) =     12.41      L. VISC  122    10.45
                         VISC (mv-ml) =      8.10      R. VISC  318     9.93
MARK-HOUWINK CONSTANTS
ALPHA      .648          IV  (dl/gm)          .294     L. CONC  127   -13.48
LOG K    -3.860          VISCOTEK MODEL    200         R. CONC  338   -19.57
```

Tab.3.2.2 GPC results of poly(2-phenoxycarbonyl norbornene) prepared *via* $MoCl_5/SnMe_4$ catalysis

EXPERIMENTAL:

Reagents: Chlorobenzene was dried and degassed from O_2 as described in 3.2.1. The catalyst $MoCl_5$ and the co-catalyst $SnMe_4$ were purchased from Aldrich and used as supplied.

Polymerization procedure: The polymerization of 2-phenoxycarbonyl norbornene with the catalyst system $MoCl_5$ / $SnMe_4$ was carried out in a glove box. All glassware was dried in an oven before use, evacuated whilst still hot and placed in the Glove Box. The monomer was evacuated, degassed and also placed in the Glove Box; then passed through alumina, weighed and placed into the reaction ampoule. A teflon magnetic follower was inserted and then chlorobenzene (1ml) added.

The catalyst $MoCl_5$ was in a stock solution 0.01 g/ml in chlorobenzene and the co-catalyst $SnMe_4$ was in a stock solution 0.01 g/ml in chlorobenzene. The ratio monomer : catalyst : co-catalyst was 100 : 0.22 : 2.

The catalyst (0.000011 mol, 0.063 g) was mixed with the co-catalyst (0.0001 mol, 0.0173 g), the mixture was stirred for 15 min and then transferred into the reaction ampoule. The mixture was then stirred for 4 hrs. An additional amount of catalyst (0.00005 mol, 0.012 g) was added and the mixture left to react overnight. The reaction ampoule was opened and a few drops of acetone were added into the mixture. The polymer was precipitated in a large excess of methanol, recovered and dried under vacuum. The procedure was repeated until white polymer was obtained (0.13 g , 12.2 % yield)

