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Cochlin, Rachel Louise

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Synthesis and Characterisation of Novel Elastomeric Polar Polymers

by

Rachel Louise Cochlin, B.Sc (Dunelm)

University of Durham

A thesis submitted in part fulfilment of the requirements for the degree of Doctor of

Philosophy at the University of Durham

September 1998

Statement of Copyright

Declaration

The work described in this thesis was carried out in the Inter-disciplinary Research Centre in Polymer Science and Technology, Department of Chemistry at the University of Durham between October 1995 and September 1998. All the work is my own, unless stated to the contrary, and it has not been submitted previously for a degree at this or any other university.

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Acknowlegdements

I would like to take this opportunity to thank all those people who have helped me throughout my PhD. It has been a difficult three years and without them, I certainly would not have made it to the end.

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I must express my gratitude for all the support staff without whom I could not have carried out my work. Thanks go to Julia and Ian for NMR data, Jarrika for elemental analysis, Ray and Gordon the glass blowers, Lara for mass spec, Gordon and Andy for GPC and DSC, and Joe and Jimmy in stores.

Thanks also go to Prof G.R. Davies for his attempts at explaining the physics involved in my work and to P. Carr for running the dielectric measurements.

A big thanks go to all the friends I have made in the IRC and in the chemistry department; without them my time here would not have been nearly as much fun.

I would like to express my dearest thanks to Andrew for his help and support over the last two years and for giving me the chance to escape from Durham every two weeks.

A final thanks must go to my family, especially to my parents for all their love and support over the past three years (and the rest!)

Thank you.

Abstract

Synthesis and Characterisation of Novel Elastomeric Polar Polymers

The work described in this thesis is a study of the synthesis of polar elastomeric polymers with a view to producing an electrostrictive polymer.

In chapter 1, the area of electrostriction and the history of the radical ring-opening polymerisation of vinylcyclopropane monomers are described. These monomers are used in the bulk of the work described in the rest of the thesis.

In chapter 2, initial studies of the production of polar, elastomeric polymers using the olefin metathesis reaction are described. Firstly, the ring opening metathesis polymerisations of two disubstituted cyclopentenes were attempted using well-defined initiators. Secondly, the acyclic diene metathesis polymerisation of 1,1-diallyl malononitrile was attempted using classical initiators. Both attempts failed to yield the desired polymers.

In chapter 3, the free-radical homopolymerisation of two vinylcyclopropane monomers containing two cyano groups is described.

In chapter 4, the attempted copolymerisation of 1,1-dicyano-2-vinylcyclopropane and butyl acrylate using emulsion free-radical copolymerisation is reported.

In chapter 5, the free-radical homopolymerisation of three monomers containing one cyano group and one ester group is described. The ester groups incorporated into the monomer were *tert*-butyl, n-butyl and hexyl esters. The monomers were successfully polymerised to give highly *trans*, atactic polymers.

In chapter 6, the free-radical, solution copolymerisation of 1,1-dicyano-2-vinylcyclopropane with 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane is described. Three copolymers were synthesised containing different percentages of each monomer. The copolymers were fully characterised.

In chapter 7, the dielectric analysis of the three homopolymers produced in the work described in chapter 5 and of two copolymers produced in the work described in chapter 6 is summarised .

Finally in chapter 8, the conclusions drawn from this work and suggestions for possible future work are outlined.

Abbreviations

NMR - nuclear magnetic resonance

GPC - gel permeation chromatography

TG - thermogravimetry

IR - infra-red

DSC - differential scanning calorimetry

DMSO - dimethyl sulphoxide

THF - tetrahydrofuran

DMF - dimethylformamide

VCP - vinylcyclopropane

MMA - methyl methacrylate

AIBN - azo-bisisobutyronitrile

BPO - benzoyl peroxide

PVDF - poly(vinylidene difluoride)

Tg - glass transition temperature

δ - chemical shift

ppm - parts per million

$\overline{Mn}$ - number average molecular weight

$\overline{Mw}$ - weight average molecular weight

Pdi - polydispersity

ε_o - permittivity of free space

ε_U - unrelaxed permittivity

ε_R - relaxed permittivity

tan δ - mechanical loss tangent

ROMP - ring-opening metathesis polymerisation

ADMET - acyclic diene metathesis

m - meso

r - racemic

Contents

Chapter 1

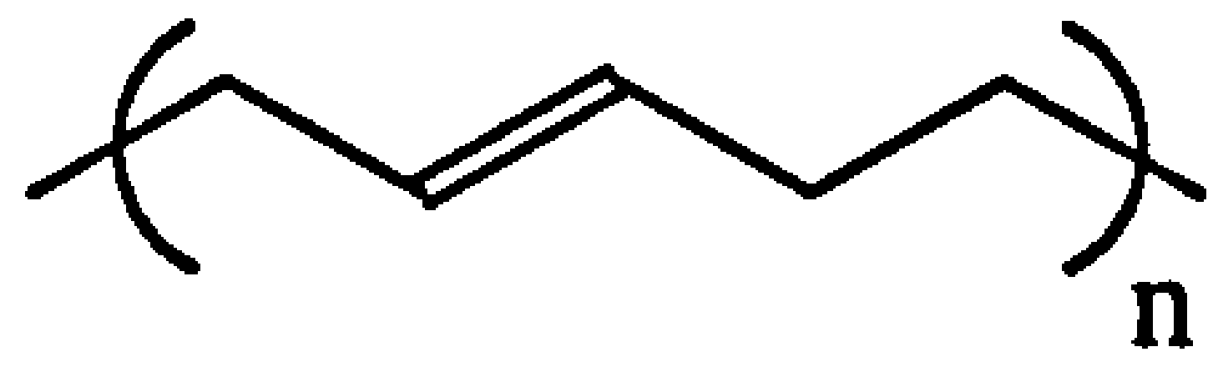
Introduction into electrostriction and free-radical polymerisation

1. Introduction into electrostriction and free-radical polymerisation

1.1 Introduction

The aim of the work described in this thesis was to produce a novel, elastomeric, polar polymer. The project was undertaken in response to a request from Professor G.R. Davies in the physics section of the IRC for the design and synthesis of novel materials for the study of electrostriction effects in polymers. The requirements of such a polymer are that it has a high concentration of polar groups and a low glass transition temperature, Tg.

In order to achieve the required elasticity it was decided to model the polymer on poly(pentadiene) which is a rubbery solid with a Tg of -90°C for the all *trans* polymer and -114°C for the all *cis* polymer.[1] These polymers have a repeat unit of five carbon atoms, two of which are joined by double bond.



To achieve high polarity, it was decided to attach cyano groups to the polymer backbone. The monomers chosen for this study were such that on polymerisation, they would yield the backbone repeat unit of poly(pentadiene) modified by pendant polar substituents.

The project was approached via two routes. Firstly the olefin metathesis reaction was applied to the ring opening metathesis polymerisation (ROMP) of two 4,4-disubstituted cyclopentenes and to the acyclic diene metathesis (ADMET) polymerisation of diallyl malononitrile. This work, along with an introduction to olefin metathesis, is described in chapter two. This approach was unsuccessful.

The second approach, which was successful, used the free-radical ring-opening polymerisation of vinylcyclopropane monomers bearing two polar groups on the cyclopropane ring. An introduction to this work follows in this chapter and the experimental work is described in chapters three to six.

Finally, in chapter seven, the investigation of the electrical properties of the polymers produced is reported.

There has been considerable interest over recent years in polar polymers with the majority of the research focused on piezo- and pyroelectric polymers. A third phenomenon that has received considerably less attention is that of electrostriction. In this work, it was hoped to produce polymers with properties suitable for the display of this phenomenon.

1.2 Electrostriction

Electrostriction has been well known for inorganic crystals and ceramics for many years, however, it has not been extensively studied in polymers. Electrostriction in polymers was observed as early as 1820 by A. C. Becquerel.[2]

In 1880, a paper published by Röntgen described an experiment to demonstrate electrostriction in rubber by the application of a field to a sheet of rubber and the measurement of the deformation caused.[3] This paper is translated and printed in a 1996 paper by Ma and Reneker.[4] Röntgen concluded that 'the elasticity of materials in the solid state is changed by electrical forces'.

The application of an electric field to any material can displace charge and lead to field-induced elastic strains. The part of the strain which is proportional to the square of the electric field is called electrostriction.

$$S = dE + \gamma E^2$$

where S is the strain, E is the applied field, d is the piezoelectric coefficient and γ is the electrostrictive coefficient.

The phenomenon of electrostriction is still not very well understood at a molecular level. However, a qualitative picture has established and is described below.

In an amorphous rubber, the polymer chains are randomly coiled with any associated dipoles randomly directed within the sample. On the application of an electric field, a force is exerted on the dipoles which tends to align them with the applied field. The movement of the dipoles is, however, restricted by the position of the chains within the sample. In order to maximise the dipole alignment, the polymer chains are forced to adopt a different organisation in space which has the result of changing the dimensions of the polymer sample. This concept is illustrated in the following cartoon.

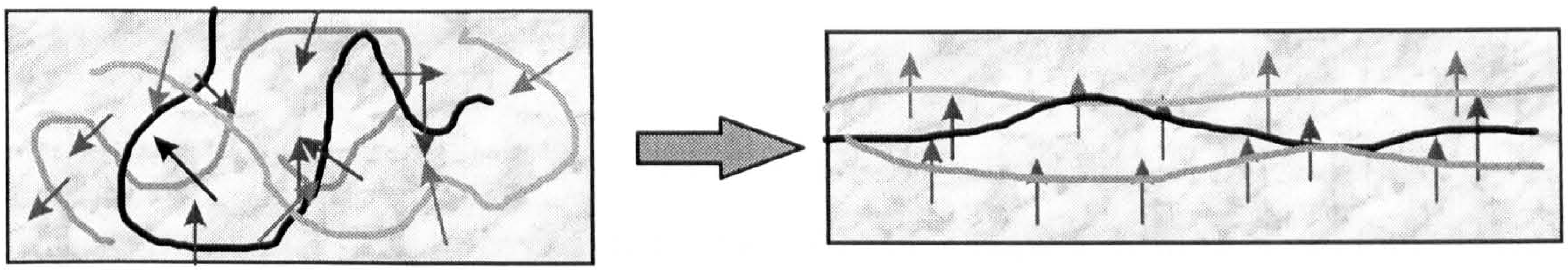


Figure 1-1 Cartoon showing the concept of electrostriction

The polymer also changes its properties since dipole alignment and chain extension produces more order in the polymer thus reducing elasticity and giving a more rigid polymer. On the removal of the electric field, the polymer relaxes and returns to its original, disordered, rubbery state.

Generally electrostriction in polymers was regarded as having no practical use since the effect was small compared to the piezoelectric effect. Even to this day, the only polymer to have received significant attention is poly(vinylidene difluoride), PVDF.

1.2.1 Poly(vinylidene difluoride)

Poly(vinylidene difluoride) (PVDF) exhibits the strongest piezo- and pyroelectric activity of all known polymers. Piezoelectricity is an electric polarisation produced by a mechanical strain and pyroelectricity is an electric polarisation produced by a change in temperature. PVDF owes its piezoelectric properties to fixed dipoles in crystalline regions of the bulk sample. It is thought that fluoroalkenes are ideal monomers with which to create piezoelectric polymers because the fluorine atom is very small and therefore, in relatively low concentrations, does not perturb the polymer crystallinity from that associated with polyethylene.

The piezoelectric properties of PVDF were first noted by H. Kawai in 1969.[5] He found that by stretching a film of PVDF at 100-150°C and then allowing it to cool in an electric field of 300 kVcm^{-1} he obtained a film with piezoelectric properties. Two years later, Bergman *et al.* reported the pyroelectric properties of PVDF.[6] They treated the polymer in the same way as Kawai and found that this protocol imparted pyroelectric properties as well.

1.2.1.1 Structure of PVDF

PVDF is a semicrystalline polymer consisting of highly polar repeat units (dipole moment ≈ 2.1D). In the melt, the polymer chains will have a random coiled conformation but, if the structure is relatively free from defects, it can crystallise into a regular conformation when cooled. This occurs by rotation about the single bonds of the backbone to achieve the most energetically favourable state. When PVDF solidifies from the melt, it forms spherulite structures consisting of about 50% lamellar crystals in an amorphous phase as shown below.[7]

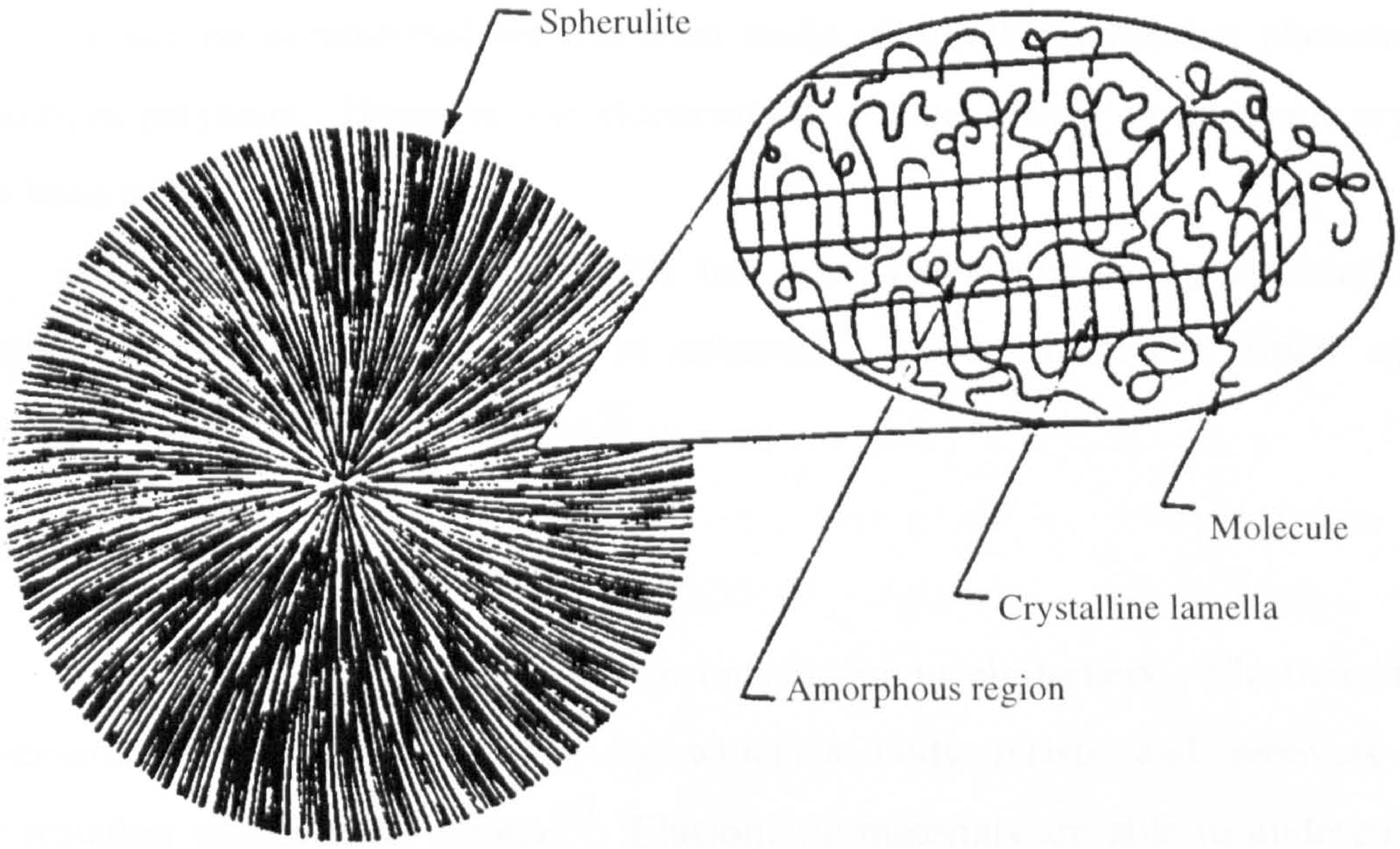


Figure 1-2 - PVDF spherulite

It was originally thought that this crystalline region alone was responsible for the electrical properties of PVDF but it is now thought that electrostriction may play a large part.[8] It is known that the crystalline regions in PVDF which are responsible for the piezoelectric effect lie within an amorphous region. It is thought that the aligned dipoles within the crystals create a field within the surrounding amorphous material and this field causes electrostriction in the amorphous PVDF.

1.2.2 Applications of polar molecular materials

Polar polymers (mostly PVDF and copolymers) have found applications which utilise their piezo- and pyroelectric properties. When comparing polymeric materials with conventional inorganic piezo and pyroelectric crystals, the polymers offer several advantages including their ease of moulding and high flexibility. The main disadvantage arises from the relatively high mechanical and electrical losses that occur.

Applications of piezoelectric materials include microphones, loud speakers, underwater transducers and headphones.[9] Applications of pyroelectric materials include IR detectors,[10] security systems and electrostatic copiers.

As yet, no commercial use has been made of the electrostrictive phenomenon arising in polymers. However, the electrostrictive effect arising in inorganic crystals has been utilised in several ways.

Lead magnesium niobate (PMN) has been introduced as an electrostrictive material and has found applications as actuators,[11] inchworms and in ‘smart’ optical systems such as deformable mirrors.[12]

1.3 The elastomeric state

Electrostriction in polymers can only occur in elastomers. Elasticity is the reversible stress-strain behaviour by which a body resists and recovers from deformation produced by a force.[13] Elastomeric materials are able to undergo large deformations without fracture and then return to their original shape.

In order for a polymer to exhibit elasticity, the polymer chains must be highly flexible so that they are able to alter their arrangements and extensions in space when subjected to a force. Also, there must be either cross links in the form of permanent chemical bonds or physical constraints such as chain entanglements. In the absence of these links, the polymer chains would permanently slip past each other on deformation; that is, they would flow and the deformation would be irreversible. Thirdly, there must be no intermolecular forces between the chains that would prevent the chains from moving reversibly past each other. For example, extensive crystallisation must not be present and the polymer must not be in the glassy state. This means that the polymer must be above its glass transition temperature.

1.4 The glass transition

The glass transition temperature is the point at which the molecular motion of amorphous polymer chains is frozen and the material becomes a glass.

There are several factors which affect the glass transition temperature. Main chain flexibility is the most important factor; polymers with flexible backbones have a low Tg. Flexibility is obtained when chains are composed of bond sequences that are able to rotate easily. Large bulky side groups tend to inhibit rotation about the main chain and thus increase Tg.

For high molecular weight polymers, Tg is essentially independent of molecular weight but as the chain length decreases then Tg will decrease. This is due to the relative increase in the number of end groups in the polymer sample. Chain ends are able to move more freely than units constrained in the polymer chain and this increase in chain end mobility contributes to a decrease in Tg.

1.5 Free-radical polymerisation

Many unsaturated monomers are able to undergo polymerisation by a free-radical chain growth process. The reactive radical produced from an initiator adds many monomer units in a chain reaction, rapidly achieving a high molecular weight and causing a steady decrease in monomer concentration throughout the reaction. The molecular weight of the polymer is relatively unchanged during the polymerisation and an increased reaction time leads to an increased yield but no increase in the molecular weight of the polymer produced.

Free-radical polymerisation involves at least three distinct reactions; namely, initiation, propagation and termination.

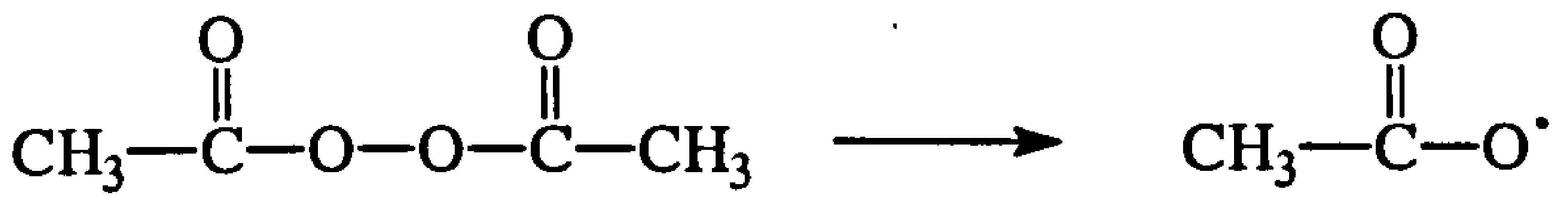
1.5.1 Initiation

Initiation occurs via two steps, the first being the generation of a radical species from an initiator and the second being the reaction of this radical with a monomer molecule. When considering the rates of initiation, it is the dissociation of the initiator that is the rate limiting step.

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

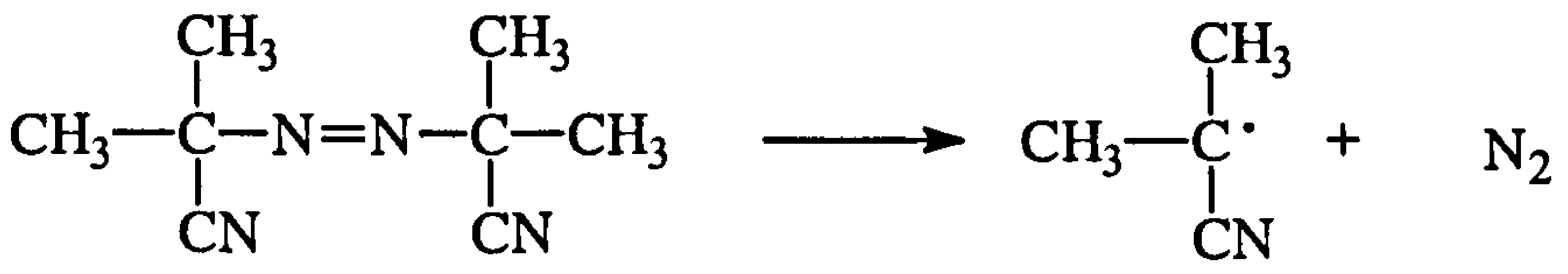
$$R^{\bullet} + M \longrightarrow M_1^{\bullet}$$

The most common method of obtaining an initiating radical is from the thermal, homolytic cleavage of a weak bond. The number of compounds that can be used is limited to those with bond dissociation energies between 100-170kJ/mol. Outside these limits, the compounds generally dissociate too quickly or too slowly to be useful initiators. Compounds containing O-O, S-S and N-O bonds possess the required range of dissociation energies. Peroxides and azo compounds are widely used as free-radical initiators.



$$CH_3-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-CH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O^{\bullet}$$

Acetyl Peroxide



$$CH_3-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{CN}{\overset{CH_3}{C}}{}^{\bullet} + N_2$$

2,2' Azobisisobutyronitrile
(AIBN)

The facile dissociation of azo compounds is not driven by a low bond dissociation energy; the C-N bond energy is ≈290 kJ/mol. The driving force behind the fission of azo compounds is the production of the highly stable nitrogen molecule. Among other initiators that have been studied are disulphides,[14] tetrazenes[15] and N_2O_4.[16]

The temperature used for the reaction, depends on the half-life of the initiator selected, for example, the half life of AIBN varies as shown below.