The polymerization was repeated with ratio monomer : catalyst : co-catalyst 100 : 1 : 2 with no further addition of catalyst but the yield decreased (5.1 %).

3.2.3 Polymerization of 2-phenoxycarbonyl norbornene using a well-defined catalyst.

The well-defined Schrock initiator $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ was used for the polymerization of 2-phenoxycarbonyl norbornene in order to try to obtain a polymer of more regular

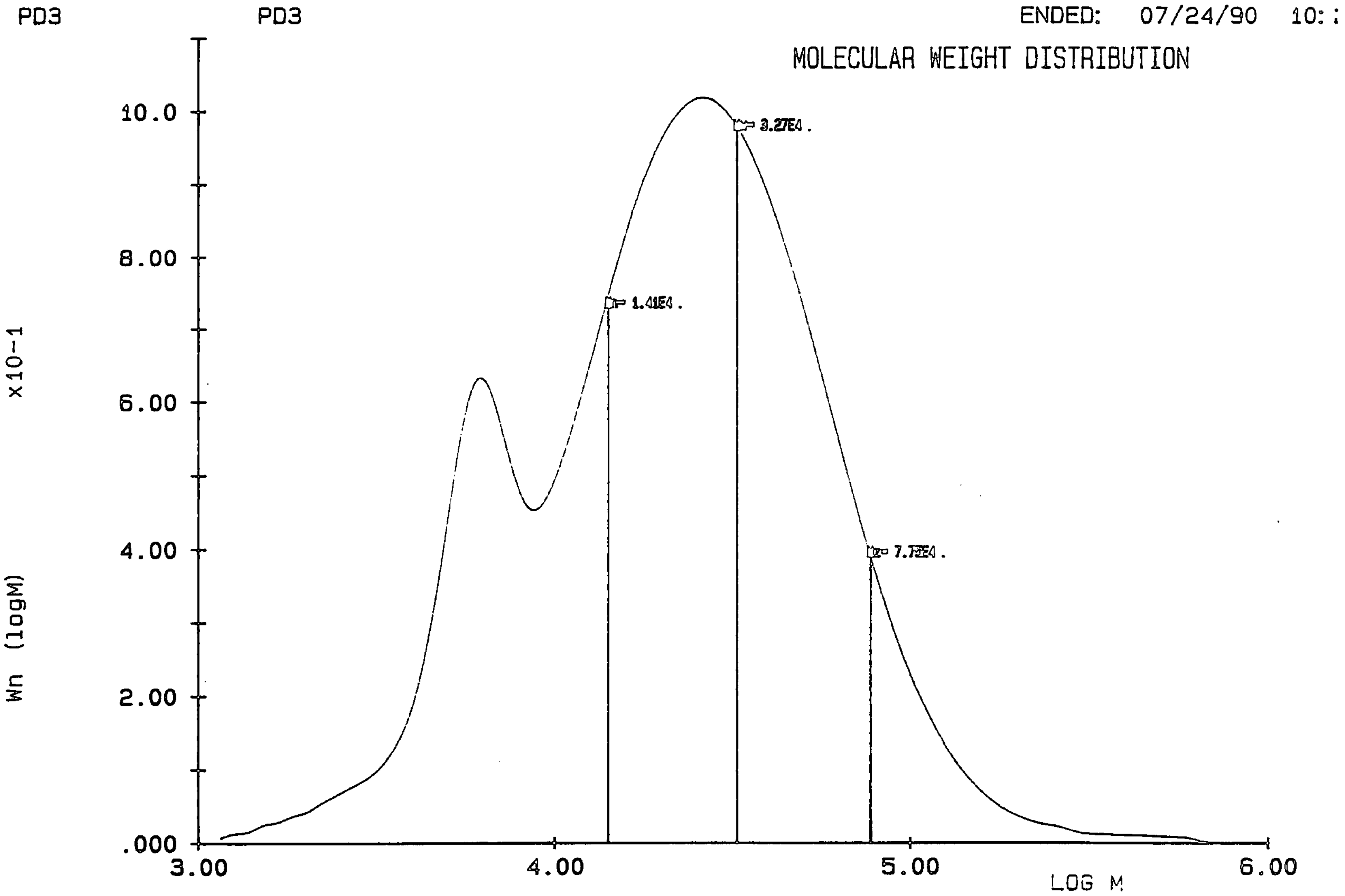
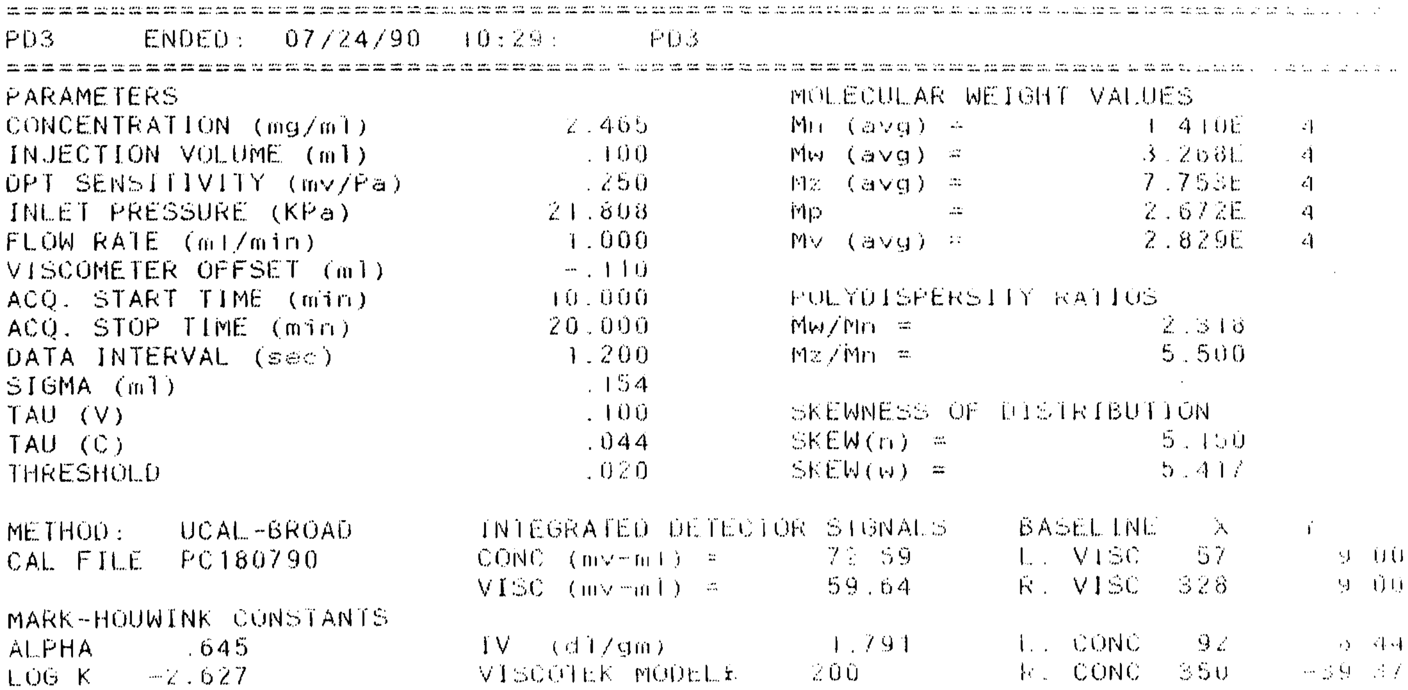
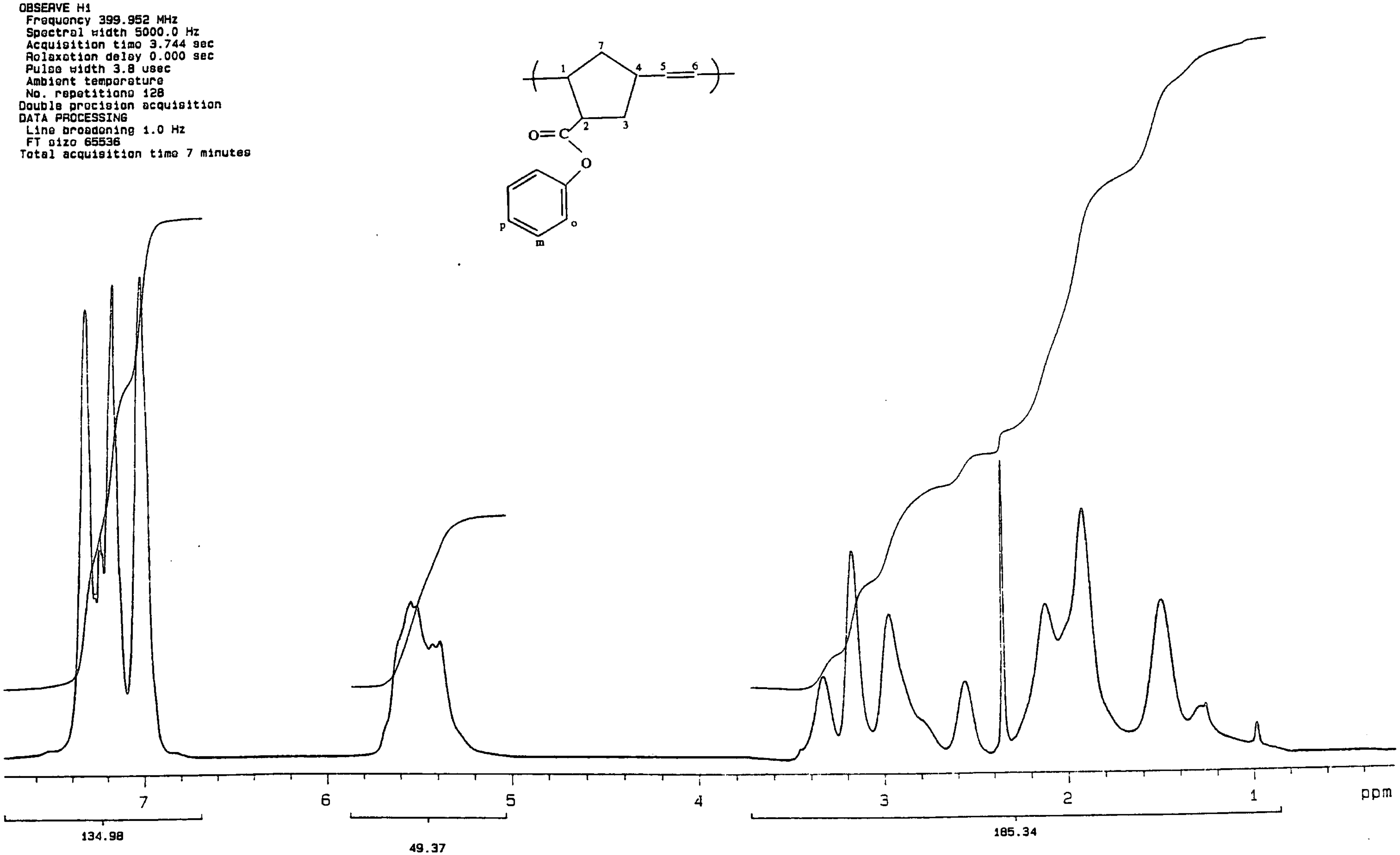


Fig.3.2.3.a Molecular weight distribution curve of poly(2-phenoxycarbonyl norbornene) prepared *via* Mo(CH-t-Bu)(NAr)(O-t-Bu)$_2$ catalysis



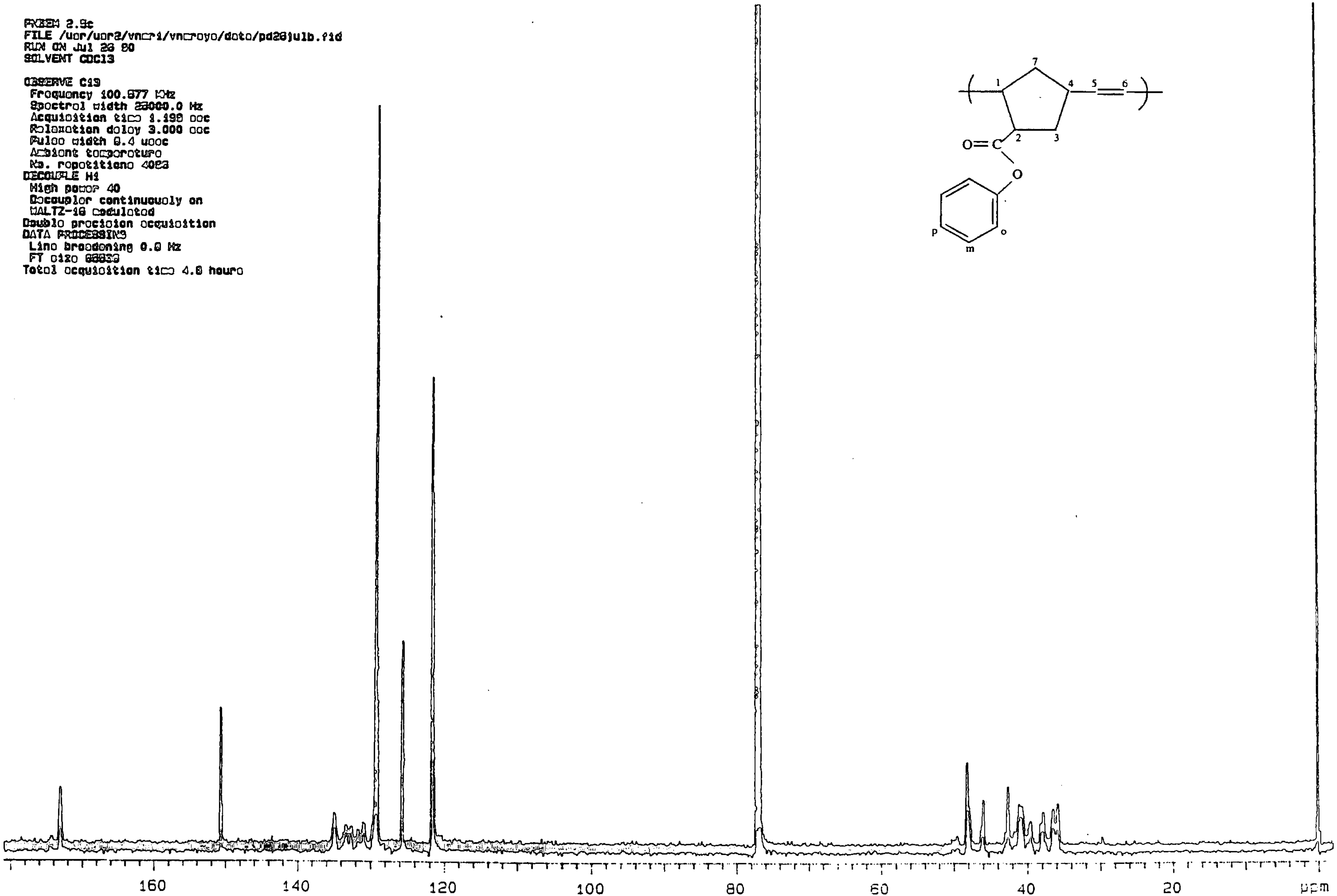
```
============================================================================
PD3      ENDED:  07/24/90  10:29:      PD3
============================================================================
PARAMETERS                                  MOLECULAR WEIGHT VALUES
CONCENTRATION (mg/ml)          2.465        Mn (avg) =         1.410E   4
INJECTION VOLUME (ml)           .100        Mw (avg) =         3.268E   4
OPT SENSITIVITY (mv/Pa)         .250        Mz (avg) =         7.753E   4
INLET PRESSURE (KPa)          21.808        Mp       =         2.672E   4
FLOW RATE (ml/min)             1.000        Mv (avg) =         2.829E   4
VISCOMETER OFFSET (ml)         -.110
ACQ. START TIME (min)         10.000        POLYDISPERSITY RATIOS
ACQ. STOP TIME (min)          20.000        Mw/Mn =              2.318
DATA INTERVAL (sec)            1.200        Mz/Mn =              5.500
SIGMA (ml)                      .154
TAU (V)                         .100        SKEWNESS OF DISTRIBUTION
TAU (C)                         .044        SKEW(n) =            5.150
THRESHOLD                       .020        SKEW(w) =            5.417

METHOD:   UCAL-BROAD      INTEGRATED DETECTOR SIGNALS    BASELINE   X      Y
CAL FILE  PC180790        CONC (mv-ml) =      72.59      L. VISC   57     9.00
                          VISC (mv-ml) =      59.64      R. VISC  328     9.00
MARK-HOUWINK CONSTANTS
ALPHA     .645            IV  (dl/gm)          1.791     L. CONC   92     6.44
LOG K   -2.627            VISCOTEK MODEL#    200         R. CONC  350   -39.47
```

Tab.3.2.3 GPC results of poly(2-phenoxycarbonyl norbornene) prepared *via* Mo(CH-t-Bu)(NAr)(O-t-Bu)$_2$ catalysis



```
OBSERVE H1
 Frequency 399.952 MHz
 Spectral width 5000.0 Hz
 Acquisition time 3.744 sec
 Relaxation delay 0.000 sec
 Pulse width 3.8 usec
 Ambient temperature
 No. repetitions 128
Double precision acquisition
DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
Total acquisition time 7 minutes
```

Fig.3.2.3.b ^{1}H-NMR spectrum of poly(2-phenoxycarbonyl norbornene) prepared *via* Mo(CH-t-Bu)(NAr)(O-t-Bu)$_2$ catalysis



```
PXEEM 2.9c
FILE /usr/usr2/vnmr1/vnmrsys/data/pd28julb.fid
RUN ON Jul 28 80
SOLVENT CDCl3

OBSERVE C13
 Frequency 100.877 MHz
 Spectral width 25000.0 Hz
 Acquisition time 1.199 sec
 Relaxation delay 3.000 sec
 Pulse width 8.4 usec
 Ambient temperature
 No. repetitions 4023
DECOUPLE H1
 High power 40
 Decoupler continuously on
 WALTZ-16 modulated
Double precision acquisition
DATA PROCESSING
 Line broadening 0.8 Hz
 FT size 65536
Total acquisition time 4.8 hours