Temperature/ °C	Half Life
50	74 hours
70	4.8 hours
100	7.2 mins

Table 1-1 Half-life of AIBN at various temperatures

Usually polymerisations using AIBN are carried out at temperatures between 50 and 70 °C to ensure that the initiator generates radicals at a convenient rate.

There are other types of initiator used in free-radical polymerisation e.g. redox initiators and photochemically cleaved initiators.

Redox initiators are systems based on mixtures of oxidising and reducing agents and they are useful because they do not require the higher temperatures necessary for thermal initiators. They initiate through single electron transfer steps that form free radial intermediates. For example, the reaction of hydrogen peroxide with ferrous iron is commonly used as a source of hydroxyl radicals.

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

Photochemical polymerisations occur when radicals are produced by ultraviolet or visible light irradiation of a reaction system. Radical generation can occur in one of two ways. Firstly, some compound in the system undergoes photoexcitation and subsequent decomposition into radicals. Secondly, some compound (a photosensitiser) undergoes excitation and in its excited state interacts with a second compound which then generates radicals.

1.5.2 Propagation

Propagation follows initiation. This is the chain growth stage where the radical monomer, $M_1^\bullet$ undergoes the successive addition of large numbers of monomer molecules.

$$M_1^\bullet + M \longrightarrow M_2^\bullet$$

$$M_2^\bullet + M \longrightarrow M_3^\bullet$$

Or in general

$$M_n^\bullet + M \longrightarrow M_{n+1}^\bullet$$

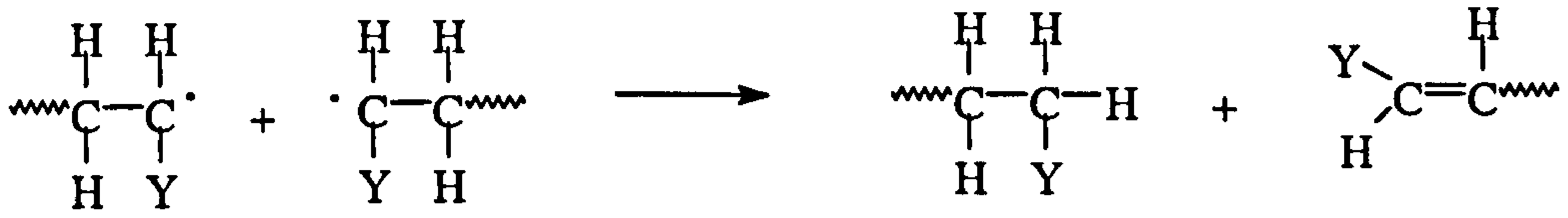
Each successive addition creates a new radical which is identical to the previous radical species except it contains one more monomer unit.

1.5.3 Termination

Termination is the stage when the chains cease to grow. This usually occurs by combination when two radical polymer ends meet and combine.

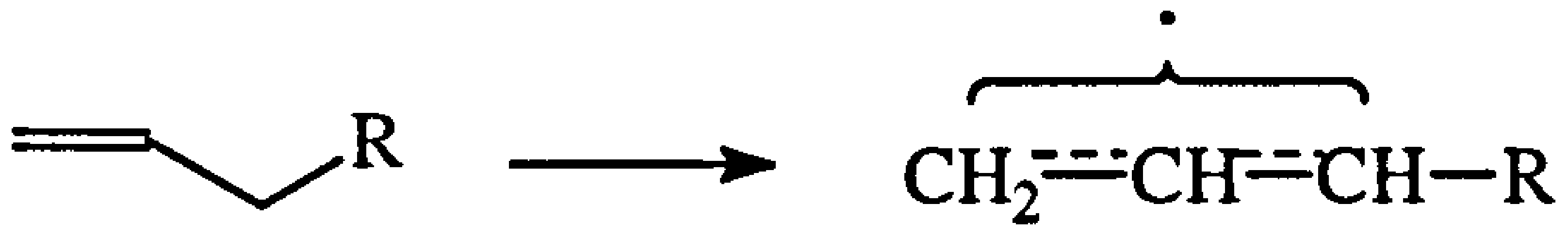
$$\sim\!\sim M^{\bullet} + {}^{\bullet}M\sim\!\sim \longrightarrow \sim\!\sim M{-}M\sim\!\sim$$

A second, less common, method of termination is disproportionation when a radical polymer end abstracts a hydrogen beta to a second polymer end creating two different polymer species; one saturated and the other unsaturated.



1.5.4 Chain transfer

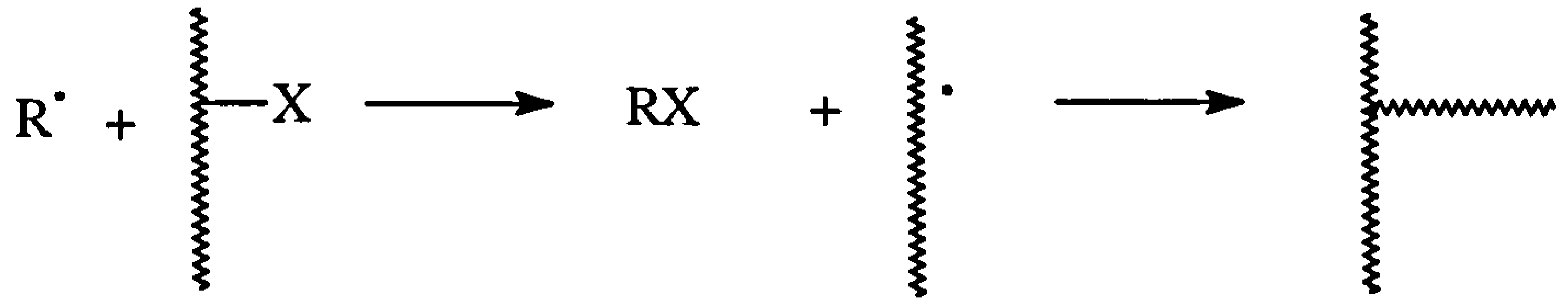
Chain transfer was first recognised by Flory in 1937.[17] It is the premature termination of the growth of the polymer chains by transfer of hydrogen or some other species to the active end of the polymer chain. At the same time it produces a new radical which may initiate the growth of further polymer chains. The effect of chain transfer on the rate of polymerisation depends on the reactivity of the new radicals formed. If the new radicals are reactive, they propagate new polymer species immediately and therefore the number of radicals present is unchanged. In some cases, the new radical formed is unreactive and does not continue to propagate new polymer chains. An example of this is provided by allylic monomers. Abstraction of an alpha-hydrogen leads to a radical which is stabilised by resonance and does not reinitiate but instead reacts with another allylic radical.



When the radical does not reinitiate, the rate of polymerisation slows and this is termed retardation.

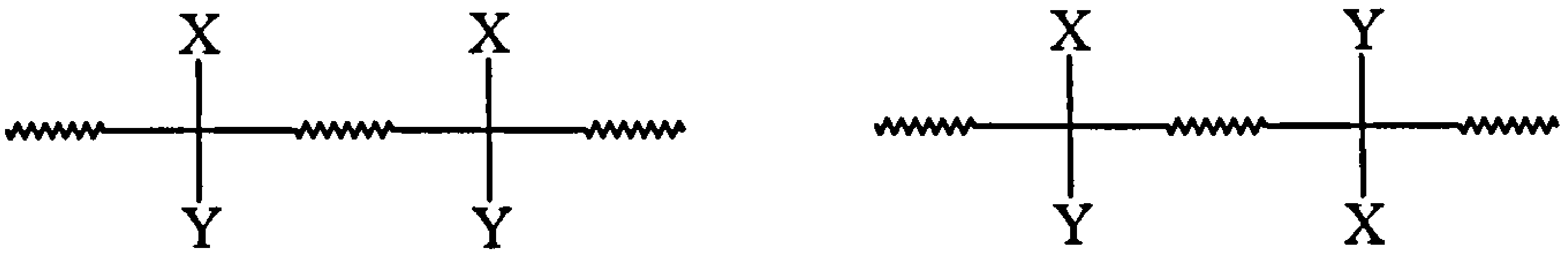
The main effect of chain transfer is to reduce the molecular weight of the polymer obtained. In some cases in industry, additives known as regulators or modifiers are added to effect chain transfer and control the molecular weight of the polymer produced.

A great number of different species are able to effect chain transfer and it is therefore a widespread phenomenon. The chain transfer agent may be a monomer molecule as described for allylic monomers, a polymer chain, a solvent molecule, an initiator molecule or an additive. If the chain transfer occurs with a polymer molecule then this leads to a radical site on the polymer which in turn leads to branching as indicated schematically below.



1.5.5 Stereochemistry

The substituted carbon atom of a monomer unit in a polymer chain is often a chiral centre and therefore has a *d* or *l* configuration depending on the stereochemistry of addition. Two adjacent chiral centres are known as a diad. Two identical chiral centres give a meso diad and chiral centres of opposite chirality give a racemic diad.



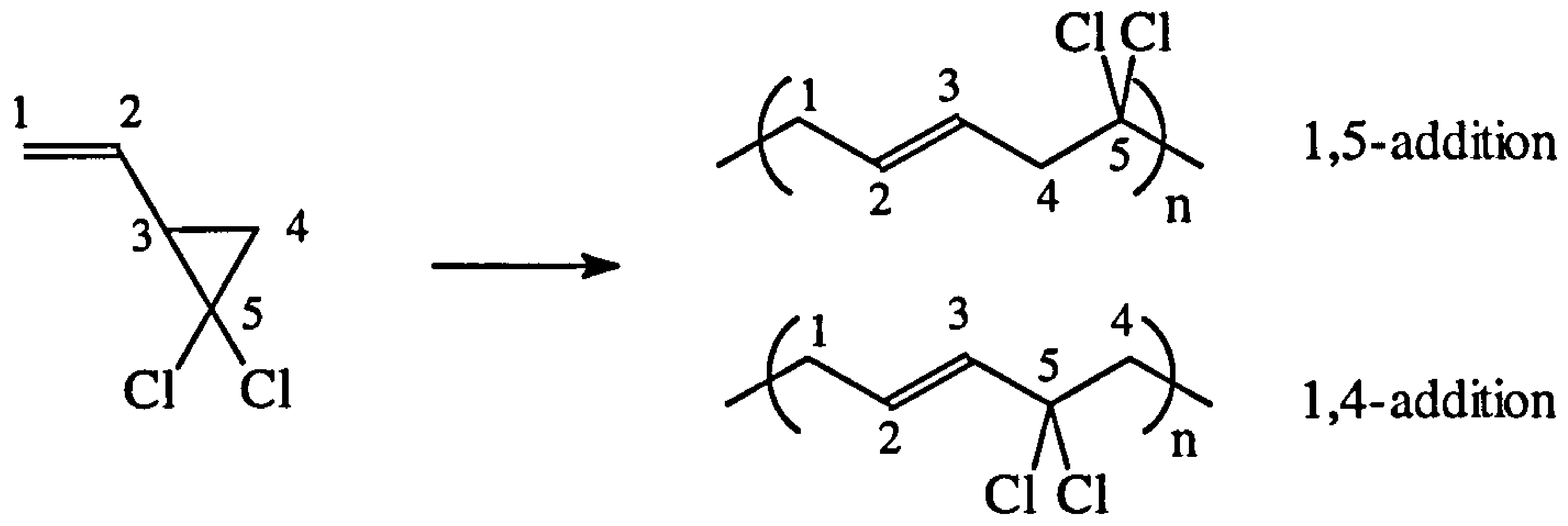
Meso Diad Racemic Diad

Isotactic polymer chains contain diads that are all meso whereas syndiotactic polymer chains contain all racemic diads. Polymers that contain a random (or statistical) sequence of meso and racemic diads are termed atactic.

Nuclear magnetic resonance (NMR) is widely used to study the microstructure of polymers. In sufficiently high resolution NMR, it is possible to detect chiral centre sequences up to heptads.

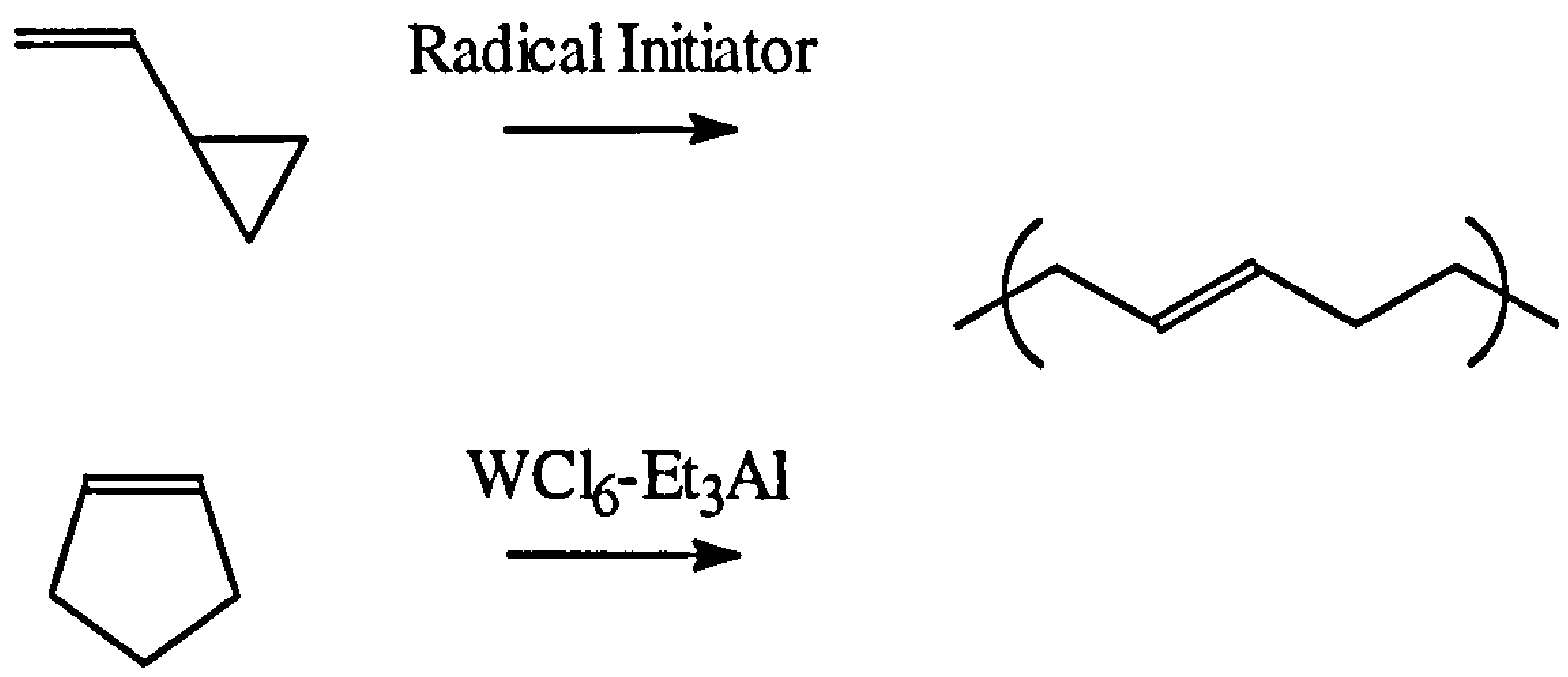
1.5.6 Free-radical polymerisation of vinylcyclopropanes

The first example of the free-radical ring opening polymerisation of vinylcyclopropanes (VCPs) was published in 1964 by Takahashi.[18] He studied the bulk and solution polymerisation of 1,1-dichloro-2-vinylcyclopropane in a tube sealed under a nitrogen atmosphere. Polymerisation failed to occur when ionic initiators were used but when benzoyl peroxide (BPO) or α,α'-azo-bisisobutyronitrile (AIBN), radical initiators, were used, a polymeric product was obtained. The purified polymer obtained from the bulk polymerisation of the monomer with BPO was found to be a white solid with a melting point of 70°C and an $\overline{Mn}$ of 7000. The chlorine content of the polymer was found to be comparable to that of the monomer suggesting that no dechlorination had occurred. Infra-red (IR) spectroscopic analysis of the polymer showed that the absorptions due to the cyclopropyl ring (1020 cm^{-1}) had disappeared and absorptions due to a *trans* double bond (965 cm^{-1}) had appeared. Takahashi proposed that both the following structures were present in the polymer, both involving ring opening.

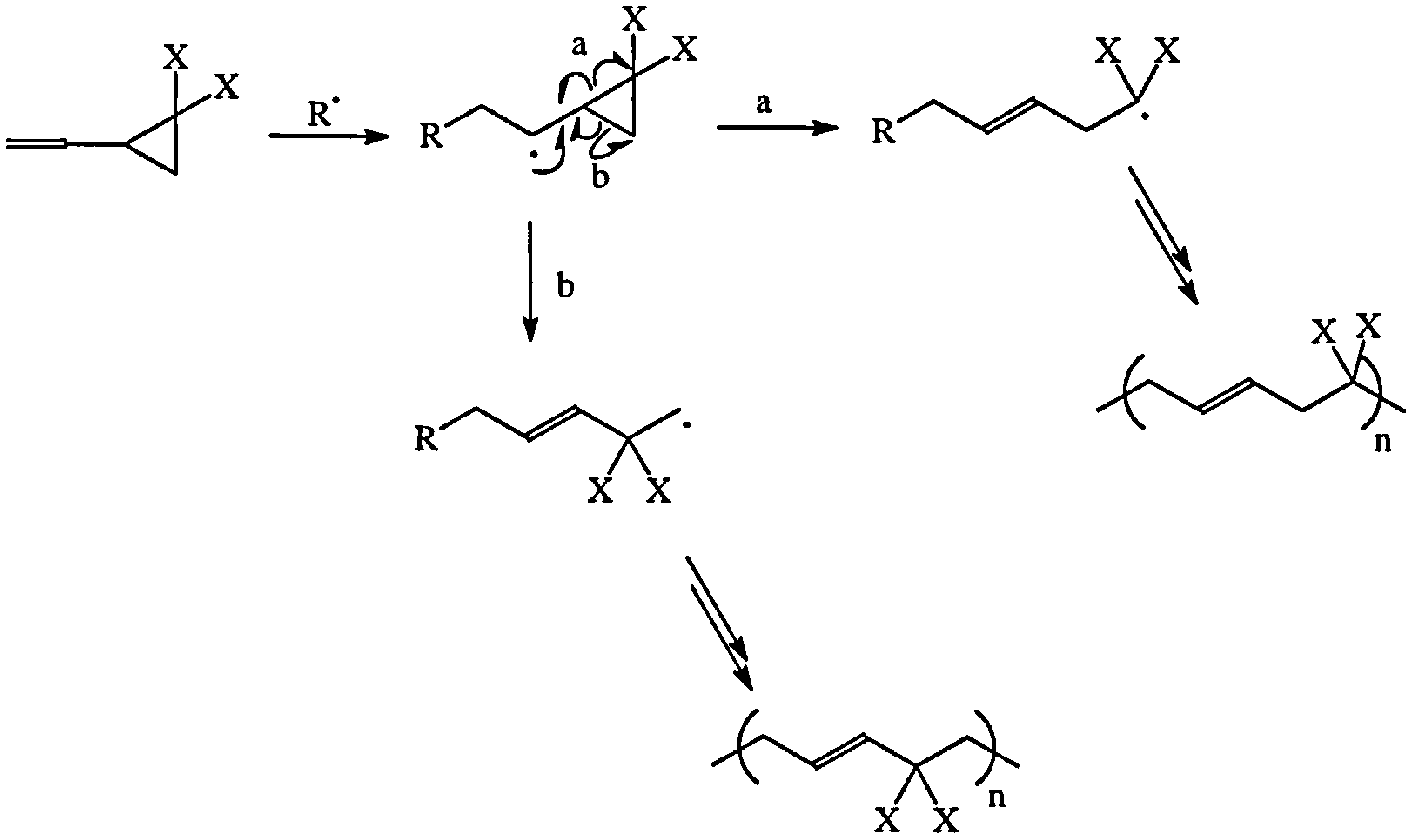


The following year, a second paper was published by Takahashi continuing his study of the radical polymerisation of vinylcyclopropanes.[19] He polymerised vinylcyclopropane using AIBN and BPO obtaining low yields (~15%) of low molecular weight polymer. He studied the IR data obtained from the polymers and again he saw the disappearance of the bands corresponding to the cyclopropyl ring and the vinyl group, and the appearance of a band corresponding to a *trans* double bond.