```

<u>Fig.3.2.3.c</u> ^{13}C-NMR spectrum of poly(2-phenoxycarbonyl norbornene) prepared *via* Mo(CH-t-Bu)(NAr)(O-t-Bu)$_2$ catalysis

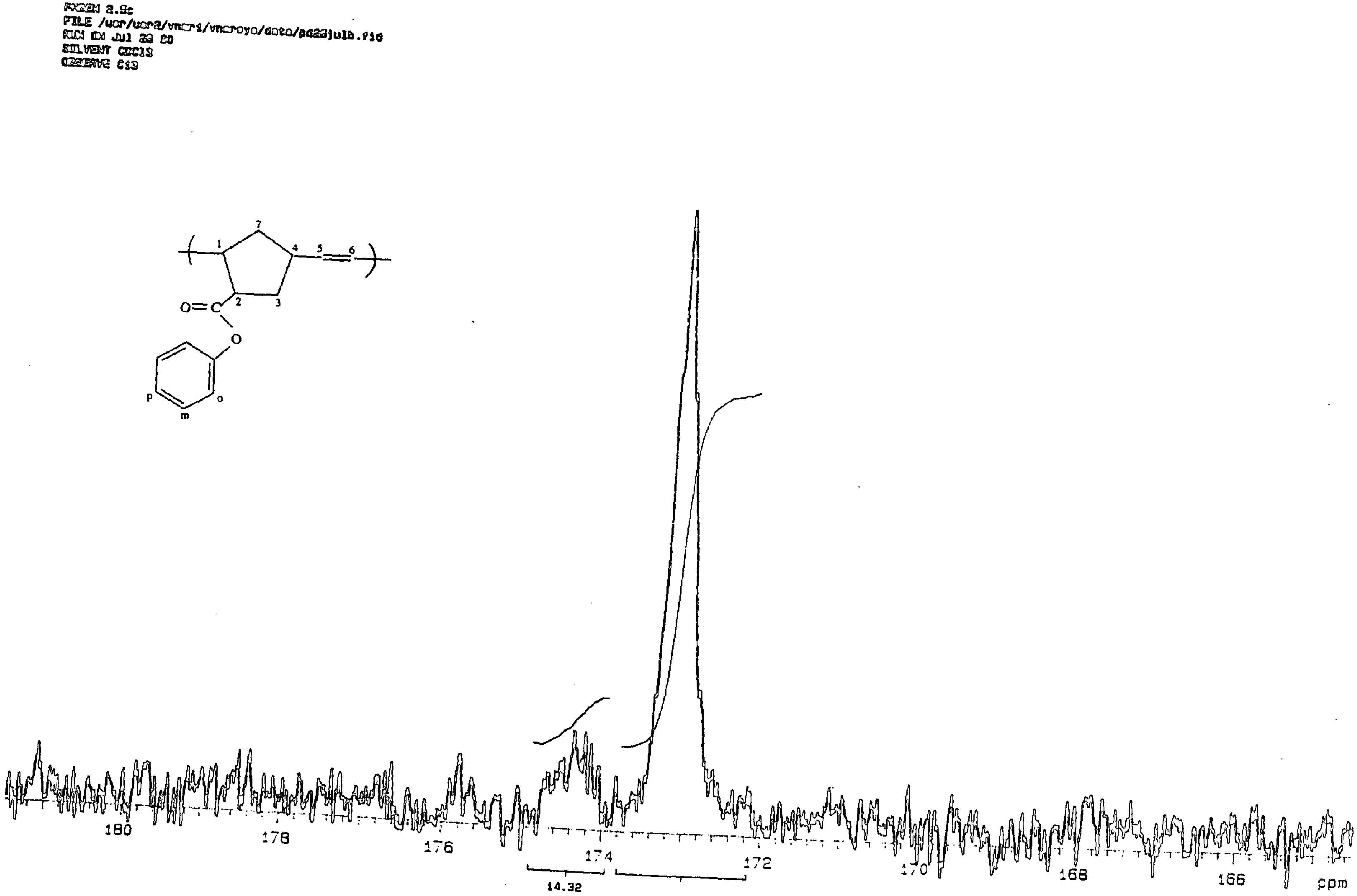
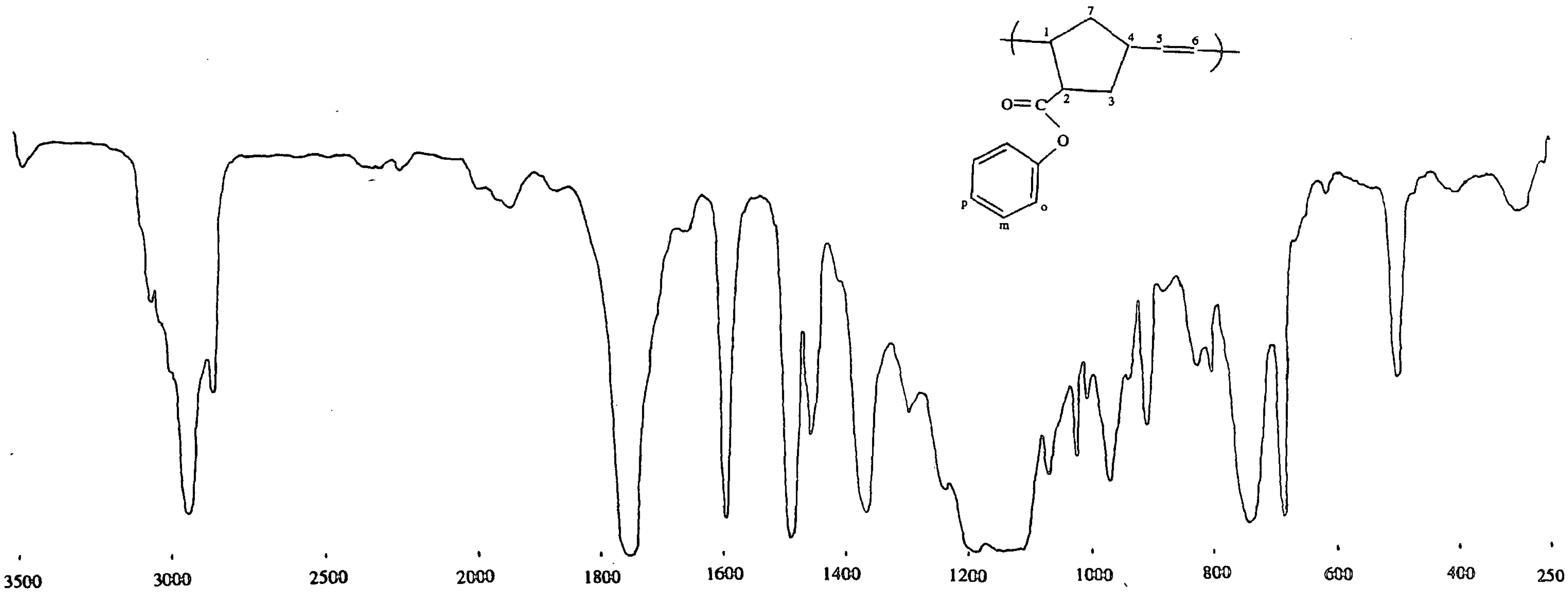


Fig.3.2.3.d Signals for the carbonyl carbon of poly(2-phenoxycarbonyl norbornene) prepared *via* Mo(CH-t-Bu)(NAr)(O-t-Bu)$_2$ catalysis



<u>Fig.3.2.3.e</u> Infrared spectrum of poly(2-phenoxycarbonyl norbornene) prepared *via* Mo(CH-t-Bu)(NAr)(O-t-Bu)$_2$ catalysis

structure with narrower molecular weight distribution than the polymers obtained by using the classical catalyst systems.

The molecular weight distribution curve (Fig.3.2.3.a) showed a bimodal distribution which leads to the conclusion that there were probably two (or more) propagation reactions in this polymerization. It is possible that this results from a reaction of the original initiating system during the process and the formation of other initiating and propagating species.

The number average molecular weight is 14,000, the weight-average molecular weight is 33,000 and the polydispersity Mw/Mn is 2.318. The number average DP is 66.

The results of the GPC are displayed on Tab.3.2.3.

The ^{1}H-NMR and ^{13}C-NMR spectra (Fig.3.2.3.b and 3.2.3.c) were similar to the spectra for the polymers which were obtained with the classical catalysts.

The peaks for the carbonyl carbons appeared at 174.1 ppm for the anti repeat unit and at 173 ppm for the syn. The integration of these two signals (Fig 3.2.3.d) is 1:7 which indicates a high selectivity of the catalyst to the endo monomer.

The infrared spectrum (Fig 3.2.3.e) was consistent with the assigned structure of the polymer, showing all the characteristic bands (see 3.2.1).

EXPERIMENTAL:

Reagents: The catalyst was prepared[67] in the transition metal chemistry research group of Dr.V.C.Gibson of the University of Durham and used as supplied.

Toluene as purchased from May & Baker Ltd,was washed with a mixture of conc.H_2SO_4 and HNO_3, refluxed over Na for 48 hrs and stored over molecular sieves in the glove box.

Benzophenone was purchased from Aldrich and used as supplied.

Polymerization procedure: The polymerization of 2-phenoxycarbonyl norbornene with the well defined catalyst Mo(CH_3-t-Bu)(NAr)(O-t-Bu) was carried out in a Glove Box. All glassware was dried in an oven, evacuated whilst still hot and transferred into the Glove Box. The ratio monomer : catalyst was 167 : 1. Toluene was passed through alumina. The catalyst was weighed (0.015g, 0.00003mol), dissolved in 4ml toluene and the solution poured into the reaction ampoule. The monomer was passed through alumina, weighed (1.07g , 0.005mol) and added dropwise into the reaction ampoule which was then sealed. The mixture was stirred overnight with a teflon magnetic follower. The reaction ampoule was opened and an excess (6.5 equivalents to the catalyst) of benzaldehyde (0.02 ml , 0.02 g) to terminate (quench) the polymerization. The polymer was precipitated in a large excess of methanol, recovered and dried under vacuum. The procedure was repeated until white polymer was obtained (0.36 g , 34 % yield).

CHAPTER 4: PHYSICAL PROPERTIES OF THE POLYMERS. CONCLUSIONS AND PROPOSALS FOR FURTHER WORK.

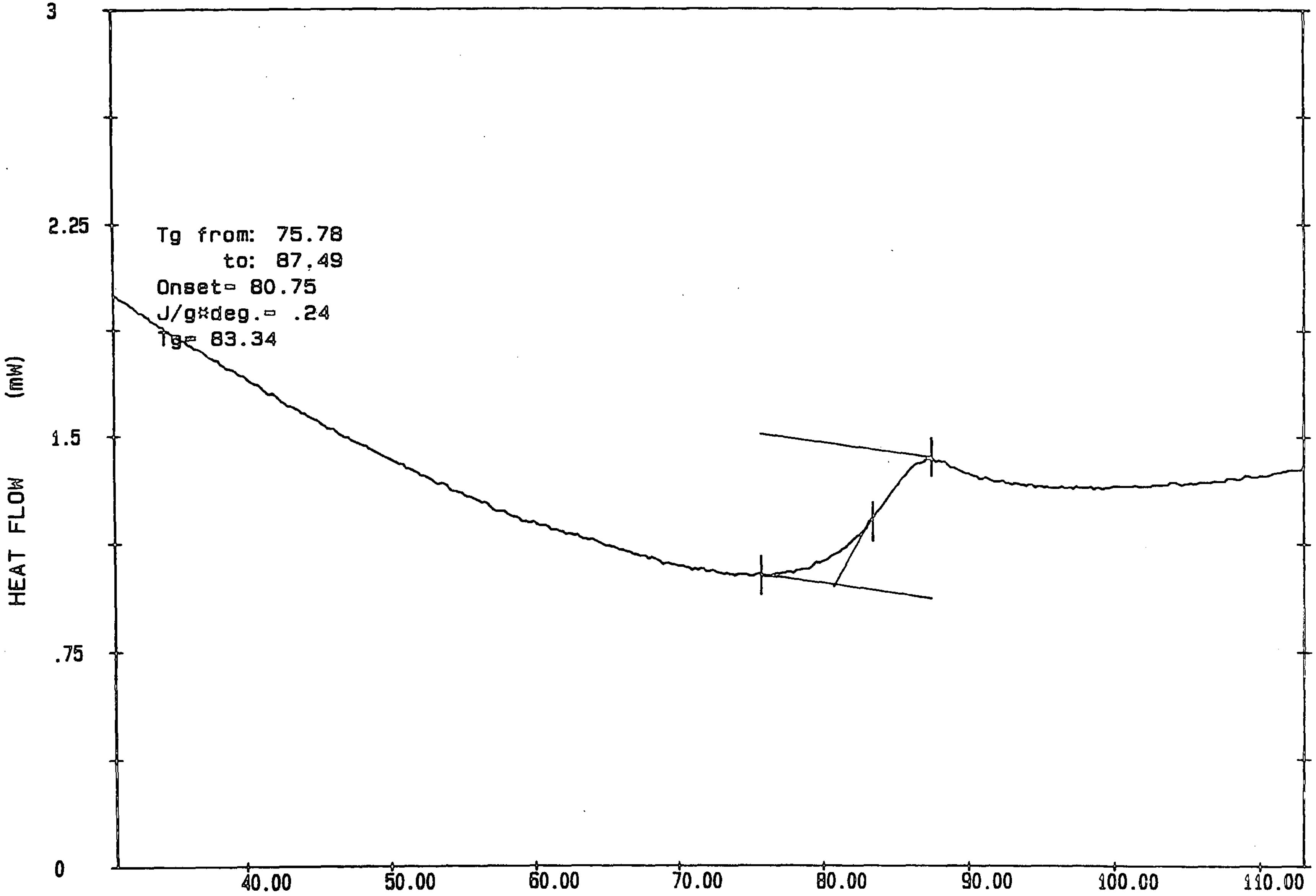
4.1 PHYSICAL PROPERTIES OF THE POLYMERS.

The thermal behaviour of the polymers, which is required to determine the limits of their working range, was investigated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

4.1.1 DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry is a technique used for investigating physical changes and chemical reactions which involve a flow of heat into or out of a sample.

In polymer science DSC is used in studies of melting processes and glass transition phenomena. For most polymers, there is a single temperature at which the onset of segmental motion occurs; it is termed the glass transition temperature, T_g. The polymer changes from a rigid, glassy solid to a rubber-like or plastic material as it passes through this temperature. For those polymers which crystallize to any extent, there is a single melting temperature, T_m, which depends to some extent on the molecular weight. Polymers containing both ordered and disordered regions usually exhibit both a glass transition temperature and a crystalline melting point. DSC deflects the enthalpy changes occurring at T_g or T_m. With the instrument used for this work, a Perkin-Elmer DSC 7, a sample (<10mg) of the polymer was placed in an aluminium sample pan and an empty pan used as a reference. The pans were placed in cells in a heating block and heated at a rate of 15°/minute. A servo mechanism supplies energy to sample and reference so as to keep their temperatures equal. The DSC output plots energy supply vs average temperature and the area under a peak is directly related to the enthalpy changes occurring.