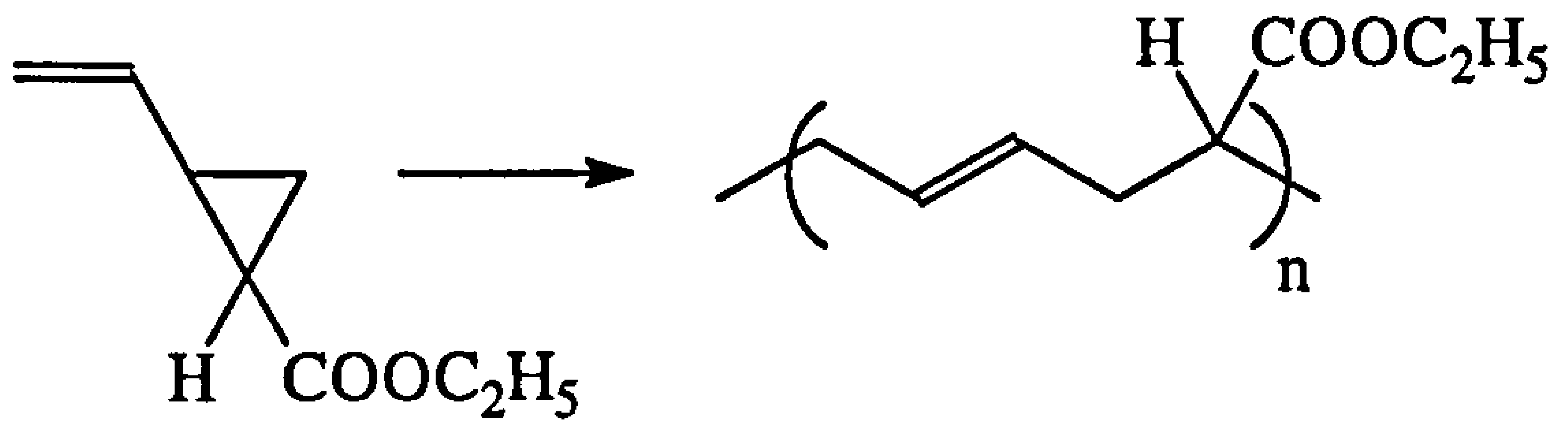
He compared the spectrum with that obtained from the ring-opening polymerisation of cyclopentene using classical initiators and saw that the polymers had essentially the same structure.



This evidence supported the theory that vinylcyclopropanes underwent radical polymerisation with the opening of both the double bond and the ring. Takahashi proposed the mechanism shown below involving both 1,5-additon (route a) and 1,4-addition (route b).

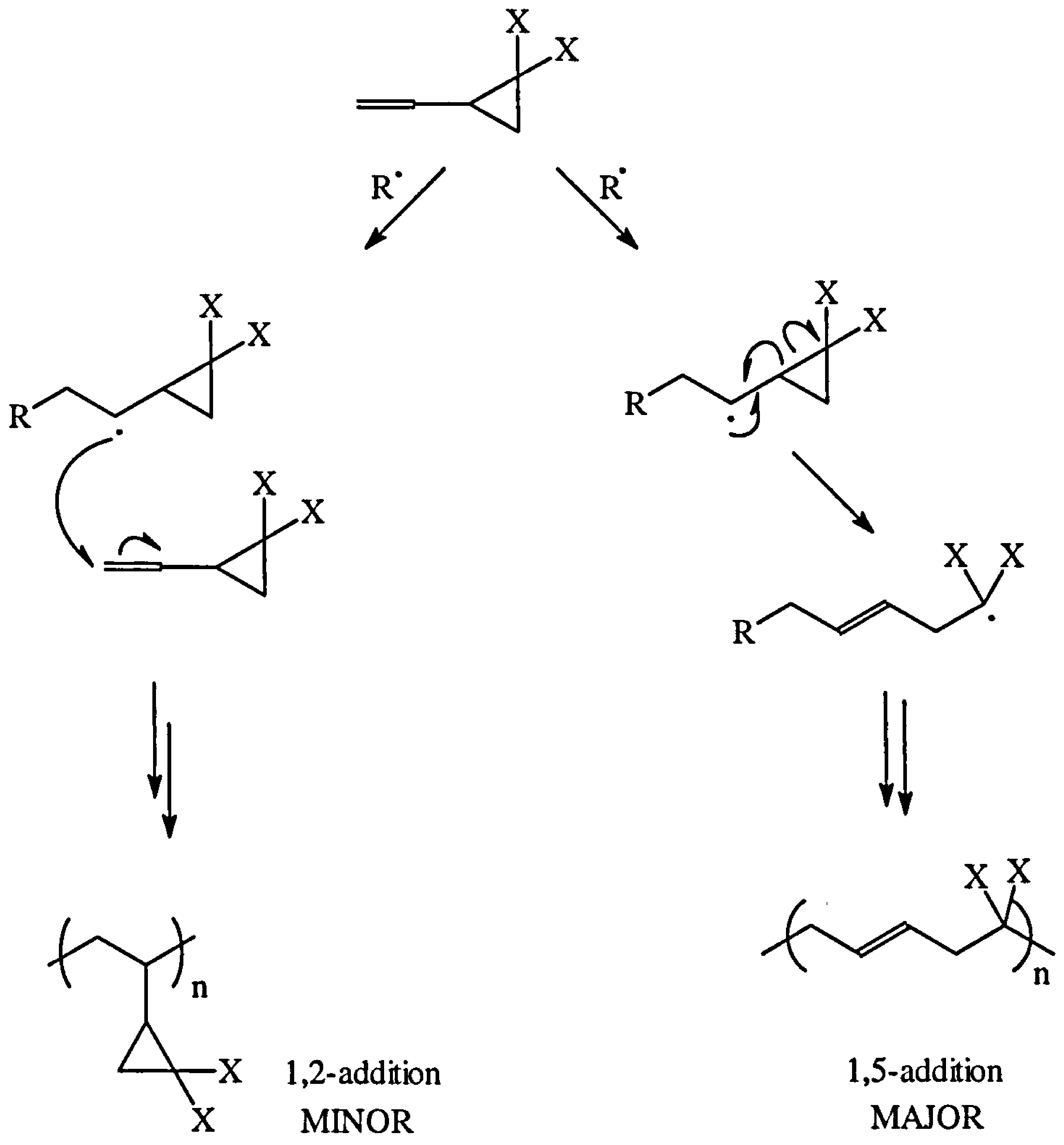


At the same time, work was carried out in the USSR by Lishanskii. In 1965, he published his work concerning the polymerisation of VCPs with polar substituents on the ring.[20] His results were only in partial agreement with those obtained by Takahashi. He polymerised 1-ethoxycarbonyl-2-vinylcyclopropane using BPO and AIBN.

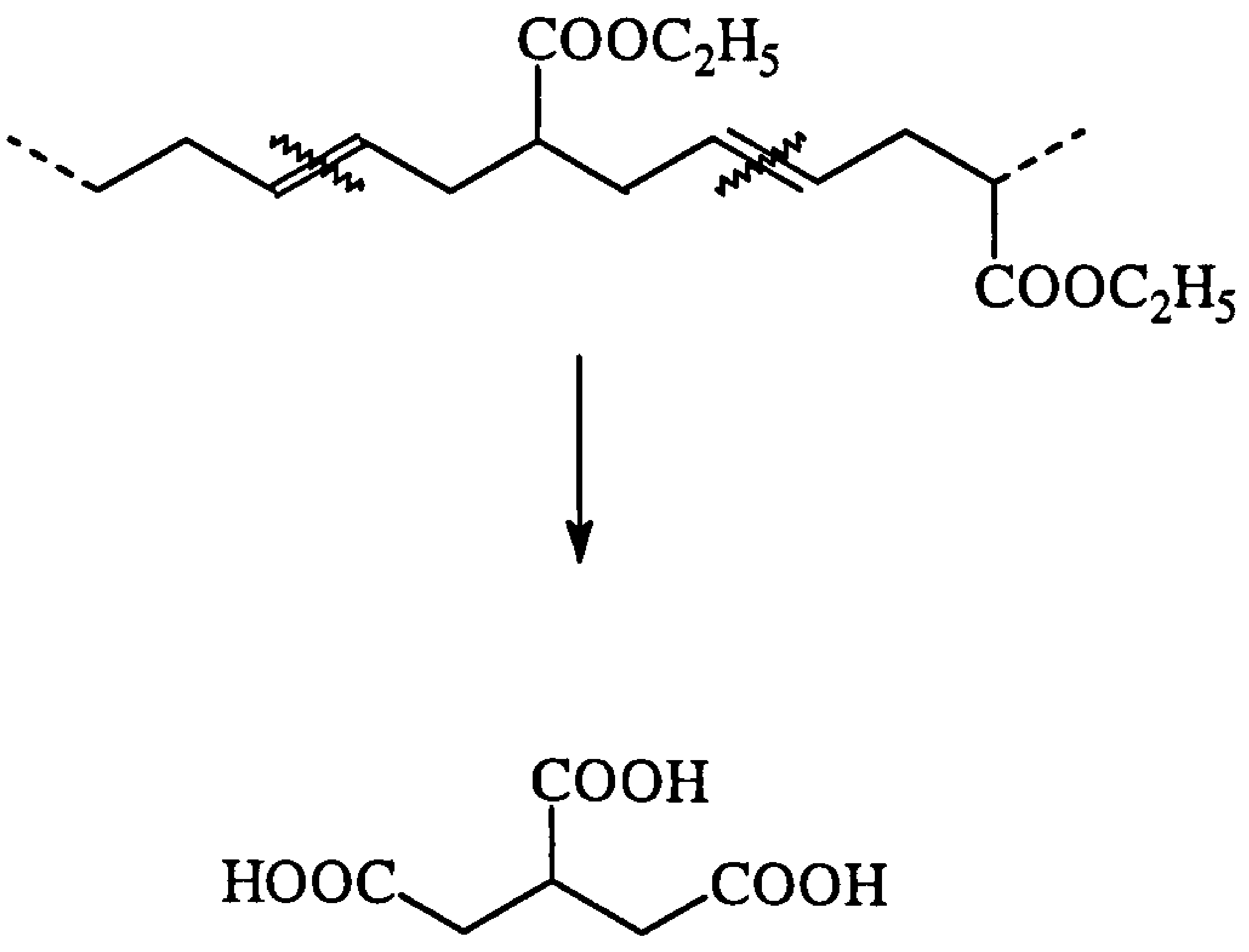


He obtained polymers in yields of up to 50% with glass transition temperatures in the region of -45°C. He proposed that the radical formed in 1,5-addition would be stabilised by conjugation with the carbonyl group thus favouring this over 1,4-addition. The formation of exclusively *trans* double bonds was explained by steric hindrance.

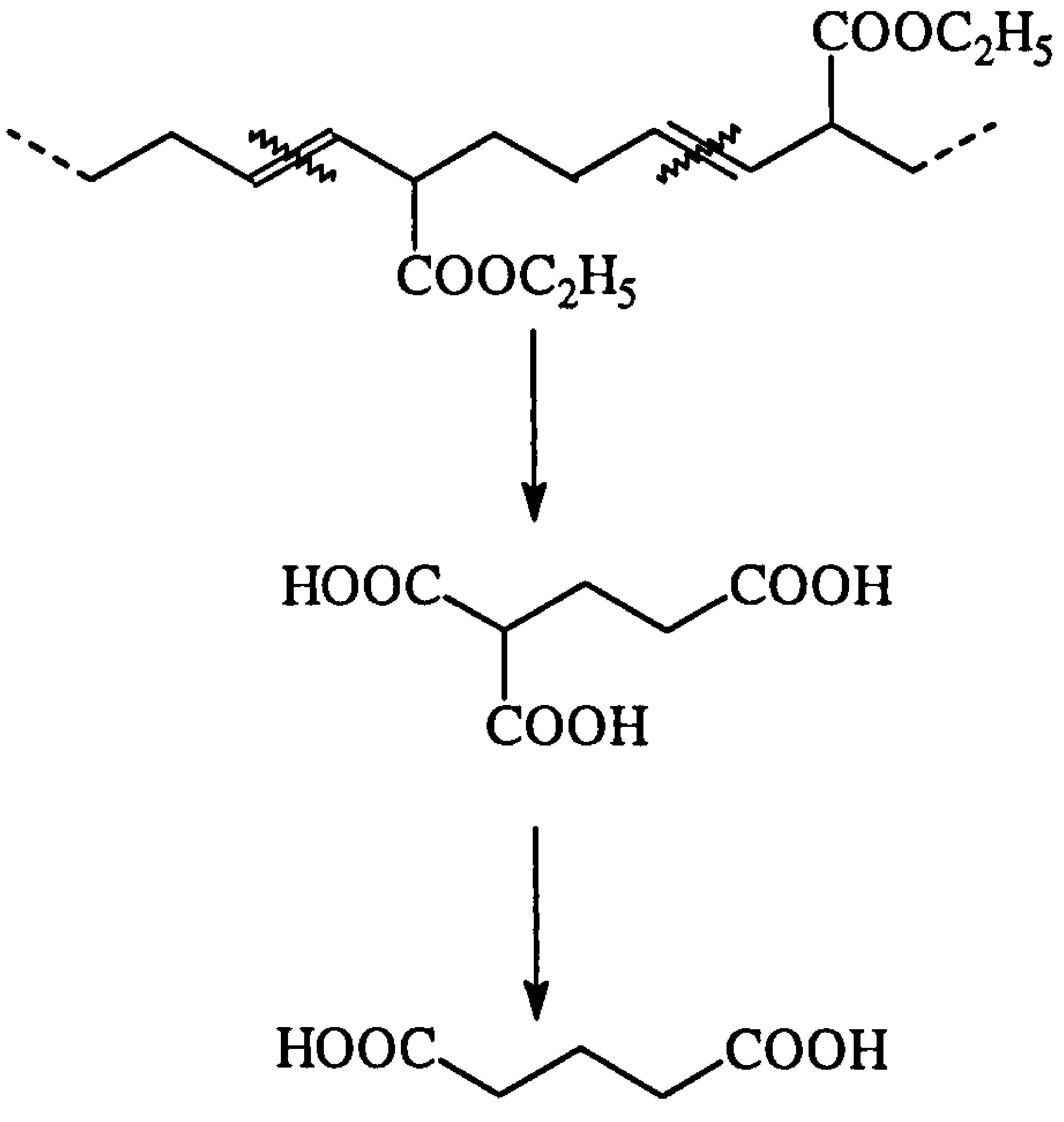
He also repeated Takahashi's work on the polymerisation of 1,1-dichloro-2-vinylcyclopropane. From the IR data obtained, Lishanskii confirmed that the main unit present in this polymer was the 1,5-addition unit where ring opening had occurred. However, he disagreed with the Japanese scientists' claim that only *trans* double bonds were present in the polymer; he argued that the spectrum complexity suggested that *cis* bonds were also present. He claimed that the steric hindrance caused by the chlorine atoms was not as great as that caused by the carboxylate group and therefore did not play as large a part in the isomerisation of the cyclopropylcarbinyl radical. He also suggested that the chlorine atoms would stabilise the radical formed in 1,5-addition making this more likely than the 1,4-addition. Also Lishanskii noted that in some cases there was a decrease in the chlorine content on going from the monomer to the polymer suggesting some elimination. He also reported that in some samples, a unit obtained from 1,2 polymerisation in which the ring is retained, was present to an extent of up to 15%. These observations are summarised below.



Subsequently, Lishanskii used ozonolysis to determine the chain structure of the polymer formed from 1-ethoxycarbonyl-2-vinylcyclopropane.[21] Polymer units formed by 1,5-addition would undergo ozonolysis and subsequent saponification to form propane-1,2,3-tricarboxylic acids.

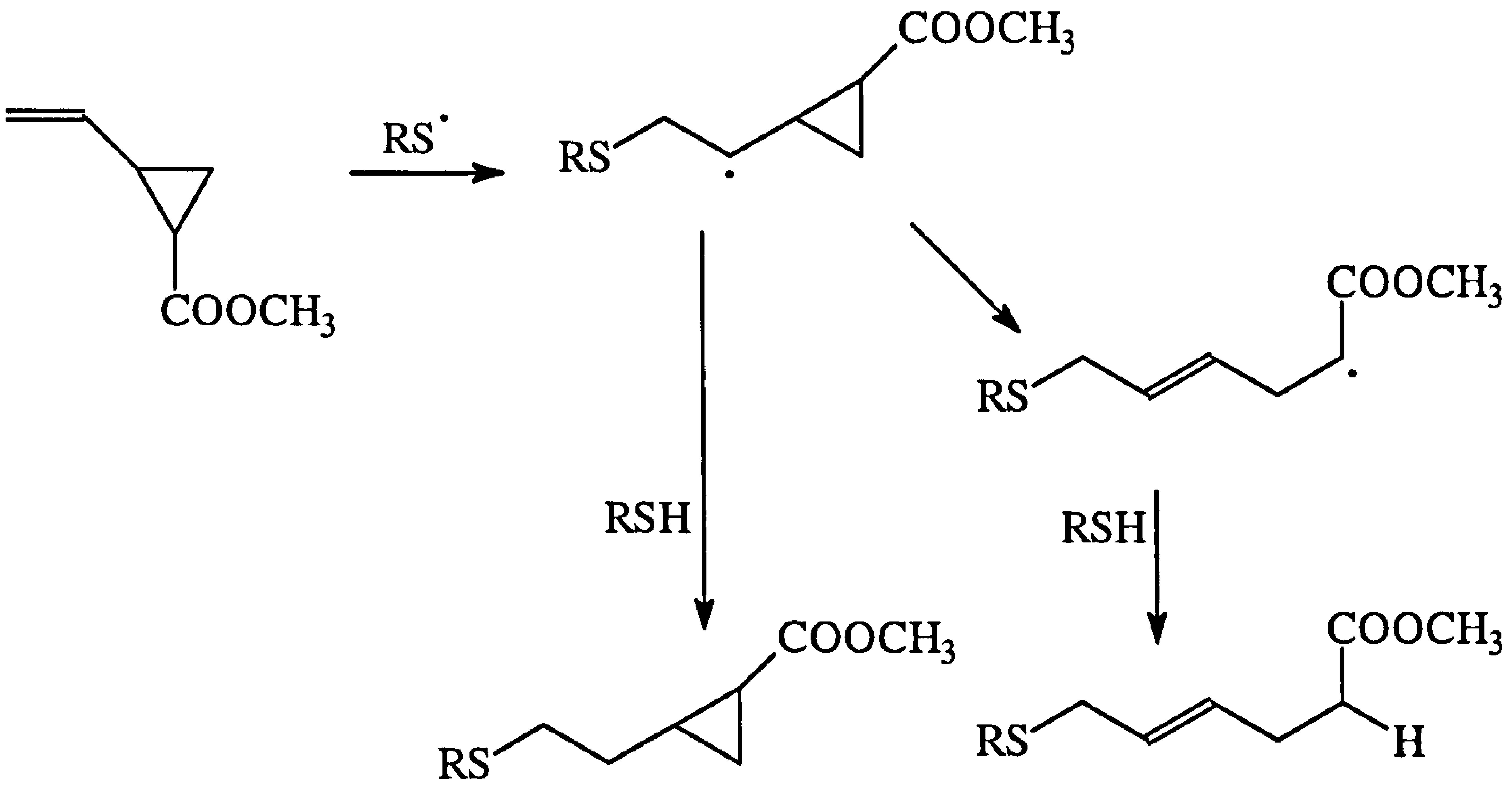


Units formed from 1,4-addition would undergo ozonolysis and saponification to form propane-1,1,3-tricarboxylic acid which could then be decarboxylated to form glutaric acid.



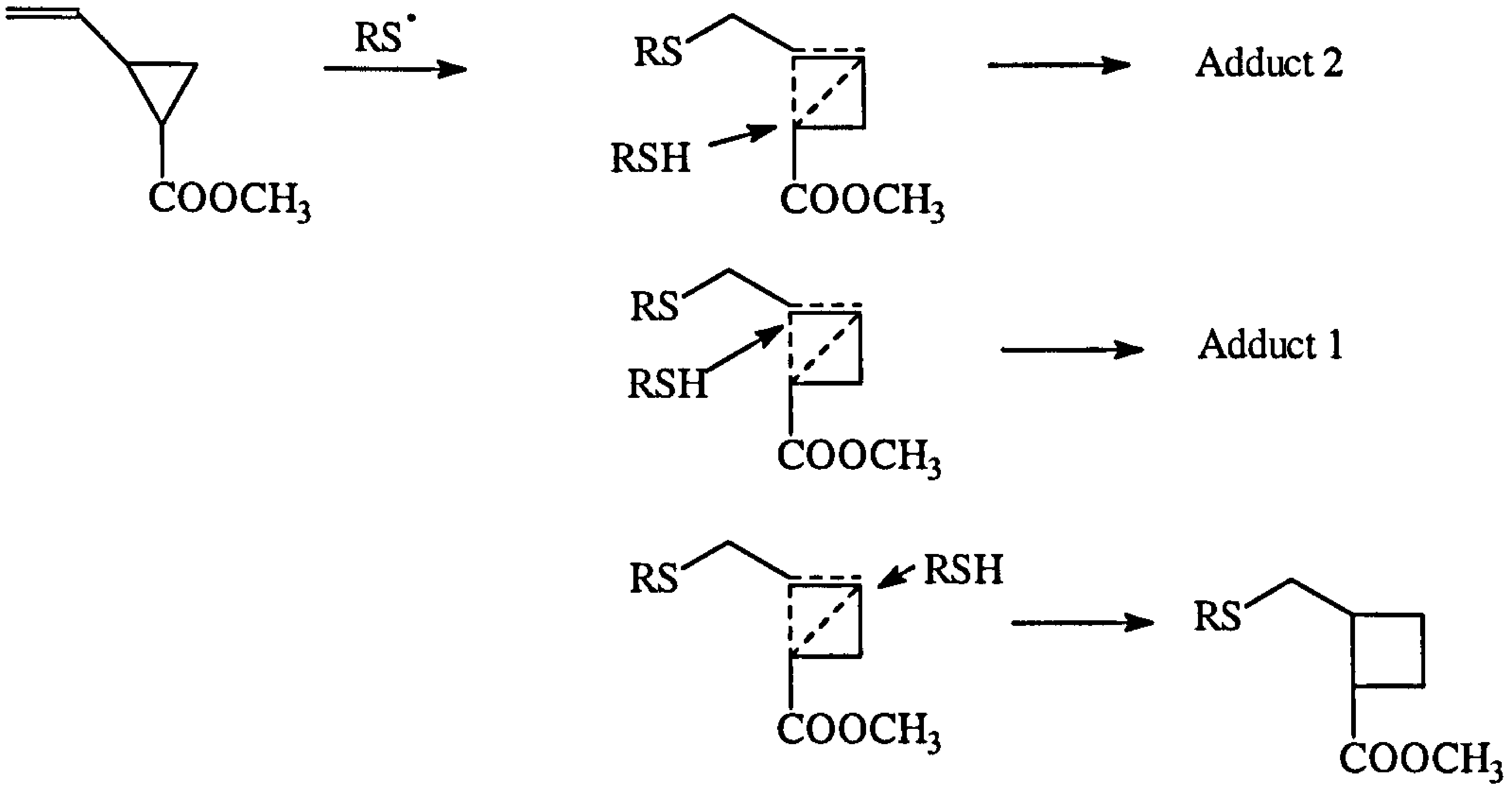
Using chromatography, it was determined that the main product was propane-1,2,3-tricarboxylic acid; no glutaric acid was present. This confirmed that 1,5-addition occurred exclusively.

Also the radical addition of thiols to 1,1-dimethoxycarbonyl-2-vinylcyclopropane was used as a model to confirm the two-stage mechanism of isomerisation polymerisation of alkenylcyclopropanes as shown below.



Adduct 1 Adduct 2

In the reaction with n-propylmercaptan (PM), both adducts 1 and 2 were observed. The ratio of the adducts varied with the ratio of PM to monomer. When the amount of PM was increased, the formation of adduct 1 increased. This is consistent with the above mechanism but inconsistent with the alternative intermediate, a 'nonclassical' radical shown below.[22]

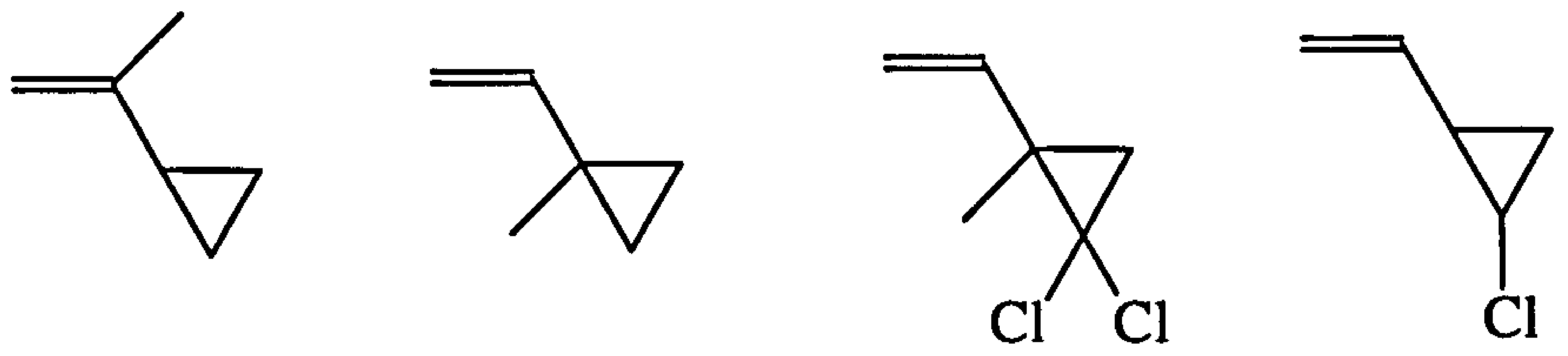


Adduct 3

An excess of PM would not lead to the stabilisation of the transition state leading to the formation of adduct 1 and so the ratio of adduct 1 to adduct 2 would not be dependent on PM : monomer ratios.

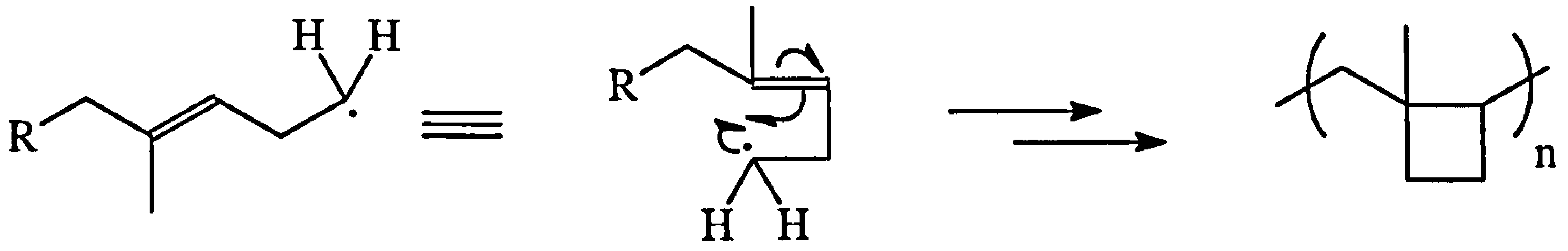
The stability and allylic rearrangement of cyclopropinyl radicals was later demonstrated in 1969 by Kochi who used electron spin resonance to provide evidence for the structure of the radical.[23]

In 1968, Takahashi described the polymerisation of the VCPs shown below.[24]

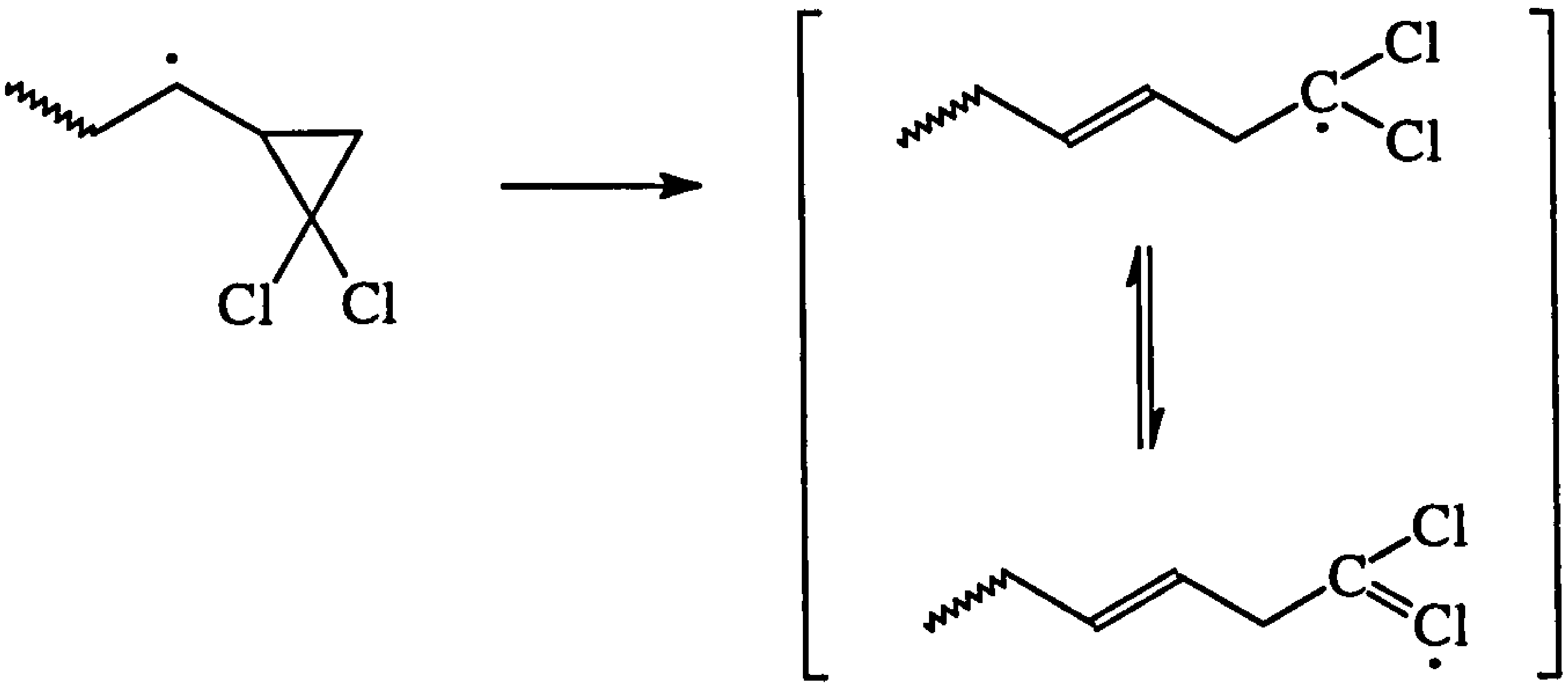


He polymerised these in bulk at 80°C using BPO and AIBN. Isopropenylcyclopropane gave polymers of low molecular weight ($\overline{Mn}$ = 1800) in yields up to 25%. 1-Methyl-1-vinylcyclopropane was not successfully polymerised yielding only a trace of polymer after 2 days reaction time. The two chlorinated monomers gave low yields of low molecular weight polymer.

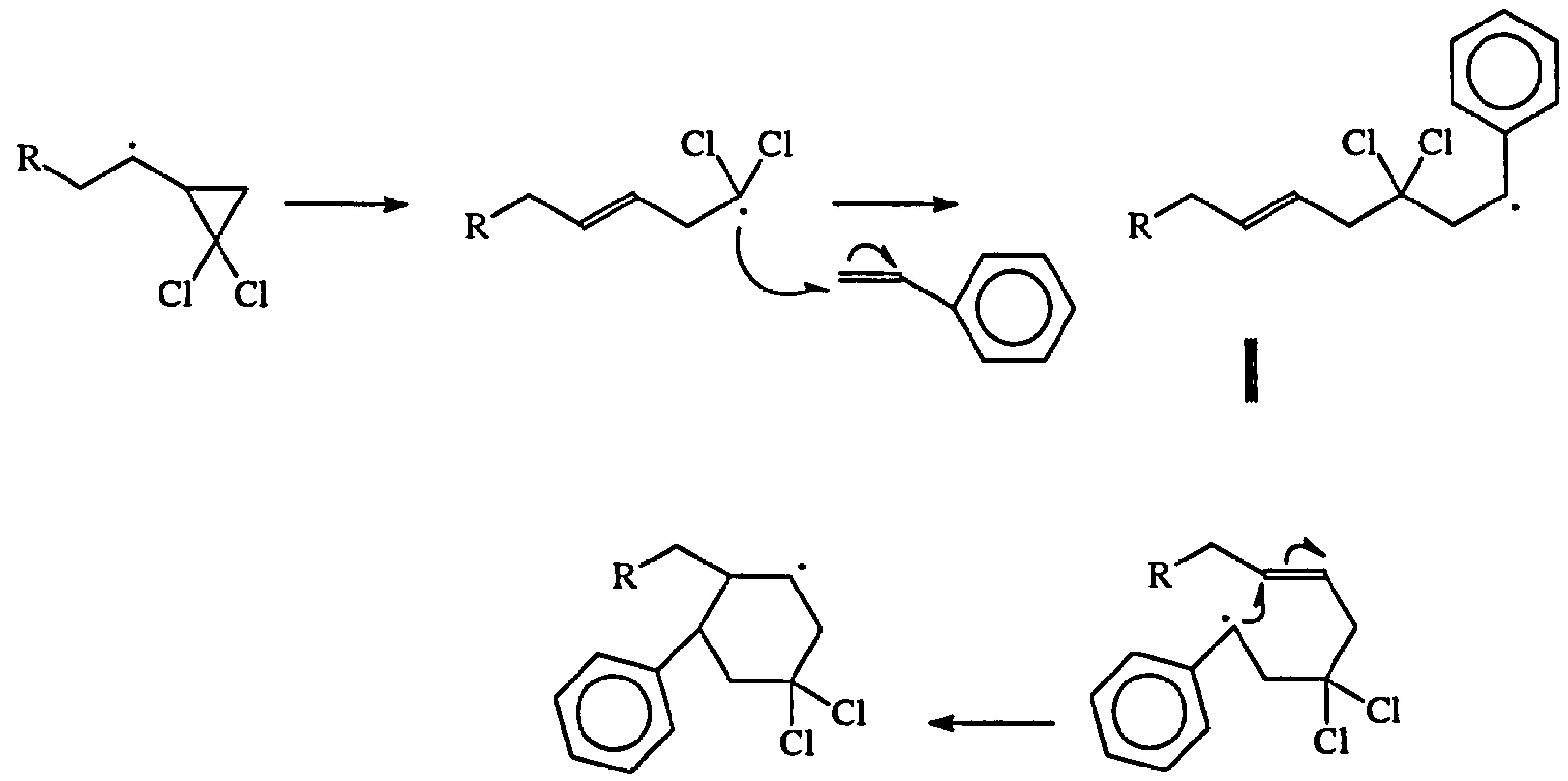
From analysis of the NMR data he concluded that the unchlorinated polymer consisted of about 80% 1,5-addition units. The remaining structural units were thought to be cyclobutane structures.



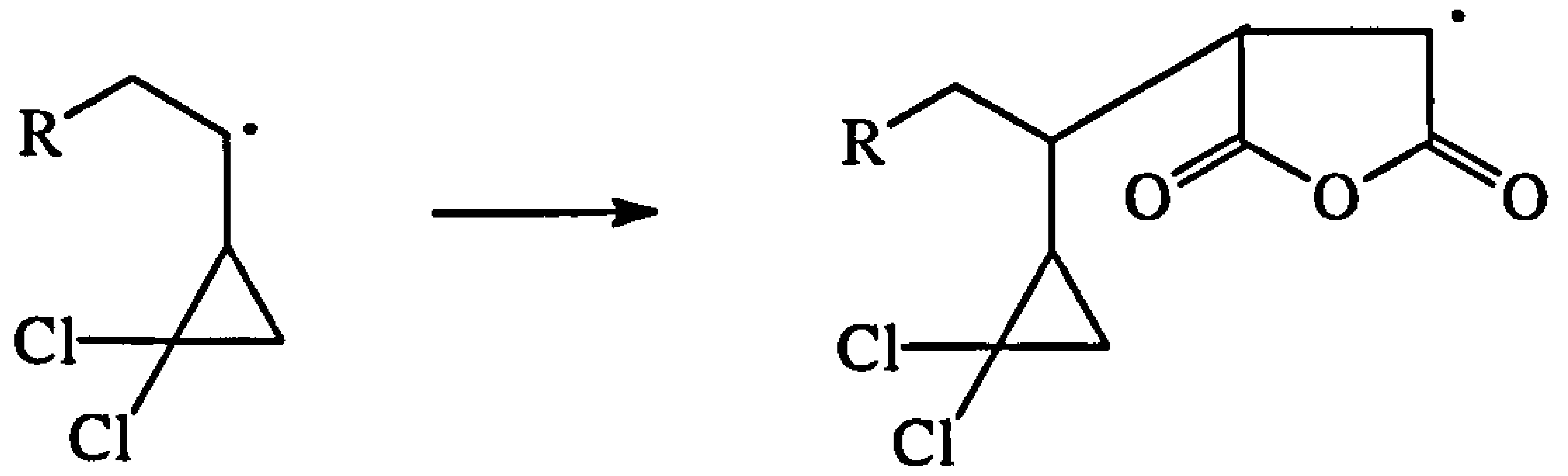
Cyclobutane units were not detected in the chlorinated polymers. This was thought to be due to the resonance stabilisation of the propagating radical chain end by the chlorine atoms.



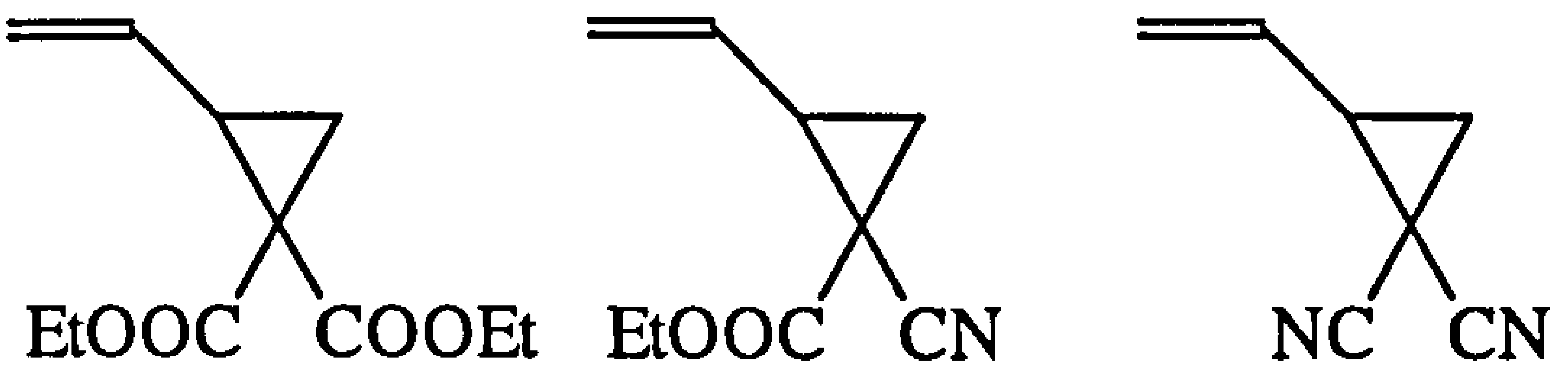
Takahashi continued his work on the polymerisation of VCPs by studying the copolymerisation of 1,1-dichloro-2-vinylcyclopropane with styrene, methylacrylate methylmethacrylate[25] and maleic anhydride.[26] He found that these copolymers contained six membered rings. For example, with styrene;



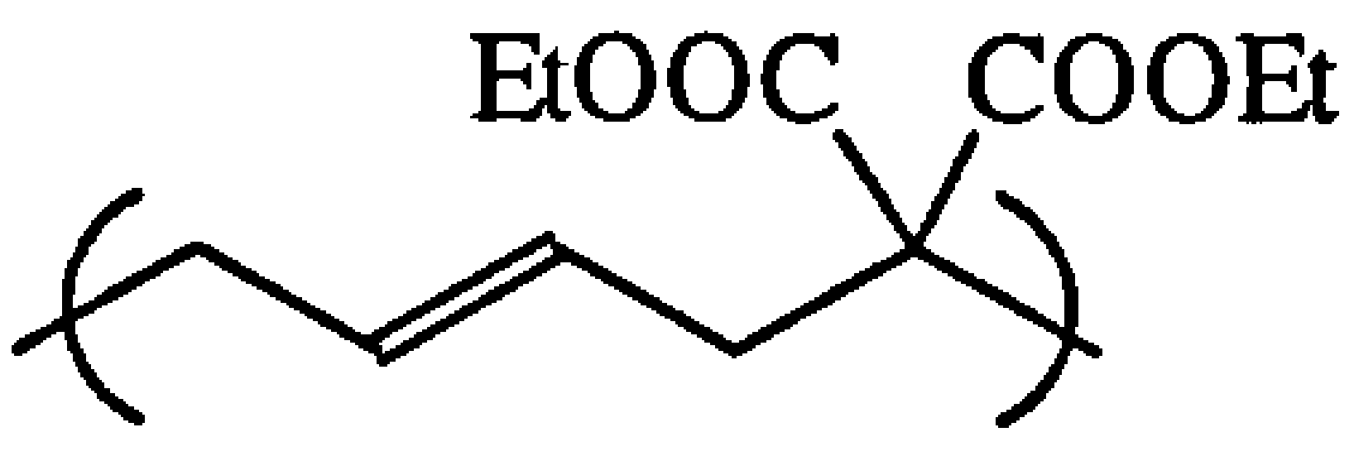
In the case of maleic anhydride / VCP copolymer, it was suspected that 1,2-addition as well as 1,5-addition was occurring. In the homopolymerisation, the rearrangement of the cyclopropylcarbinyl to the allyl radical occurs more quickly than the addition of the monomer to the radical leading to predominantly 1,5-type addition. In the case of the copolymer, it would appear that the maleic anhydride is able to add rapidly to the cyclopropylcarbinyl radical leading to 1,2-type structural units.



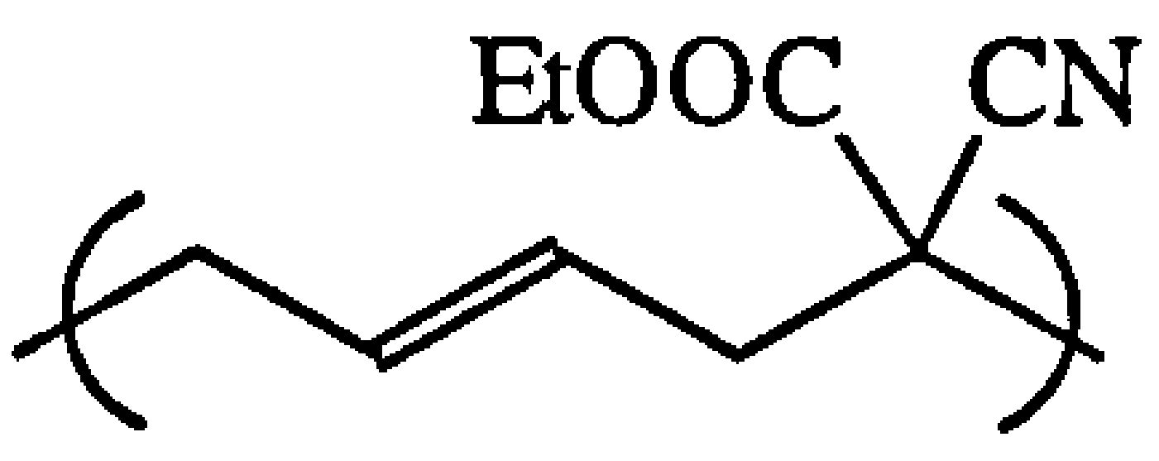
Seven years later, Cho published what he described as 'the first truly clean and facile radical 1,5-type polymerisations of certain vinyl disubstituted cyclopropanes.'[27] He polymerised the following monomers at 55°C using AIBN.