Date: Aug 06, 1990 09: 47am
Scanning Rate: 15.0 C/min
Sample Wt: 7.797 mg Path: \PE\
File: PDA *PD*

IRC DURHAM

Fig.4.1.1.a T_g of poly(2-phenoxycarbonyl norbornene) obtained *via* WCl_6 / $SnMe_4$ catalysis

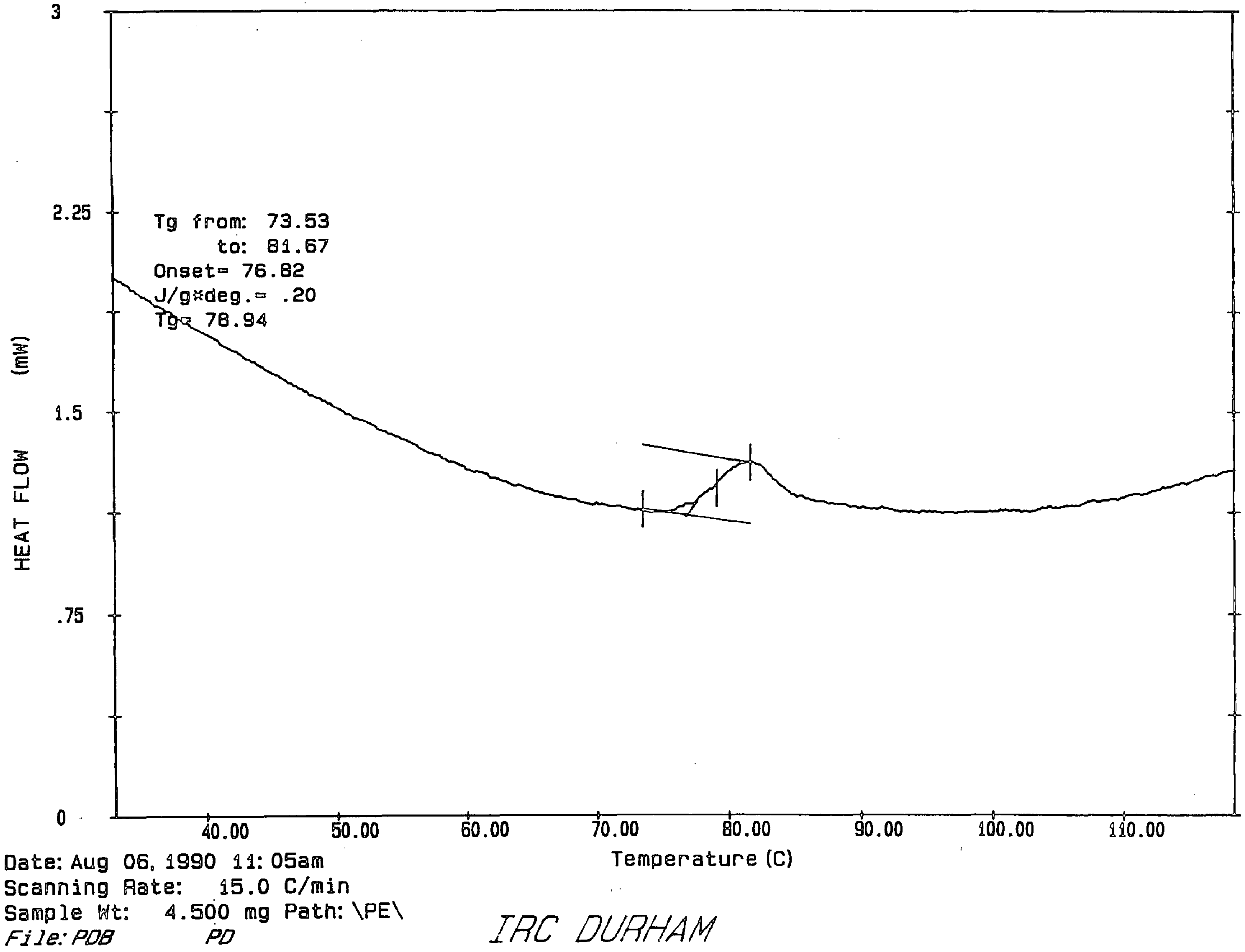


Fig.4.1.1.b T_g of poly(2-phenoxycarbonyl norbornene) obtained *via* $MoCl_5$ / $SnMe_4$ catalysis

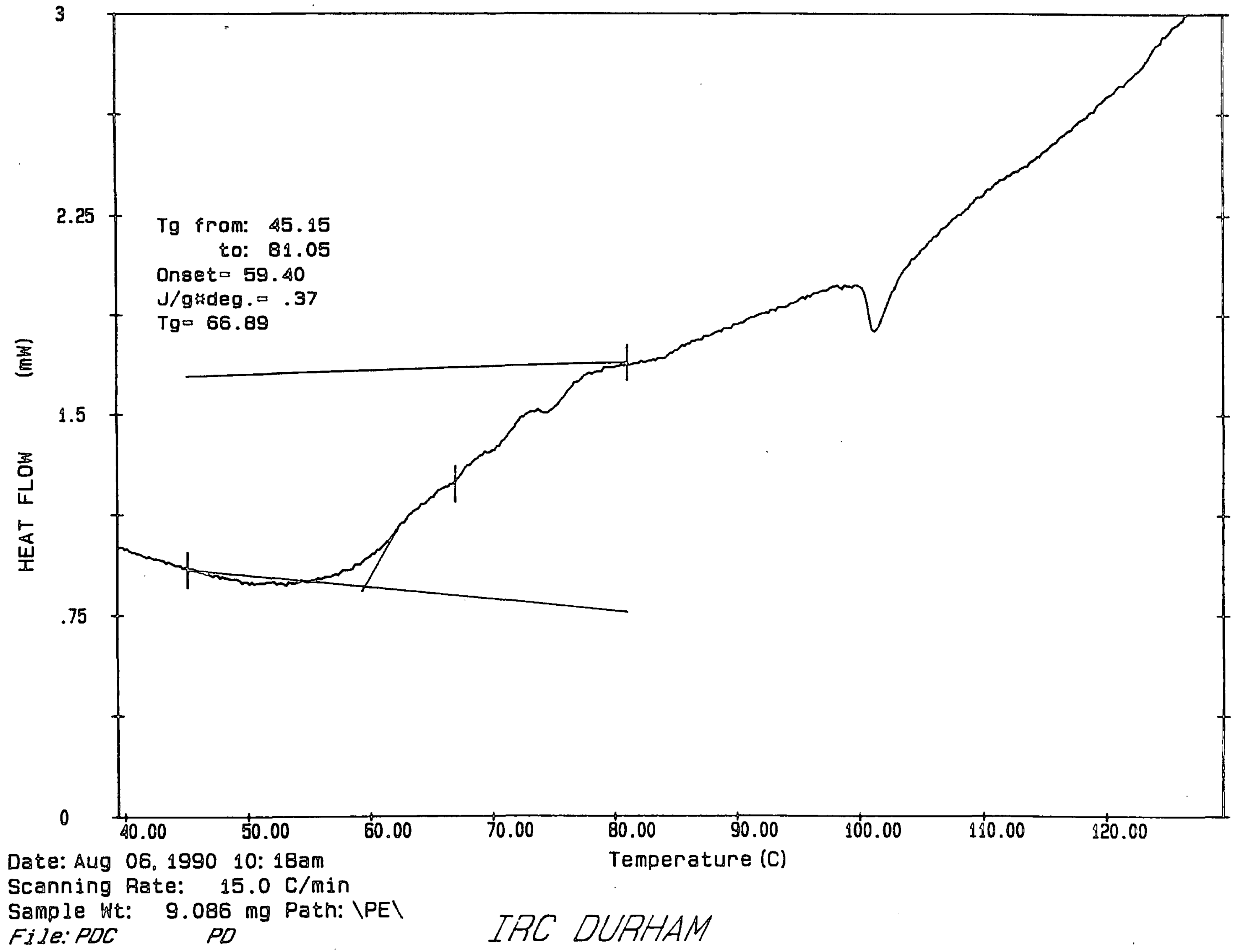
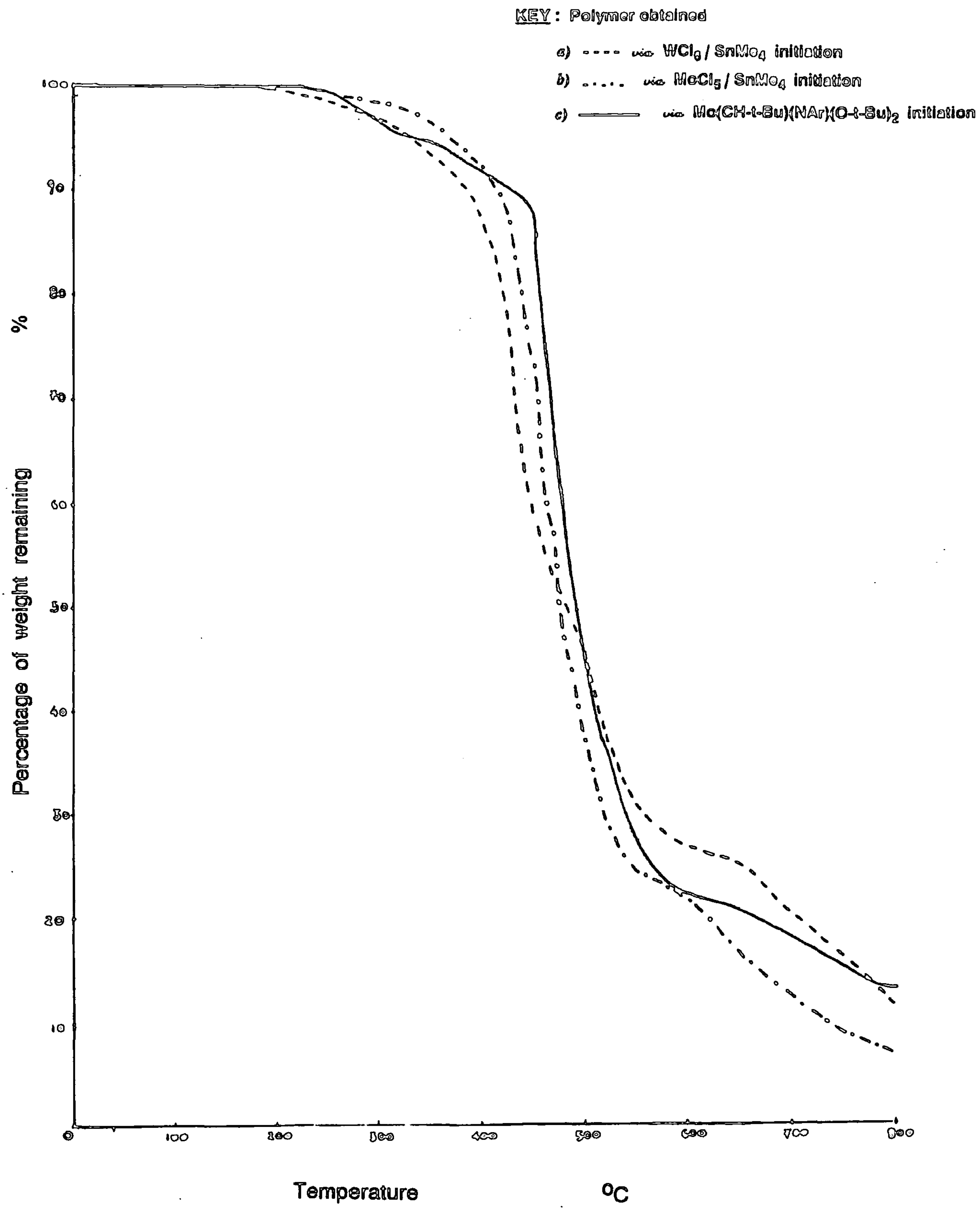


Fig.4.1.1.c T_g of poly(2-phenoxycarbonyl norbornene) obtained *via* Mo(CH-t-Bu)(NAr)(O-t-Bu)$_2$ catalysis

Fig.4.1.2 Thermogravimetric analysis (TGA)



The glass transition temperature is observed as a deflection in the base line. The T_g for the polymer obtained *via* WCl_6 / $SnMe_4$ catalysis was 83°C (Fig.4.1.1.a), for the polymer obtained *via* $MoCl_5$ / $SnMe_4$ catalysis was 79°C (Fig 4.1.1.b) and for the polymer obtained *via* $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ catalysis was 67°C (Fig 4.1.1.c), in this latter case there was a very small exotherm at about 100°C which we have not been able to explain. The T_gs observed at 83, 79 and 67°C were for samples with M_n of 268,000, 76,000 and 14,000; the differences are readily explained in terms of molecular weight for the first two samples and possibly the third sample although in this case the difference of ca.20°C may indicate a different tacticity.

4.1.2 THERMOGRAVIMETRIC ANALYSIS

In thermogravimetric analysis a sensitive balance is used to follow the weight change of the sample as a function of temperature. Typical applications of TGA include the assessment of thermal stability and decomposition temperature. A Stanton Redcroft TG 760 was used in this work. A sample of the polymer (<10mg) was placed on the balance and the instrument programmed to heat at a rate of 10°C/min from room temperature to 800°C. The decomposition temperature was taken as the temperature at which 10% weight loss had occurred. The plots (temperature vs % weight remaining) for the polymers which obtained *via* different catalyst systems are displayed in Fig.4.1.2. All the samples show a similar profile with an onset of degradation in air at just over 200°C.