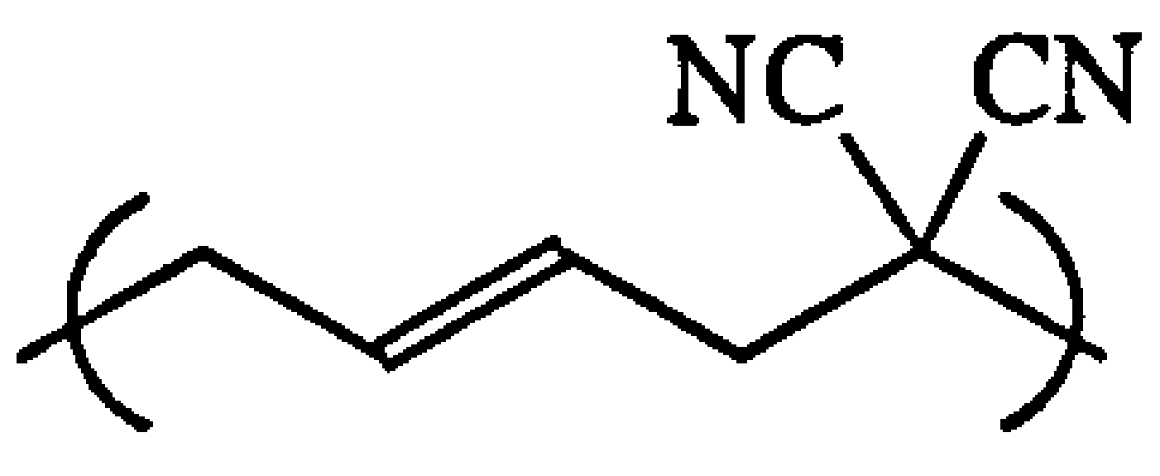
For the first time, high yields (up to 60%) of high molecular weight polymers were obtained. The authors studied NMR and IR data and concluded that the polymers were exclusively 1,5-addition products and all the double bonds had the *trans* configuration. Two years later a second paper published by Cho confirmed his previous results and gave more analytical data on the polymers obtained.[28] Glass transition temperatures were measured and the reported values are shown below.



$T_g = 40^{o}C$



$T_g = 29^{o}C$

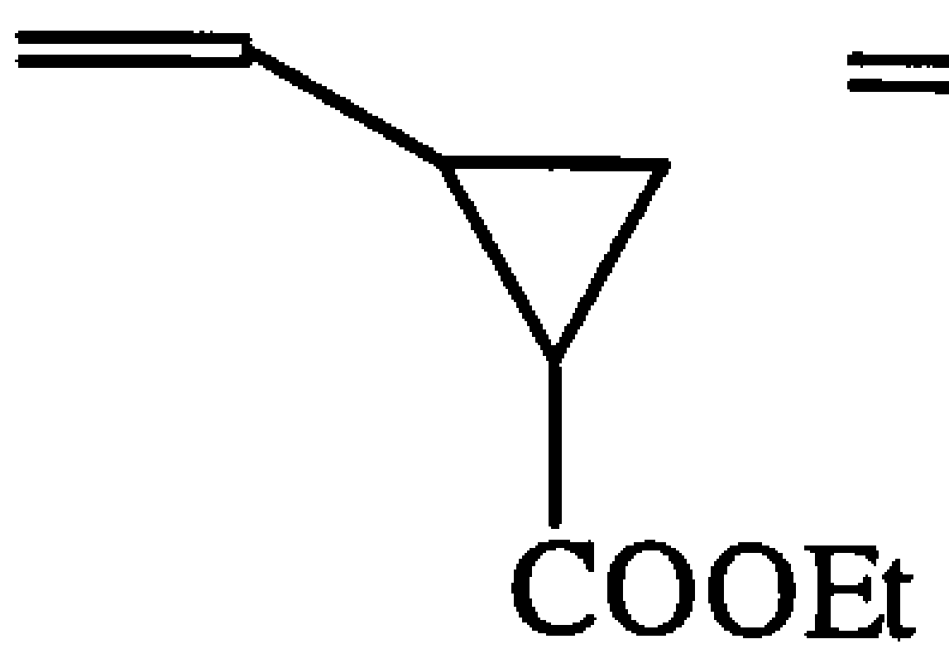


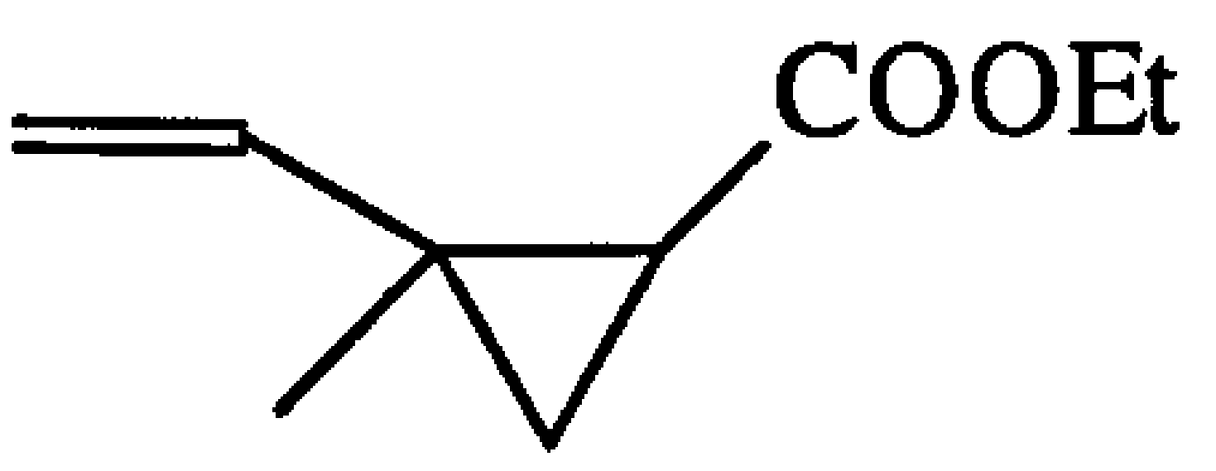
$T_g = 25^{o}C$

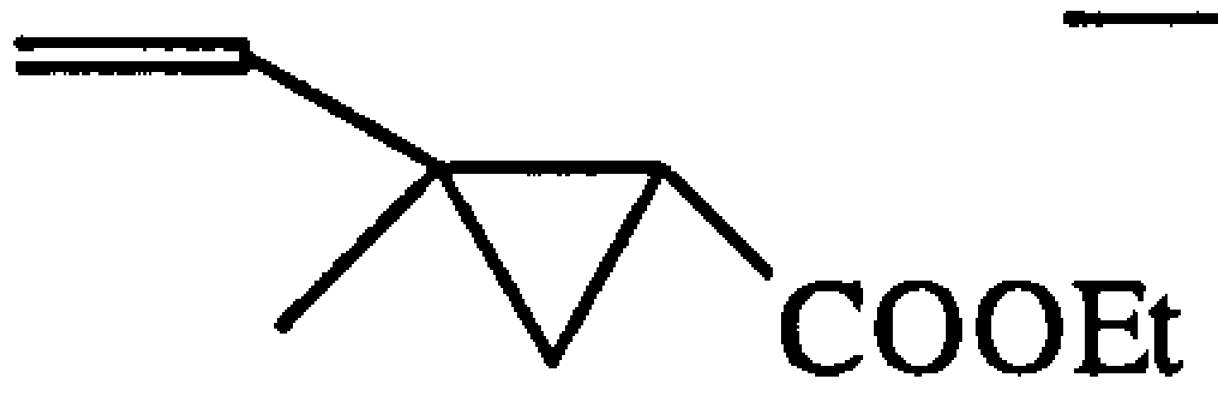
Cho also copolymerised the monomers with acrylonitrile, styrene and vinyl acetate. He found lower conversions were achieved but did not do a detailed analysis of the structure of the polymers obtained.

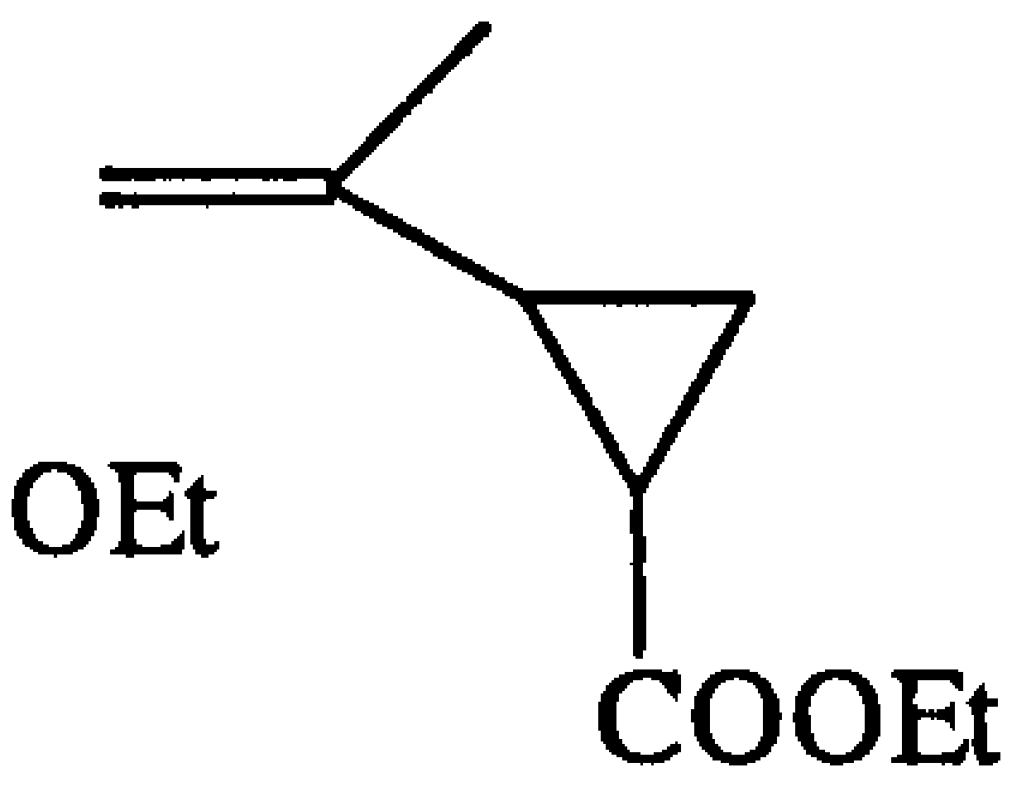
In 1984, Cho continued his work and studied the polymerisation of 1-phenyl-2-vinylcyclopropane and 1,1-diphenyl-2-vinylcyclopropane.[29] He found that the diphenyl monomer polymerised only in low conversion and this was thought to be due to the excessive stabilisation of the radical.

The polymerisation of VCP derivatives bearing ester groups was studied in 1987 by Endo.[30] The following monomers were studied;



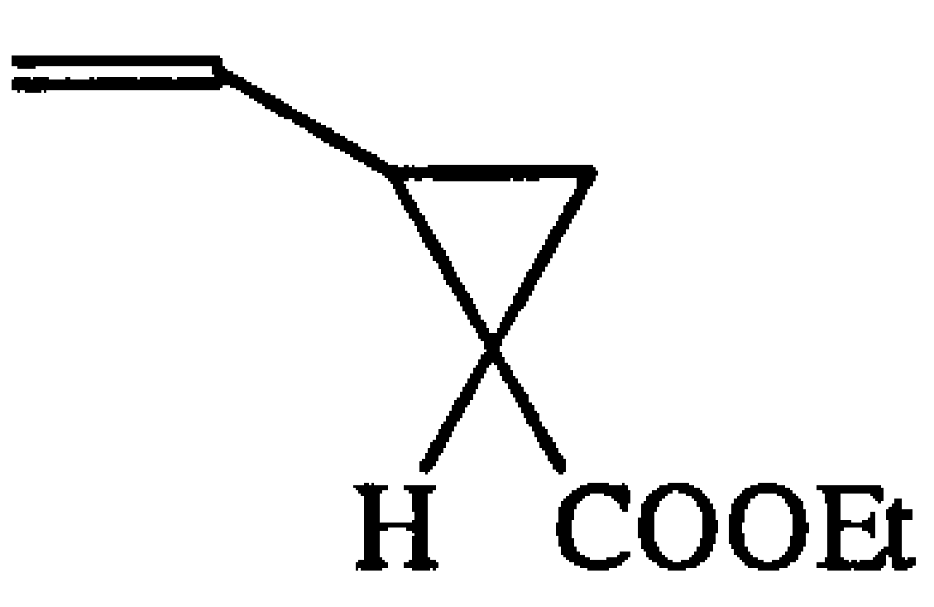


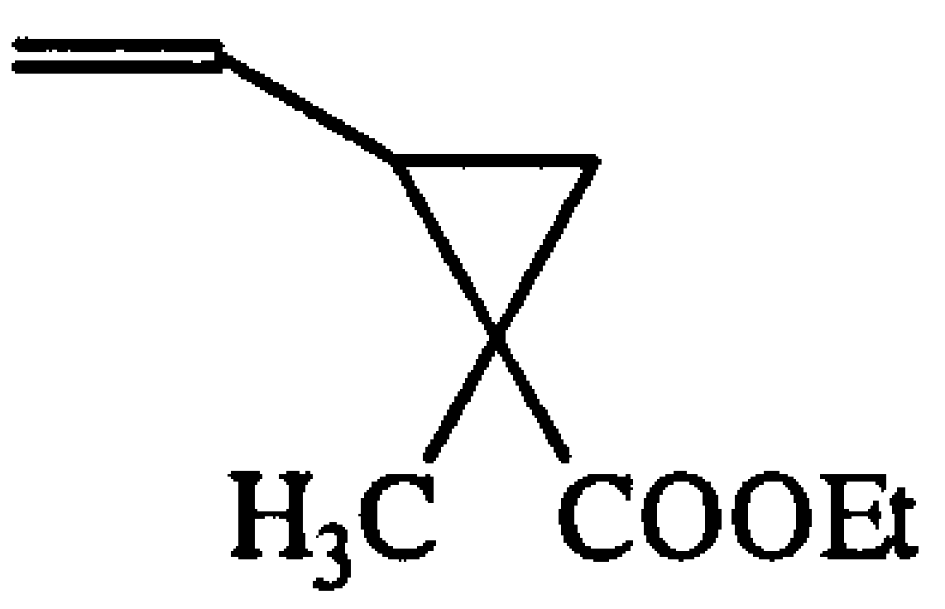


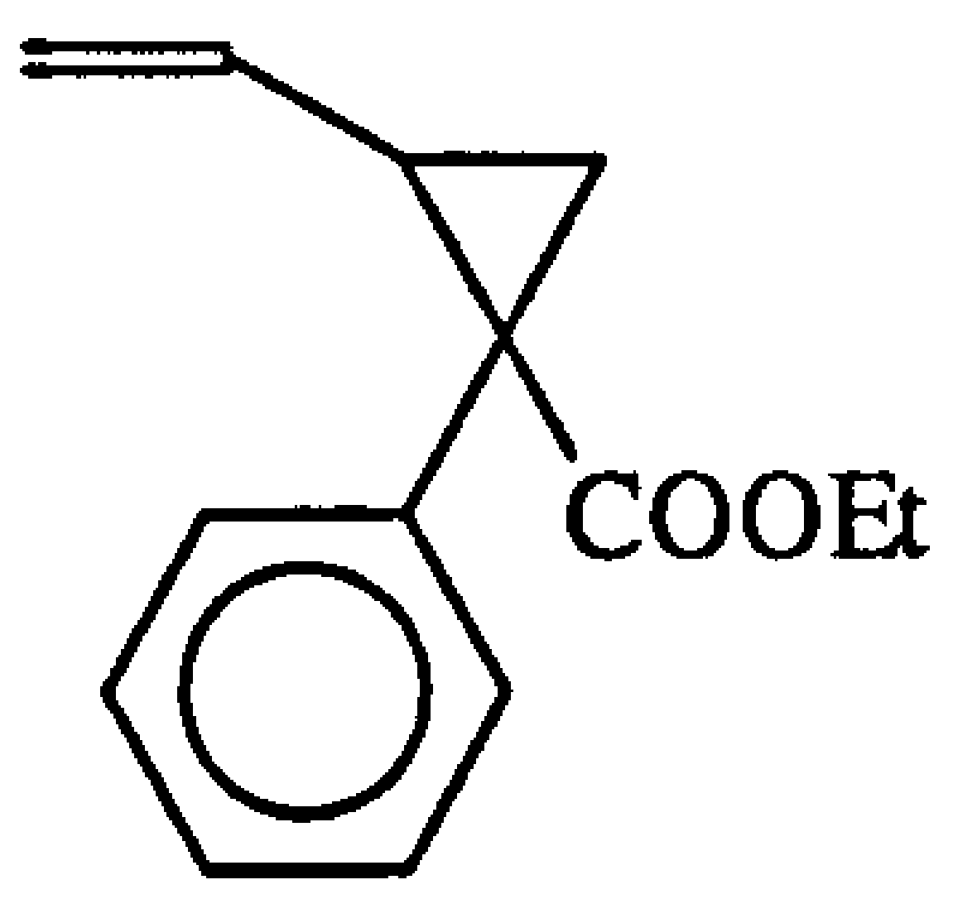


Yields were fairly low (<30%) but high molecular weight ($\overline{Mn}$ ~ 35-122,000) products were obtained. The rates of polymerisation were studied and it was found that the steric bulk of the methyl groups hindered attack of the propagating radical and reduced the rate of polymerisation.

Endo also studied the effect of substituents on the ring on the rate of polymerisation using the following monomers.[31]



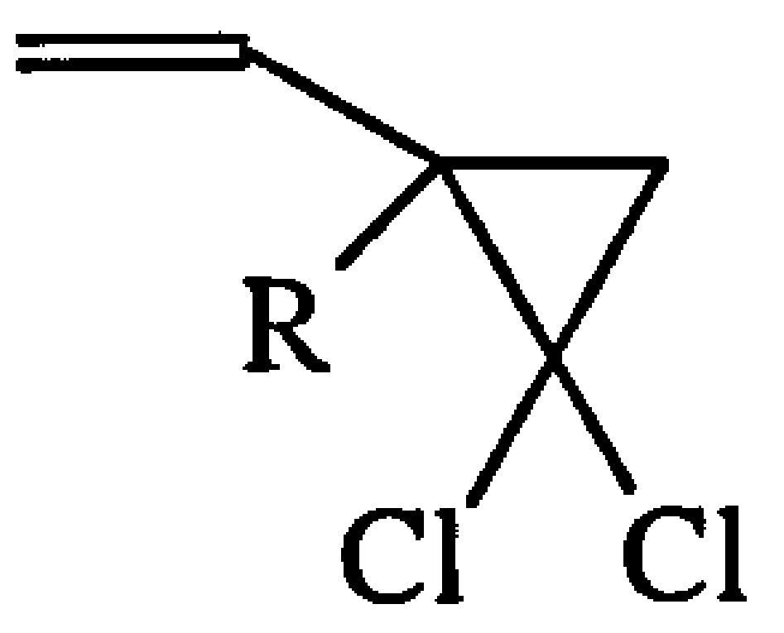




The rate was found to be H > CH_3 > C_6H_5 and this was thought to be due to two factors. Firstly, as the substituents increase in size, steric hindrance increases thus decreasing the ease with which the cyclopropylcarbinyl radical can rearrange to the allyl radical. Secondly, the stability of the propagating allyl radical increases from H to C_6H_5 reducing its reactivity.

Endo continued his work by studying 1,1-diethoxycarbonyl-, -dicyano- and -diacetyl-2-vinylcyclopropanes.[32] He attempted the polymerisations at 60°C using AIBN. He found that the diethoxycarbonyl monomer polymerised in low yields to give the 1,5-addition polymer as reported by Cho. The dicyano monomer polymerised in low yields when benzene was used as the solvent but did not polymerise when DMF was used. The diacetyl monomer did not polymerise.

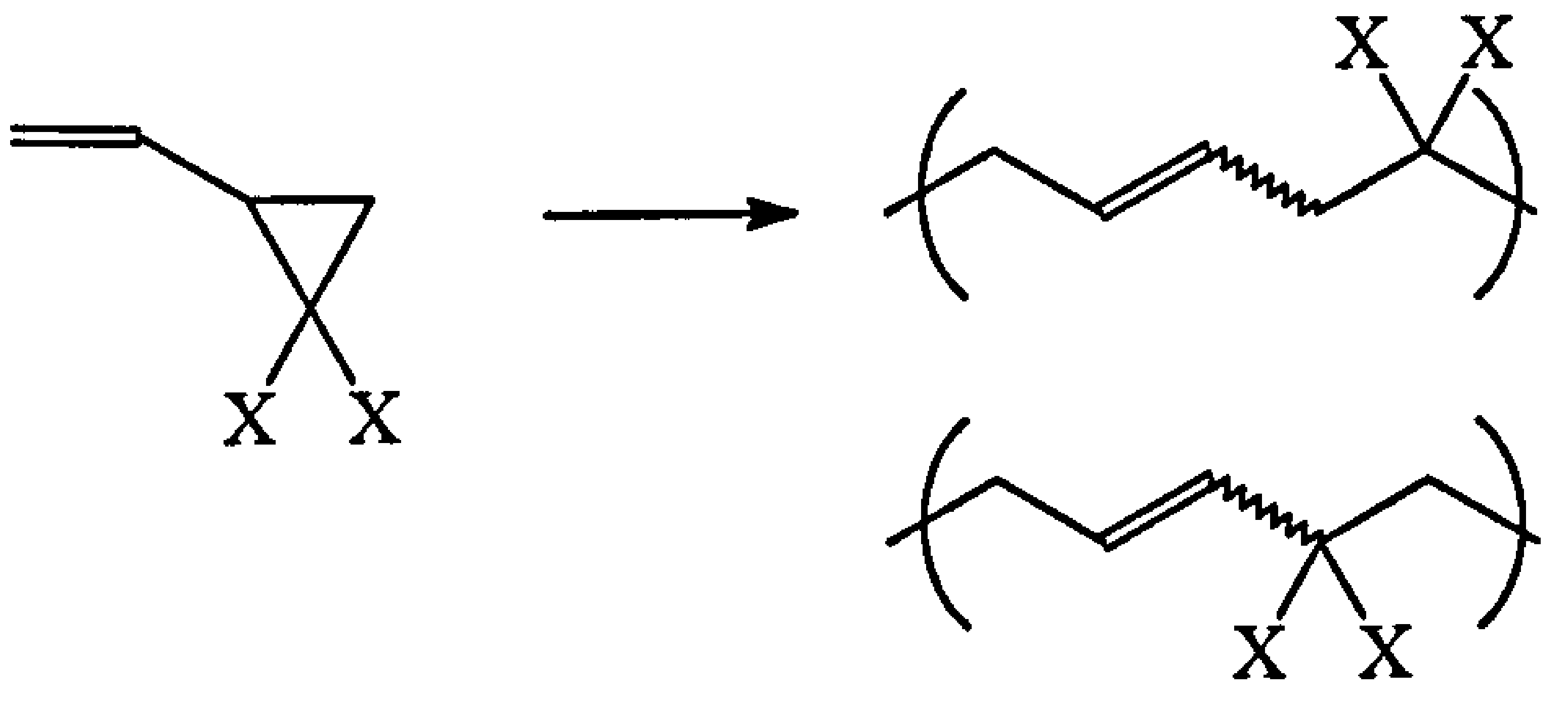
A series of chlorinated monomers was also studied by Endo.[33]



R = H
R = CH_3
R = Cl

All of these monomers were shown to polymerise cleanly by 1,5-type addition.

In 1993, Sando published a paper which contained a detailed analysis of the structure of the polymers obtained from the polymerisation of the dicyano-, dichloro- and diethoxycarbonyl-2-vinylcyclopropane monomers.[34] He claimed that three types of units were present in the polymers.



1

2

(Unknown) 3

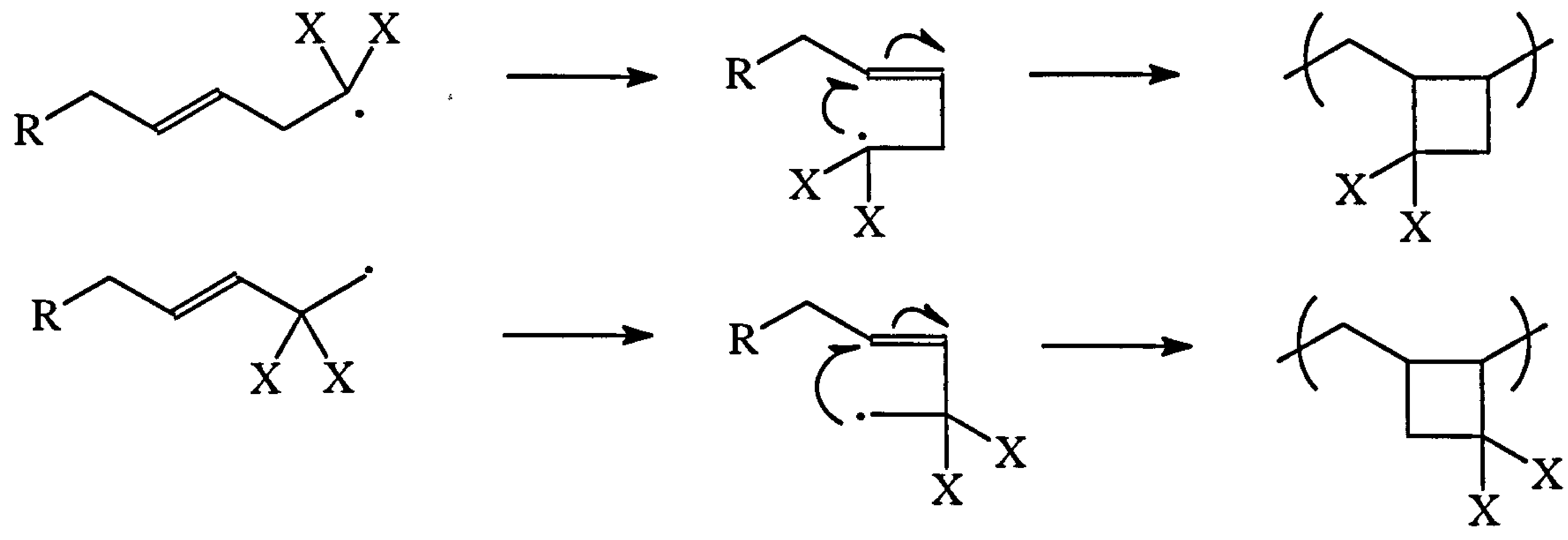
The percentages of each unit present in the polymers is shown in the table below.

X =	% **1**	% **2**	% **3**
Cl	55	21	24
COOEt	58	0	42

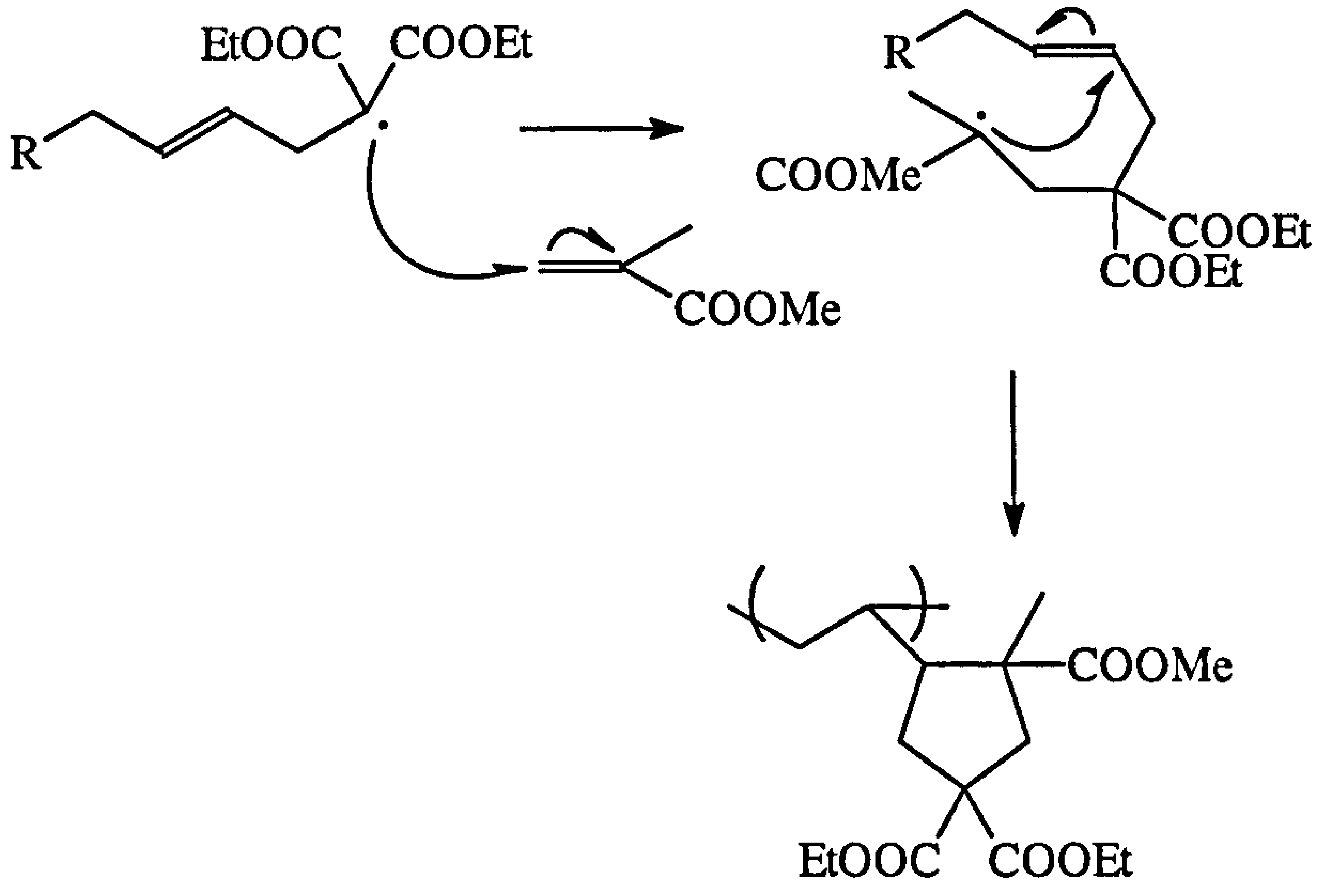
Table 1-2 Percentages of the various units present 1,1-dicyano- and 1,1-diethoxycarbonyl-2-vinylcyclopropane polymers

Details were not obtained for the cyano polymer due to its insolubility in a solvent suitable for NMR analysis. It was thought that no 1,4-addition product (**2**) was observed for the diethoxycarbonyl polymer due to the high radical-stabilizing effect of the substituent leading to selective cleavage of the ring.

It was suggested that the unknown structure was the cyclobutane unit previously suggested by Takahashi in 1968. Sando suggested two possible isomers.

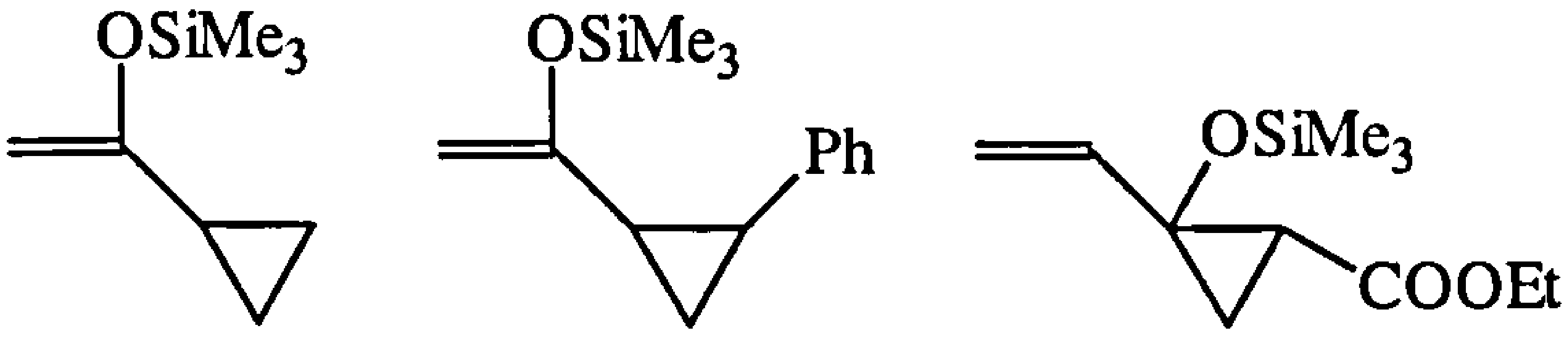


Sando went on to study the copolymerisation of the diethoxycarbonyl monomer with methacrylate.[35] The copolymerisation previously carried out by Takahashi had formed polymers with structures that had not been fully characterised. He had suggested the presence of a six-membered ring but had not proved its existence. Sando suggested that the formation of a five-membered ring would be more likely (see below) although from NMR it was not possible to prove conclusively which ring had formed.

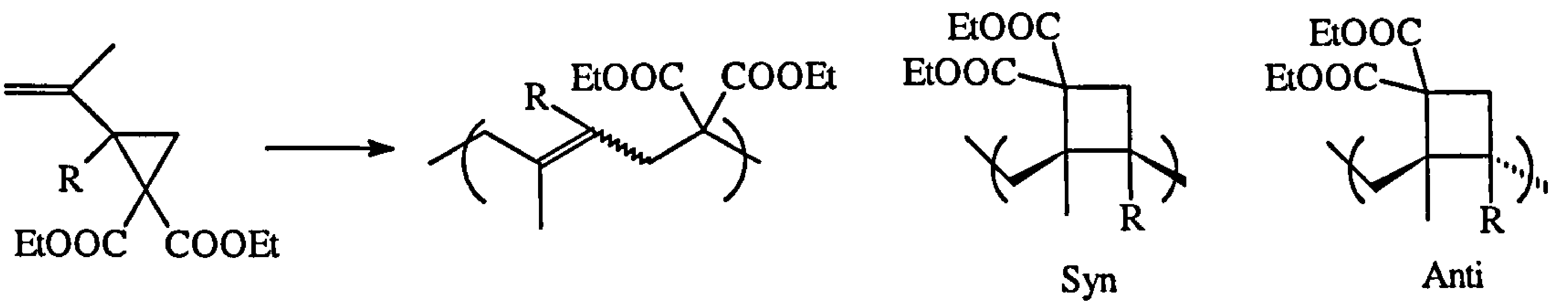


In 1994, Sugiyama observed the formation of the cyclobutane units.[36] He polymerised 1,1-diphenoxycarbonyl-2-vinylcyclopropane using AIBN and formed polymers with glass transition temperatures in the range 76-84°C and molecular weights in the range $\overline{Mn}$ = 90-420,000. Sugiyama was studying these polymers for use as dental materials requiring a high Tg and a low volume shrinkage during polymerisation. Sugiyama found that as the monomer concentration decreased and the temperature increased, the number of cyclobutane units in the polymer chain increased. This lead to a decrease in the molecular weight and viscosity of the polymer.

Mizukami went on to use the 1,5-ring-opening polymerisation of vinylcyclopropanes to prepare poly(silyl enol ethers) from the following monomers.[37]



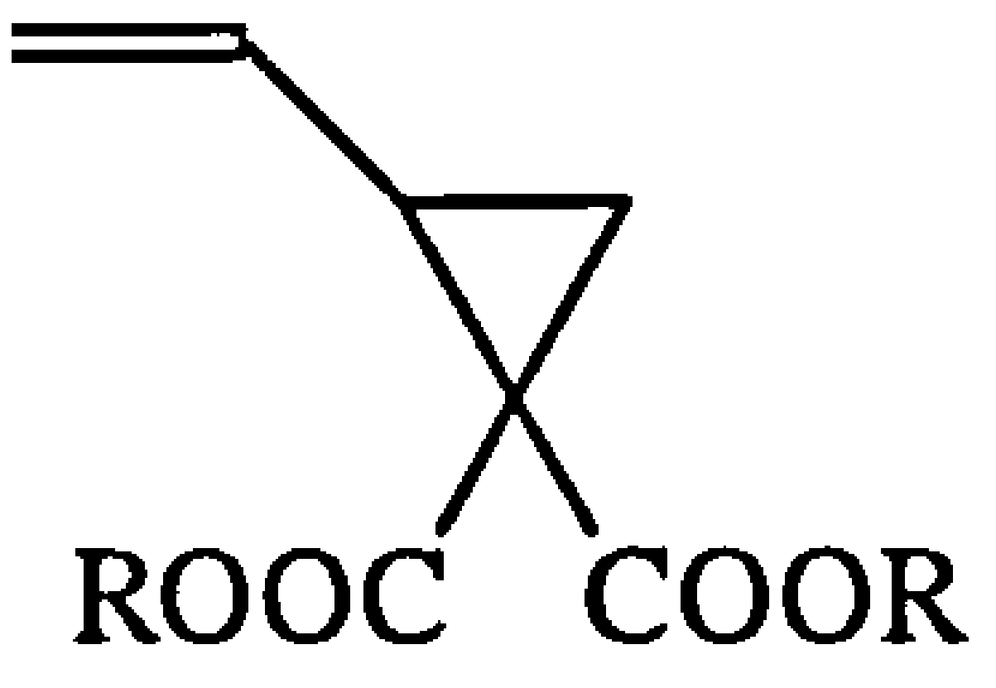
In 1995, Sanda continued his work and studied the polymerisation of the following monomers.[38]



R = H, Me

When R was a methyl group only *trans* double bonds were formed as the steric repulsion of the two methyl groups would be high in the *cis* isomer. When R was hydrogen, a *cis* : *trans* ratio of 33:67 was observed. Sanda was surprised that the cyclobutane units formed when R was methyl as he expected the bulkiness to inhibit the ring formation.

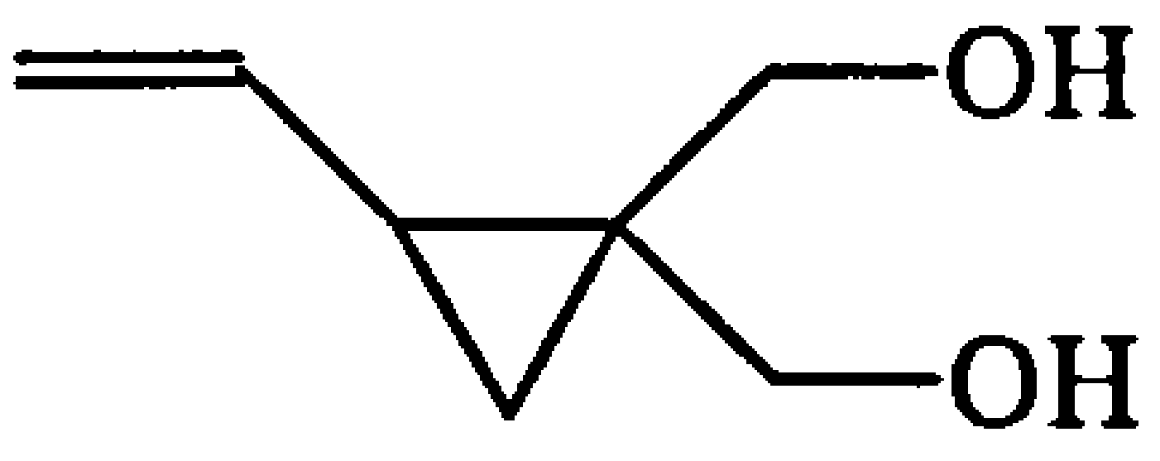
More recently, Zeuner has published a paper concerning the polymerisation of the following monomers.[39]

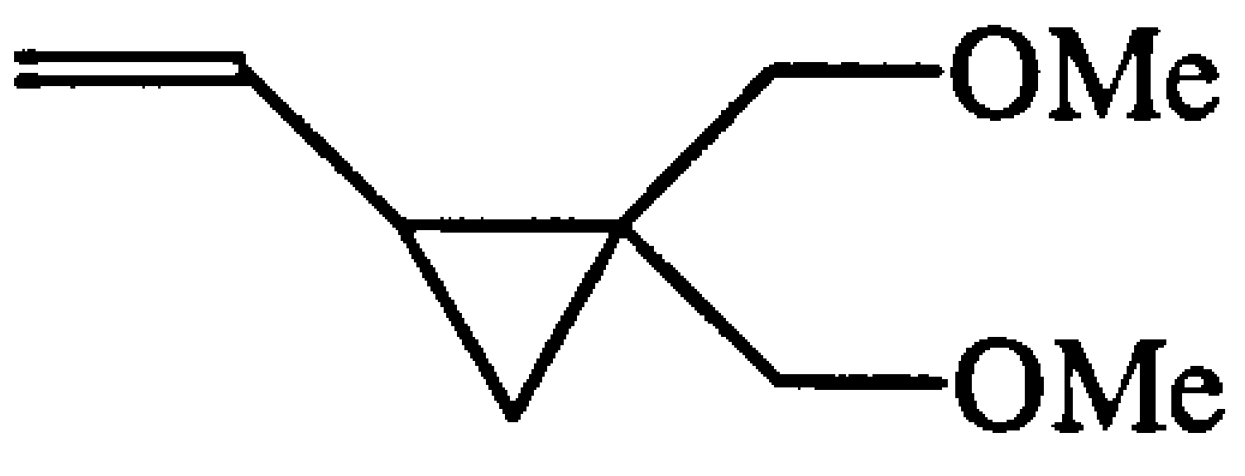


R = C_2H_5, C_6H_5, 3-CH_3-C_6H_4, 4-C_9H_{19}-C_6H_4
C_6H_5-CH_2

Using AIBN and di-*tert*-butyl peroxide (DtBPO), he polymerised the monomers in bulk and obtained polymers with a molecular weight range of $\overline{Mn}$ = 70000-260000 in yields up to 84%. In all cases, polymerisation yielded highly *trans* products. Using DtBPO at high temperatures lead to a polymer with about 20% cyclobutane units.