4.2 CONCLUSIONS AND PROPOSALS FOR FURTHER WORK

The work described in this thesis illustrates that poly(2-phenoxycarbonyl norbornene) can be prepared *via* ring opening metathesis polymerization of 2-phenoxycarbonyl norbornene using the classical catalyst systems $WCl_6/SnMe_4$ and $MoCl_5/SnMe_4$, as well as the well-defined Schrock catalyst $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$.

The tungsten-based classical catalyst gives the best yield (90 %), while the molybdenum-based classical catalyst gives the poorest yield (12%), observation which leads to the conclusion that the first catalyst system is more tolerant to the functional group of the monomer than the second system is. On the other hand, when the well-defined catalyst was used, the polymer showed a bimodal molecular weight distribution. In this case, a possible explanation could be that although the polymerization was initiated by the well-defined catalyst, during the procedure other initiating species were formed and as a result the polymerization continued under different catalytic conditions. An interesting observation is the selectivity of the well-defined catalyst to the endo isomer of 2-phenoxycarbonyl norbornene, which is the reverse of that observed for $WCl_6/SnMe_4$.

The study of the microstructure of the polymers was difficult because of the complexity of the ^{13}C-NMR spectra . Although a cis-trans atactic structure was postulated, further information such as the ratio of cis to trans double bonds and the distribution head-tail, head-head, tail-tail units could not be obtained.

This work establishes that phenoxycarbonyl substituted norbornene monomers readily undergo ring-opening metathesis polymerization with conventional catalysts. Any future continuation of this work might involve the separation of the endo and exo isomers in order to obtain simpler and more readily interpreted spectra. A wider range of initiation conditions could be investigated, which might also lead to the formation of polymers with better defined microstructure.