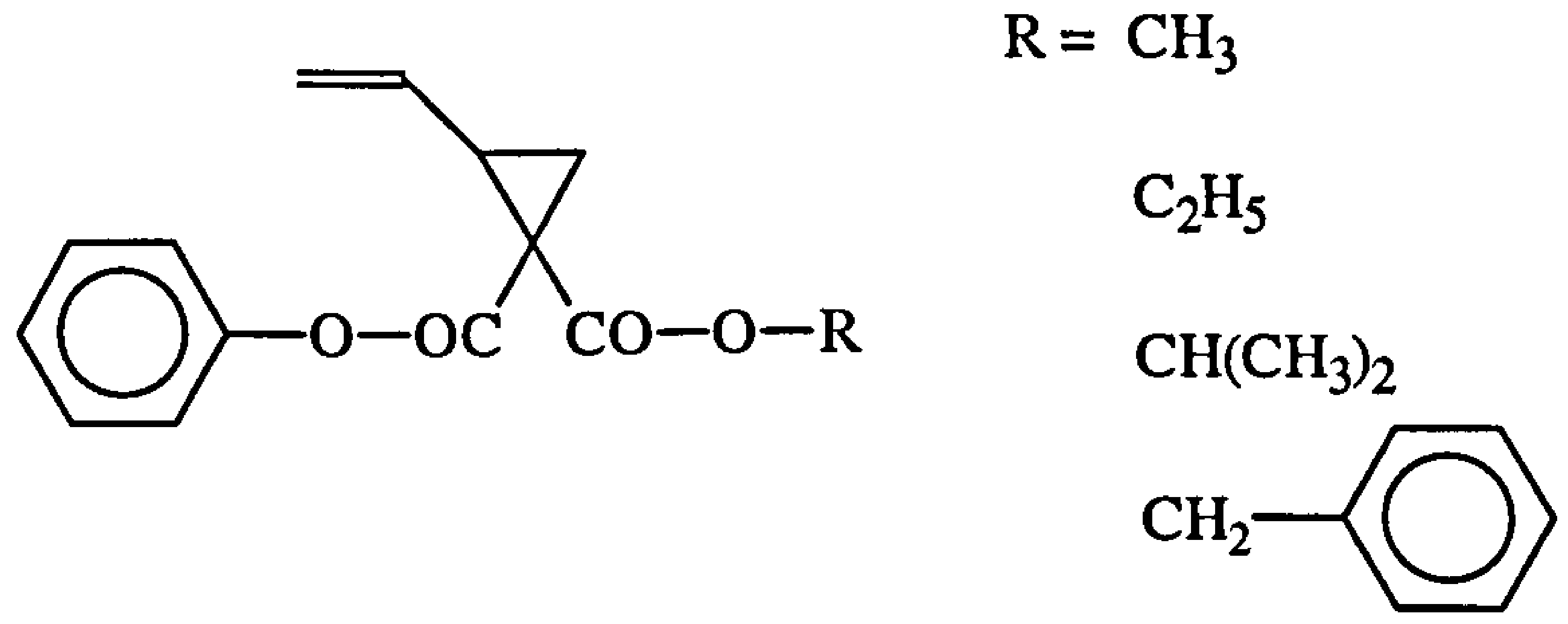
The ring-opening polymerisation of vinylcyclopropanes is still being investigated by several groups. Endo has published a paper on the polymerisation of vinylcyclopropanes bearing hydroxymethyl and methoxymethyl groups.[40]





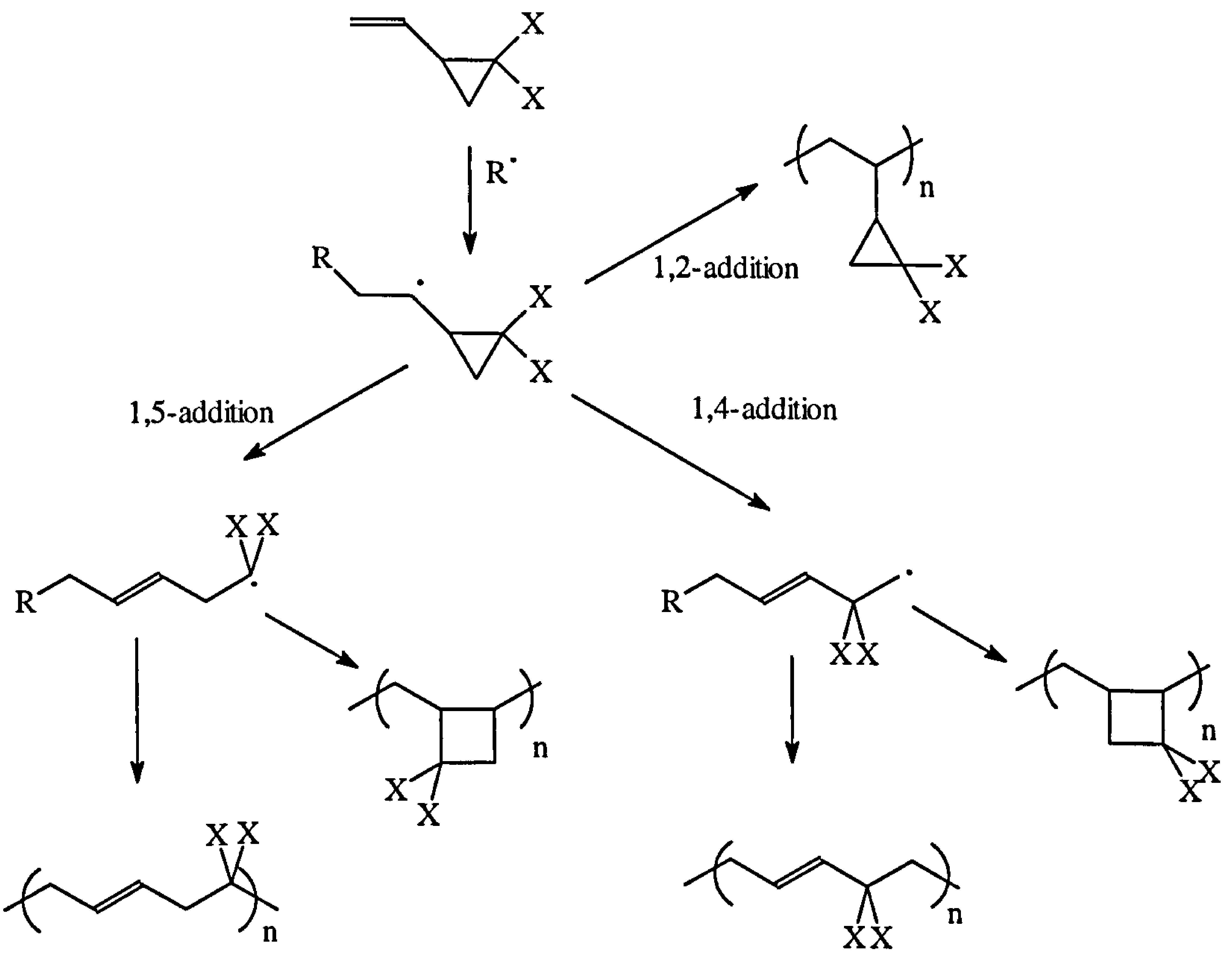
Three structures were identified in the resulting polymer; the 1,5- and the 1,4-addition products, and a unit without the olefinic moiety formed from intramolecular cyclisation.

Moszner has recently published a paper describing the polymerisation of the following asymmetric substituted 1-phenoxy-2-vinylcyclopropanes.[41,42]



The glass transition temperature of the polymers produced ranged between 41 and 61°C. Mozner reported the formation of a 1,5-ring-opened unit and a cyclobutane unit as have been previously reported for other monomers.

It can be seen that the ring-opening polymerisation of vinylcyclopropanes is not straight forward and many different structures are formed. The various structures that have been identified to date are shown below.



Several other species have been observed in the copolymerisation of vinylcyclopropanes with conventional monomers, for example 6- and 5-membered rings.

The work reported in this thesis will attempt to reproduce the polymerisation of 1,1-dicyano-2-vinylcyclopropane and to study the polymerisation of several vinylcyclopropane monomers that have not been previously investigated in order to produce polar polymers with glass transition temperatures below room temperature.

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Chapter 2

Polymerisation using the olefin metathesis reaction

2. Polymerisation using the olefin metathesis reaction

2.1 Introduction

The aim of the work reported in this chapter was to produce polar, elastomeric polymers using the olefin metathesis reaction. Firstly, the synthesis of two 3-cyclopentene-1,1-dicarboxylate monomers and their attempted polymerisation by ring opening metathesis (ROMP) is described. Secondly, the synthesis of 1,1-diallyl malononitrile and its attempted polymerisation by acyclic diene metathesis (ADMET) is reported.

2.2 Olefin metathesis

Metathesis refers to the interchange of atoms, or groups of atoms, between two molecules. The olefin metathesis reaction involves catalytically induced breaking and making of carbon-carbon double bonds. In 1964, Banks and Bailey reported the first example of the metathesis of linear alkenes,[1] which they named 'olefin disproportionation'. The process is shown schematically below.

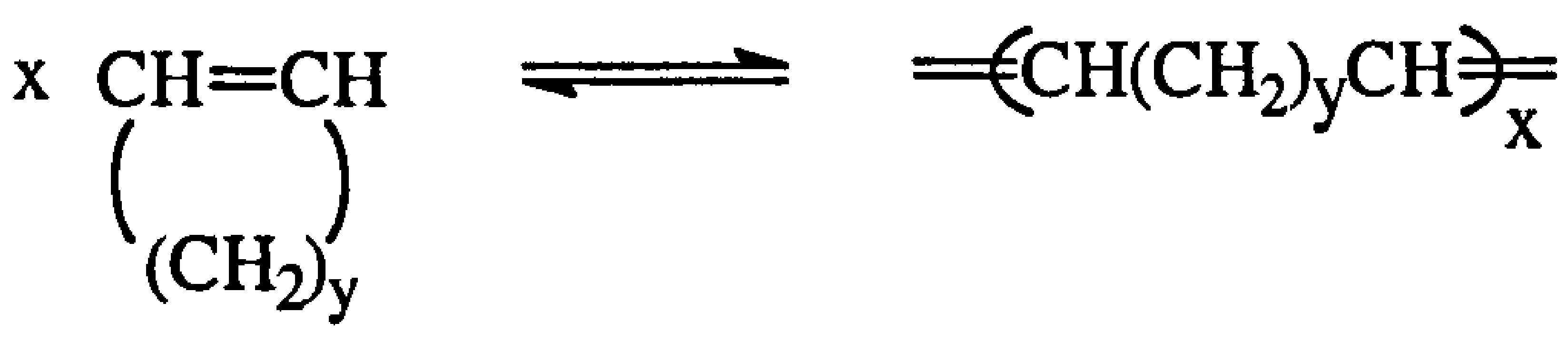
$$2\ \mathrm{RHC{=}CHR'} \rightleftharpoons \mathrm{RHC{=}CHR} + \mathrm{R'HC{=}CHR'}$$

This type of reaction was generally carried out on supported oxide catalysts, most commonly containing tungsten, molybdenum or rhenium, at elevated temperatures (~160°C).

2.3 Ring opening metathesis polymerisation (ROMP)

The scope of the olefin metathesis reaction was expanded when it was found that strained cyclic olefins could undergo ring-opening polymerisation reactions.

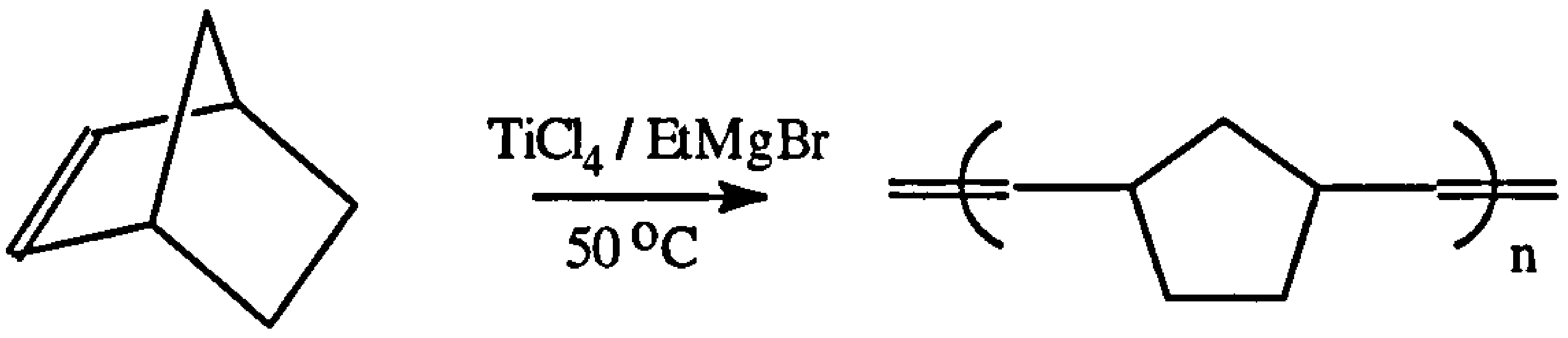
When the alkene is cyclic, olefin metathesis leads to ring scission and the cyclic monomer is converted to a linear unsaturated polymer in a process known as ring opening metathesis polymerisation (ROMP), see below.



$$x\ \underbrace{\mathrm{CH{=}CH}}_{(\mathrm{CH_2})_y} \rightleftharpoons =\!\!\left(\mathrm{CH(CH_2)_yCH}\right)_x\!\!=$$

2.3.1 History

Examples of ROMP had appeared as early as 1955 when Anderson and Merckling described the polymerisation of norbornene.[2]



They did not, however, appear to appreciate the structure of the polymer and the importance of the reaction. It was not until 1960 that the polymer was shown to be a polyalkenylene.[3]

In 1957 Eleuterio filed patents describing the synthesis of linear polymers via ROMP of a wide variety of cycloolefins, such as cyclopentene and norbornene using a catalyst prepared from molybdenum oxide on alumina.[4] In the case of cyclopentene, highly stereoregular *trans*-poly(pentadiene) was formed in low yield.

In 1963, Dall'Asta and Natta studied the polymerisation of cycloalkenes using various catalysts to produce stereoregular polymers.[5] They went on to investigate tungsten and molybdenum halides as catalysts with organolithium compounds as activators and again produced stereoregular poly(pentadiene) by ROMP.[6]

Initially, it was not realised that the disproportionation of acyclic alkenes and the ring opening polymerisation of cyclic alkenes were examples of the same reaction type. Probably this was due to the differences in the catalysts and the reaction temperatures used for the two reactions. Usually disproportionation was carried out on supported oxide catalysts such as MoO_3/Al_2O_3 at elevated temperatures whereas ROMP was carried out at room temperature using catalysts such as $MoCl_5/Et_3Al$ in inert solvents. However, in 1967, Calderon discovered that the same catalyst ($WCl_6/EtAlCl_2/EtOH$) could be used for both reactions and he realised that the reactions proceeded by a common mechanism.[7] He then introduced the term 'olefin metathesis' to describe this common reaction.

2.3.2 Catalysts

There are a number of catalysts which are known to initiate the olefin metathesis reaction. Organometallic compounds containing molybdenum and tungsten are generally the most active initiators, but some compounds containing the following transition metals have been shown to be active.

IVB (4)	VB (5)	VIB (6)	VIIB (7)	VIII (8)	VIII (9)
Ti	V	Cr			
Zr	Nb	Mo		Ru	Rh
Hf	W	W	Re	Os	Ir

Table 2-1 Transition metals with compounds shown to be active for olefin metathesis

The initiators can be divided into two main types; classical and well-defined.

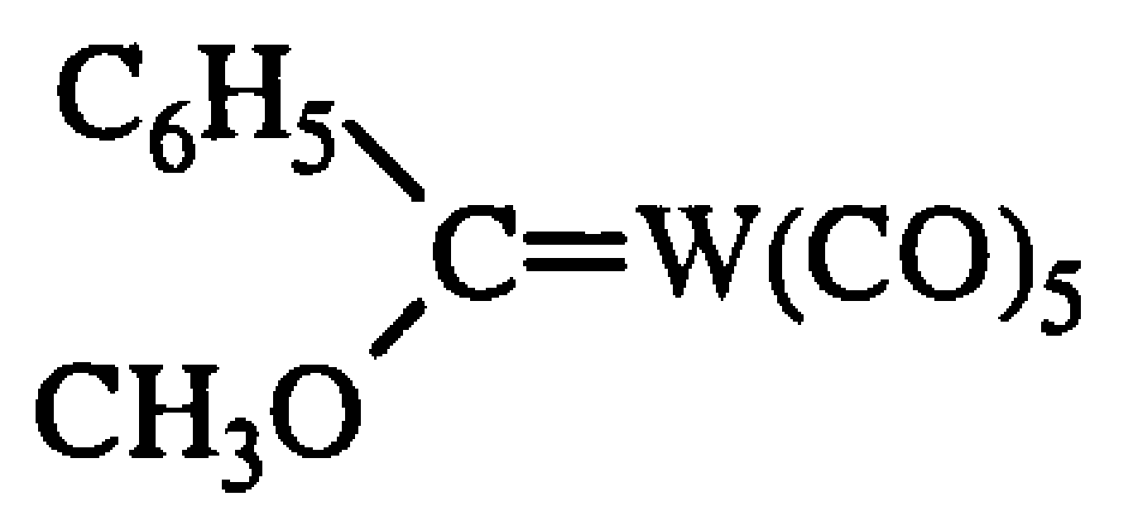
2.3.2.1 Classical initiators

Classical initiators are ill-defined, dual component systems and usually are derived from the chlorides, oxides or oxychlorides of molybdenum, tungsten or rhenium. In some cases, these catalysts are effective by themselves but more commonly, they require a cocatalyst, often a Lewis acid and/or alkylating agent. In some cases a third component, typically containing oxygen, is required as a promoter. Examples of these classical initiator systems are $WCl_6/EtAlCl_2/EtOH$ and $WOCl_4/Me_4Sn$. It is thought that a metal carbene is generated by the reaction between the two main components but the mechanism is complex and many side reactions are possible. As a result, the exact nature of the active site is unknown or ill-defined. This in turn means that there is little control over the molecular weight or stereochemistry of the polymer. There is also an element of irreproducibility because the production of the initiating carbene is dependent on physical parameters such as temperature and concentration. Another disadvantage of classical initiators is their limited tolerance of functional groups.

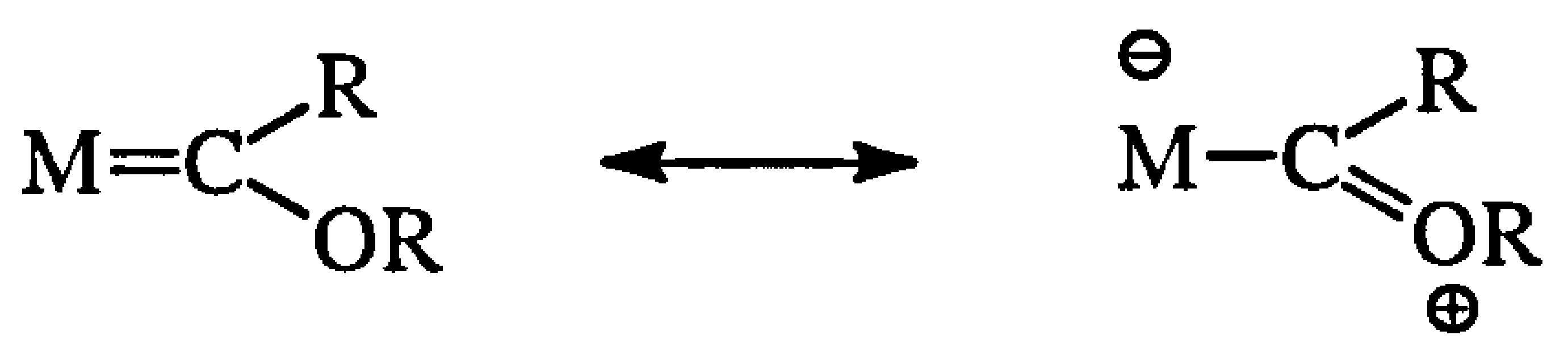
2.3.2.2 Well-defined initiators

In contrast to classical systems, well-defined initiators are able to offer considerable control over molecular weight and stereoregularity.

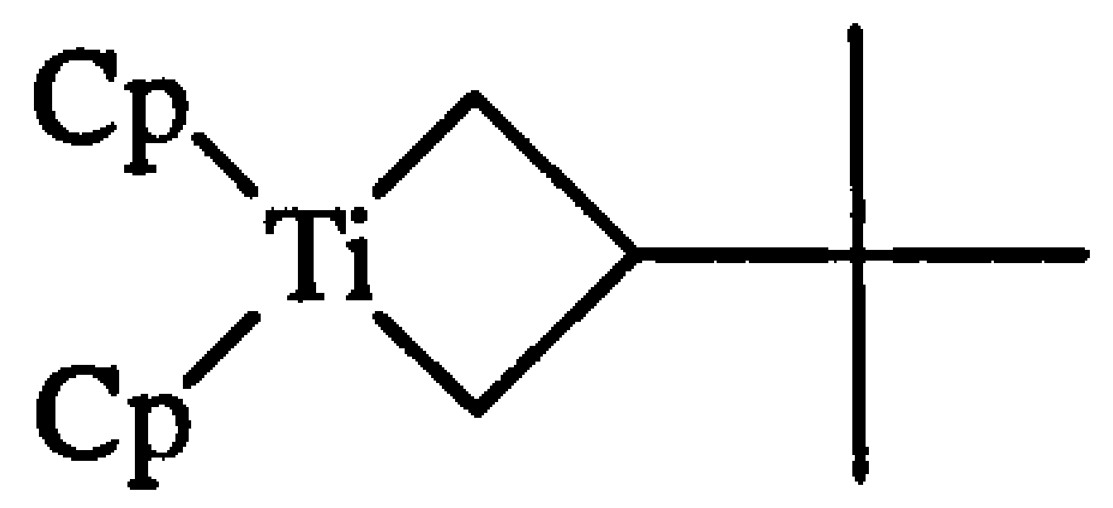
The first carbene species that was found to be capable of inducing olefin metathesis was discovered in 1964 by Fischer.[8]



This carbene had low activity as a catalyst and only induced metathesis in strained olefins such as cyclobutene.[9] The chemistry of the Fischer carbene is influenced by the hetero-atom substituent which is conjugated with the metal d-orbitals through the ligand π-orbitals leading to a significant reduction in the metal-carbon bond order as shown below.

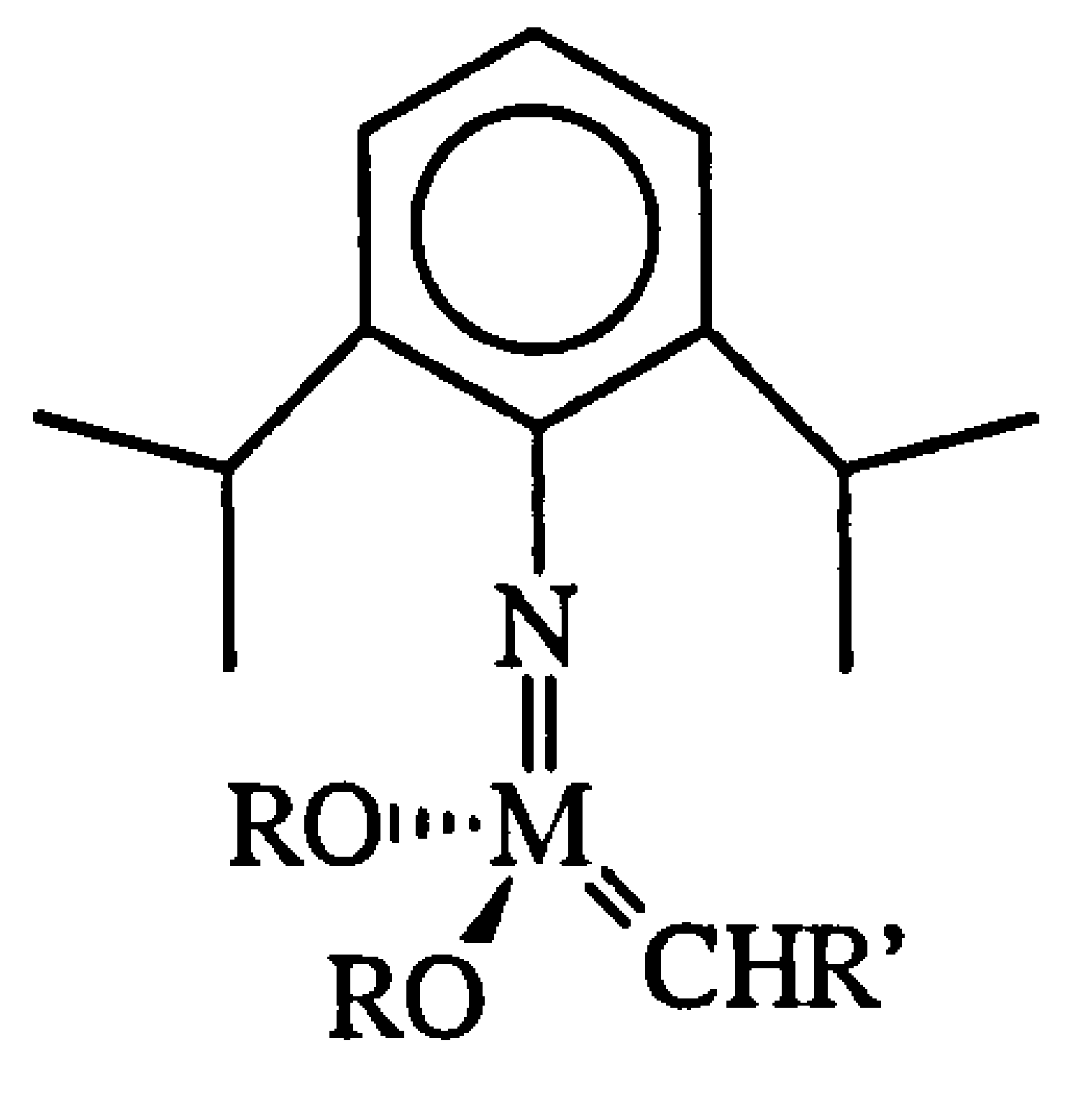


The first example of a living polymerisation system for the ring-opening of cyclic olefins was published by Grubbs and Gilliom.[10] They polymerised norbornene using the titanacyclobutane metallacycle shown below.