APPENDIX A

INSTRUMENTATION

^1H and ^{13}C NMR spectra were recorded on a Varian VXR 400 NMR spectrometer at 399.952 MHz (^1H) and 100.577 MHz (^{13}C).

^{19}F NMR spectra were recorded on a Bruker AC 250 FT NMR spectrometer at 235.3 MHz.

Infrared spectra were recorded on Perkin-Elmer 457 or 577 grating spectrometers.

GC chromatograms were obtained using a Hewlett-Packard 5890 Series II gas chromatograph.

Mass spectra were recorded on a VG Analytical Model 7070E Mass spectrometer. Combined gas chromatography/mass spectra were recorded on the same spectrometer coupled to a Hewlett-Packard 5790A GC.

Gel permeation chromatography was carried out using a Viscotek Differential Refractometer/Viscosometer Model 200 (column packing PL_{gel} 10μ mixed styrene-divinyl benzene beads).

Differential scanning calorimetry was performed using a Perkin-Elmer DSC 7 differential scanning calorimeter.

Thermogravimetric analysis was performed using a Stanton Redcroft TG760 thermobalance.

APPENDIX B

RESEARCH COLLOQUIA, SEMINARS, LECTURES AND CONFERENCES

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing:

a) all research colloquia, seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student (those attended are marked *)

b) all research conferences attended by the author during the period when research for the thesis was carried out.

UNIVERSITY OF DURHAM

Board of Studies in Chemistry

a) COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS 1ST AUGUST 1989 TO 31ST JULY 1990

ASHMAN, Mr. A. (Durham Chemistry Teachers' Centre) The National Curriculum - an update	11th October, 1989
*BADYAL, Dr. J.P.S. (Durham University) Breakthoughs in Heterogeneous Catalysis	1st November, 1989
BECHER, Dr. J. (Odense University) Synthesis of New Macrocylic Systems using Heterocyclic Building Blocks	13th November, 1989
* BERCAW, Prof. J.E. (California Institute of Technology) Synthetic and Mechanistic Approaches to Ziegler-natta Polymerization of Olefins	10th November, 1989
BLEASDALE, Dr. C. (Newcastle University) The Mode of Action of some Anti-tumour Agents	21st February, 1990
BOLLEN, Mr. F.(Formerly Science Advisor, Newcastle LEA) Whats's New in Satis, 16-19	27th March, 1990
*BOWMAN, Prof. J.M. (Emory University) Fitting Experiment with Theory in Ar-OH	23rd March, 1990
BUTLER, Dr. A. (St. Andrews University) The Discovery of Penicillin: Facts and Fancies	7th December, 1989
CAMPBELL, Mr. W.A. (Durham Chemistry Teachers' Centre) Industrial catalysis - some ideas for the National Curriculum	12th September, 1989
CHADWICK, Dr. P. (Dept. of Physics, Durham University) Recent Theories of the Universe (with Reference to National Curriculum Attainment Target 16)	24th January, 1990
CHEETHAM, Dr. A.K. (Oxford University) Chemistry of Zeolite Cages	8th March, 1990
* CLARK, Prof. D.T. (ICI Wilton) Spatially Resolved Chemistry (using Natures's Paradigm in the Advanced Materials Arena)	22nd February, 1990
* COLE-HAMILTON, Prof. D.J. (St. Andrews University) New Polymers from Homogeneous Catalysis	29th November, 1989

*CROMBIE, Prof. L. (Nottingham University) The Chemistry of Cannabis and Khat	15th February, 1990
DYER, Dr. U. (Glaxo) Synthesis and Conformation of C-Glycosides	31st January, 1990
FLORIANI, Prof. C. (University of Lausanne, Switzerland) Molecular Aggregates - A Bridge between homogeneous and Heterogeneous Systems	25th October, 1989
*GERMAN, Prof. L.S. (USSR Academy of Sciences - Moscow) New Syntheses in Fluoroaliphatic Chemistry: Recent Advances in the Chemistry of Fluorinated Oxiranes	9th July, 1990
GRAHAM, Dr. D. (B.P. Reserch Centre) How Proteins Absorb to Interfaces	4th December, 1989
*GREENWOOD, Prof. N.N. (University of Leeds) Novel Cluster Geometries in Metalloborane Chemistry	9th November, 1989
*HOLLOWAY, Prof. J.H. (University of Leicester) Noble Gas Chemistry	1st February, 1990
HUGHES, Dr. M.N. (King's College, London) A Bug's Eye View of the Periodic Table	30th November, 1989
*HUISGEN, Prof. R. (Universität München) Recent Mechanistic Studies of [2+2] Additions	15th December, 1989
IDDON, Dr. B. (Univeristy of Salford) Schools' Christmas Lecture - The Magic of Chemistry	15th December, 1989
JONES, Dr. M.E. (Durham Chemistry Teachers' Centre) The Chemistry A Level 1990	3rd July, 1990
JONES, Dr. M.E. (Durham Chemistry Teachers' Centre) GCSE and Dual Award Science as a starting point for A level Chemistry - how suitable are they?	21st November 1989
JOHNSON, Dr. G.A.L. (Durham Chemistry Teachers' Centre) Some aspects of local Geology in the National Science Curriculum (attainment target 9)	8th February, 1990
KLINOWSKI, Dr. J. (Cambridge University) Solid State NMR Studies of Zeolite Catalysts	13th December 1989
*LANCASTER, Rev. R. (Kimbolton Fireworks) Fireworks - Principles and Practice	8th February, 1990
LUNAZZI, Prof. L. (University of Bologna) Application of Dynamic NMR to the Study of Conformational Enantiomerism	12th February, 1990

* PALMER, Dr. F. (Nottingham University) Thunder and Lightning	17th October, 1989
PARKER, Dr. D. (Durham University) Macrocycles, Drugs and Rock 'n' roll	16th November, 1989
* PERUTZ, Dr. R.N. (York University) Plotting the Course of C-H Activations with Organometallics	24th January, 1990
* PLATONOV, Prof. V.E. (USSR Academy of Sciences - Novosibirsk) Polyfluoroindanes: Synthesis and Transformation	9th July, 1990
* POWELL, Dr. R.L. (ICI) The Development of CFC Replacements	6th December, 1989
POWIS, Dr. I. (Nottingham University) Spinning off in a huff: Photodissociation of Methyl Iodide	21st March, 1990
RICHARDS, Mr. C. (Health and Safety Executive, Newcastle) Safety in School Science Laboratories and COSHH	28th February, 1990
* ROZHKOV, Prof. I.N. (USSR Academy of Sciences - Moscow) Reactivity of Perfluoroalkyl Bromides	9th July, 1990
* STODDART, Dr. J.F. (Sheffield University) Molecular Lego	1st March, 1990
SUTTON, Prof. D. (Simon Fraser University, Vancouver B.C.) Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium	14th February, 1990
THOMAS, Dr. R.K. (Oxford University) Neutron Reflectometry from Surfaces	28th February, 1990
THOMPSON, Dr. D.P. (Newcastle University) The role of Nitrogen in Extending Silicate Crystal Chemistry	7th February, 1990

b) RESEARCH CONFERENCES

NEW ORGANIC MATERIALS International Symposium

University of Durham 10-12 September 1990

Organized by the Royal Society of Chemistry

Perkin Division and Macro Group (UK)

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