The disadvantage of these initiators was the relatively high temperature required (>50°C) in order to polymerise even reactive monomers such as norbornene. They were also very intolerant of functional groups owing to the highly electrophilic nature of the metal centre.

In 1986, Schrock reported a new class of transition metal complexes which were active in olefin metathesis.[11] The basic structure of these initiators is shown below.

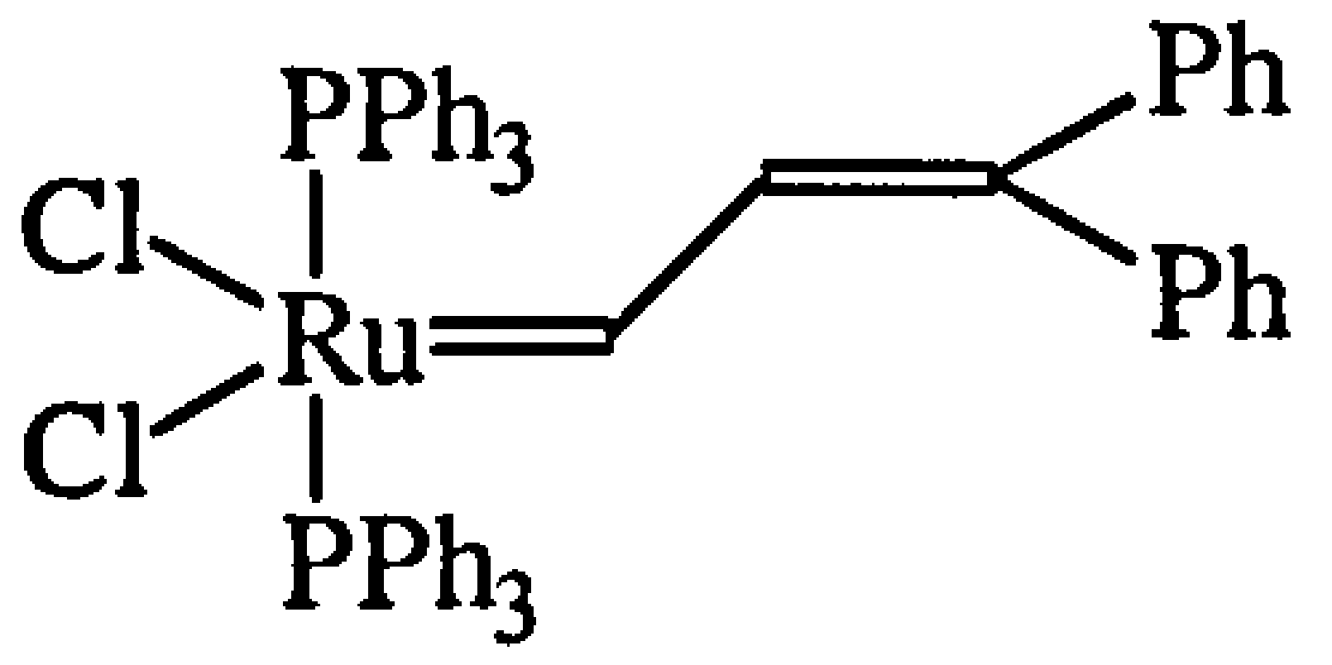


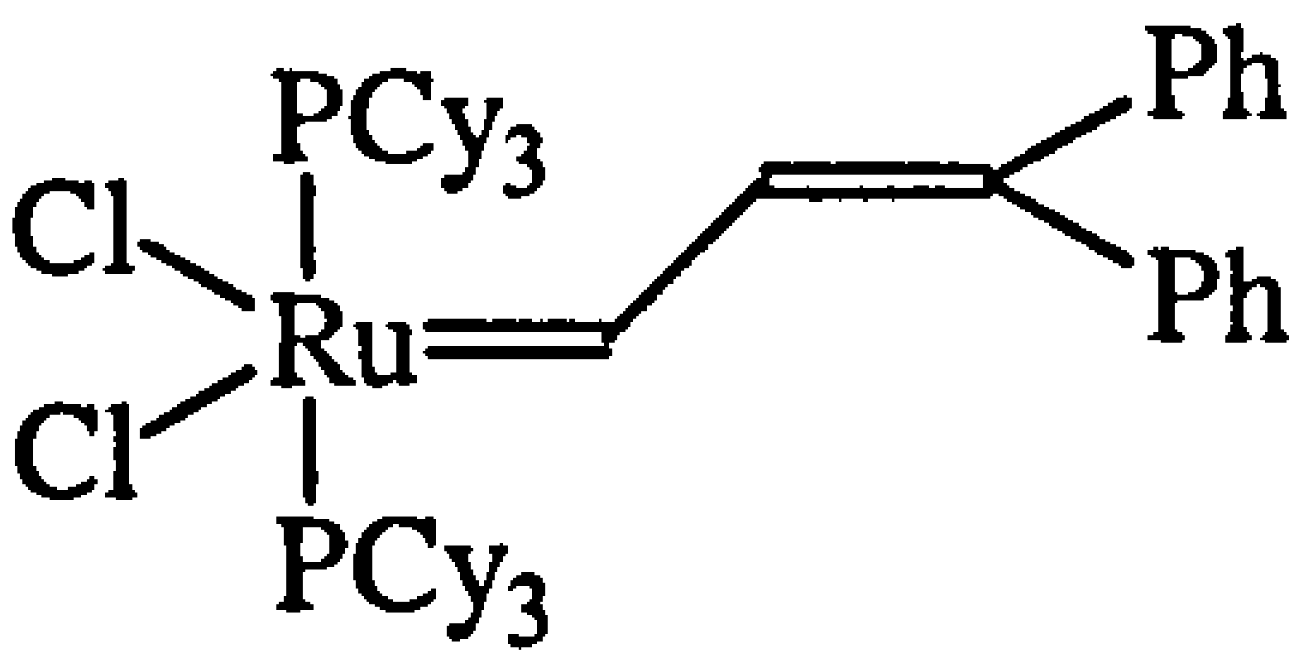
The four co-ordination of the metal atom in these complexes allows a substrate to attack forming a five co-ordinate intermediate metallocyclobutane. The bulky alkoxide and imido ligands shield the metal centre and prevent bimolecular reactions that could destroy the alkylidene ligand which is the site of metathesis reactions.

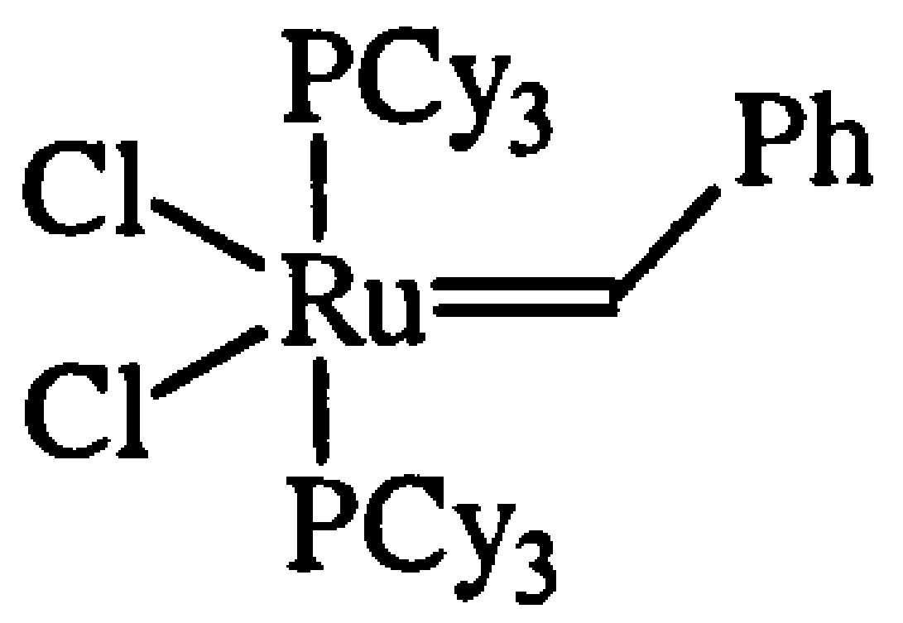
The activity of the initiator can be controlled by replacing the methyl groups on the *tert*-butoxide ligands with trifluoromethyl groups. The increased electronegativity of the trifluoromethyl groups pulls electron density away from the metal centre and subsequently away from the alkylidene double bond making the active centre more electrophilic and therefore more reactive towards incoming nucleophiles.

The two most commonly used metals in Schrock initiators are tungsten and molybdenum. The tungsten analogue is more reactive but, as a result of this increased activity, tolerates few functional groups. The molybdenum analogue is less reactive but is able to polymerise monomers containing a greater variety of functionality.

Recently, Grubbs and co-workers have prepared well-defined ruthenium olefin metathesis initiators which are considerably more tolerant to functional groups than the Schrock initiators and can even be used in protic solvents such as methanol and water.[12]



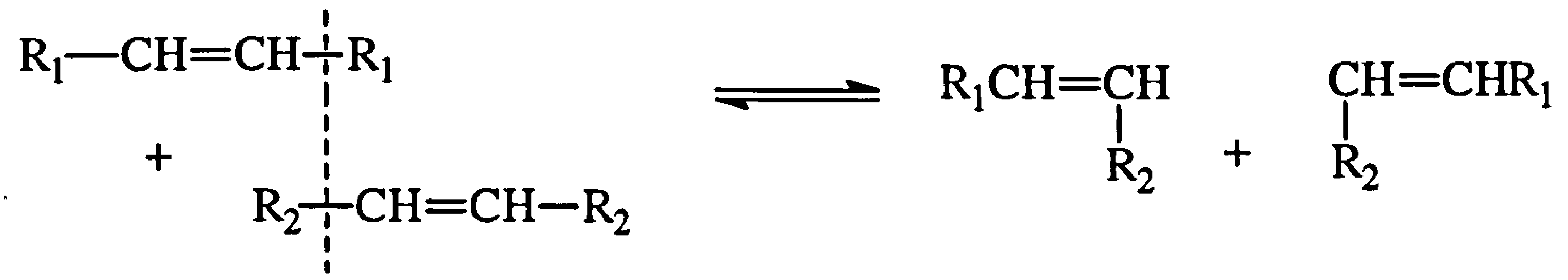




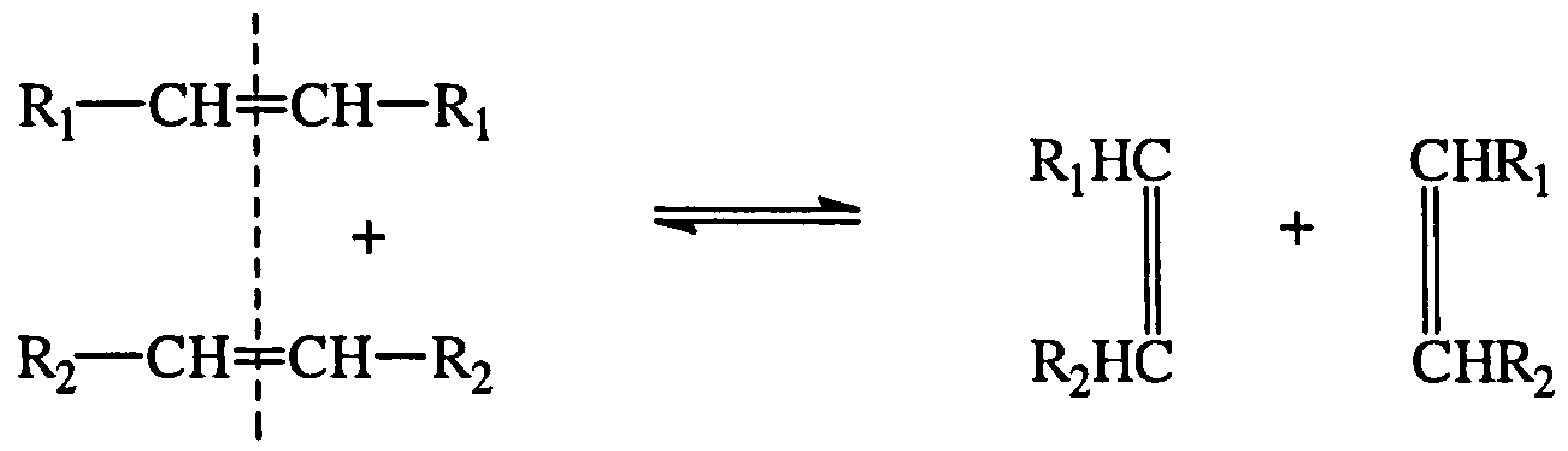
2.3.3 Mechanism of olefin metathesis

There are two pathways that could explain the products of olefin metathesis reactions; transalkylation or transalkylidenation.

Transalkylation involves cleavage of a C-C single bond as shown below.

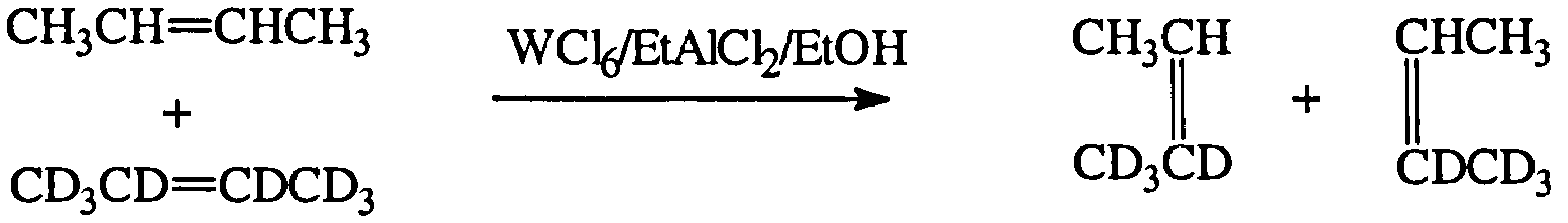


Transalkylidenation involves cleavage of the C=C double bond. See below.



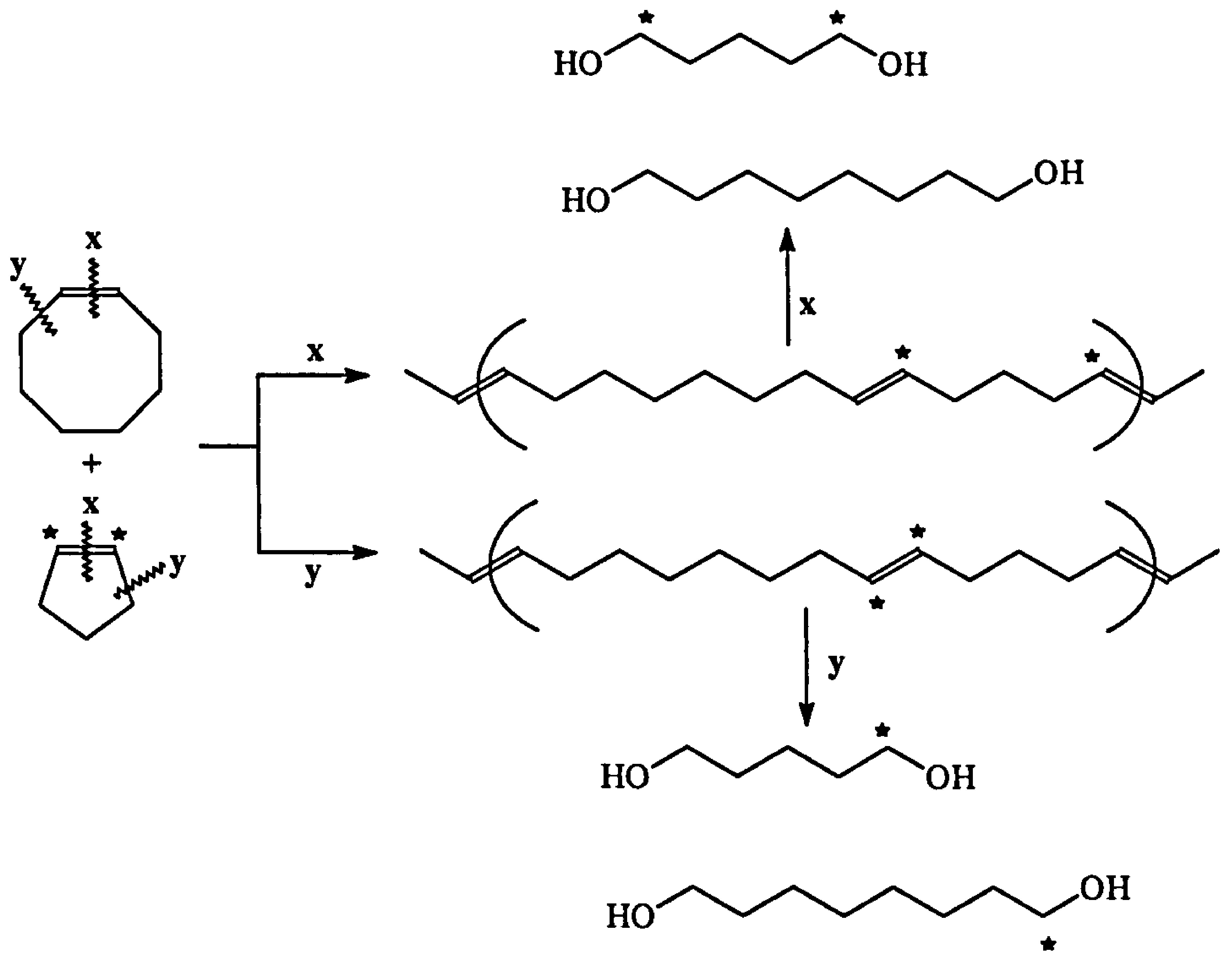
$$\mathrm{R_1{-}CH{=}CH{-}R_1 + R_2{-}CH{=}CH{-}R_2 \rightleftharpoons R_1HC{=}CHR_2 + R_1HC{=}CHR_2}$$

As early as 1967 Calderon showed that transalkylidenation was occurring by studying the reaction of but-2-ene with but-2-ene-d8.[13] The only product was but-2-ene-d4; this can be explained if the double bonds are completely broken and reformed in the reaction as shown below.



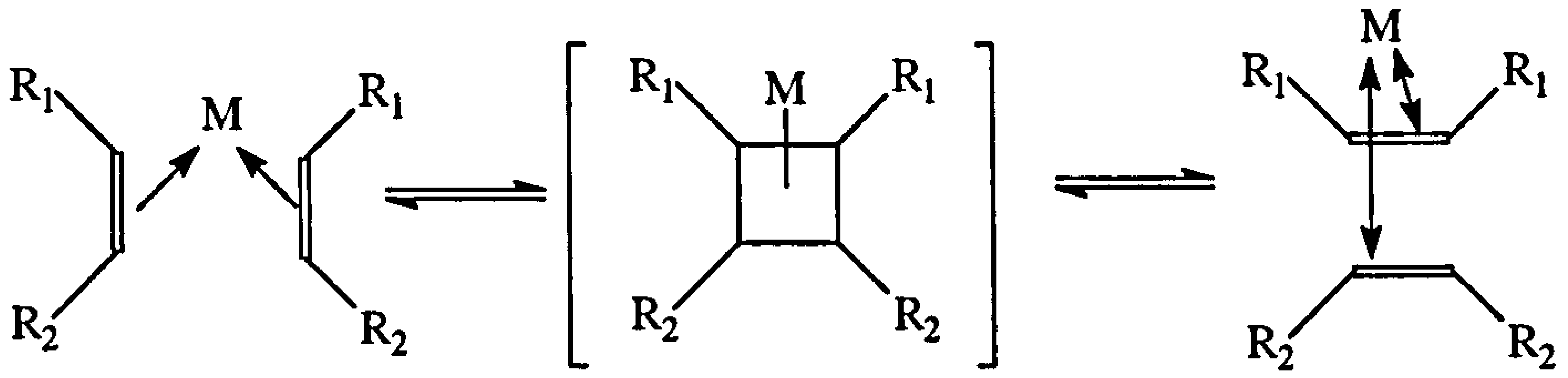
$$\mathrm{CH_3CH{=}CHCH_3 + CD_3CD{=}CDCD_3 \xrightarrow{WCl_6/EtAlCl_2/EtOH} CH_3CH{=}CDCD_3 + CHCH_3{=}CDCD_3}$$

This explanation was confirmed in 1971 when Dall'Asta copolymerised cyclooctene and ^{14}C labelled cyclopentene shown in the scheme below.[14]

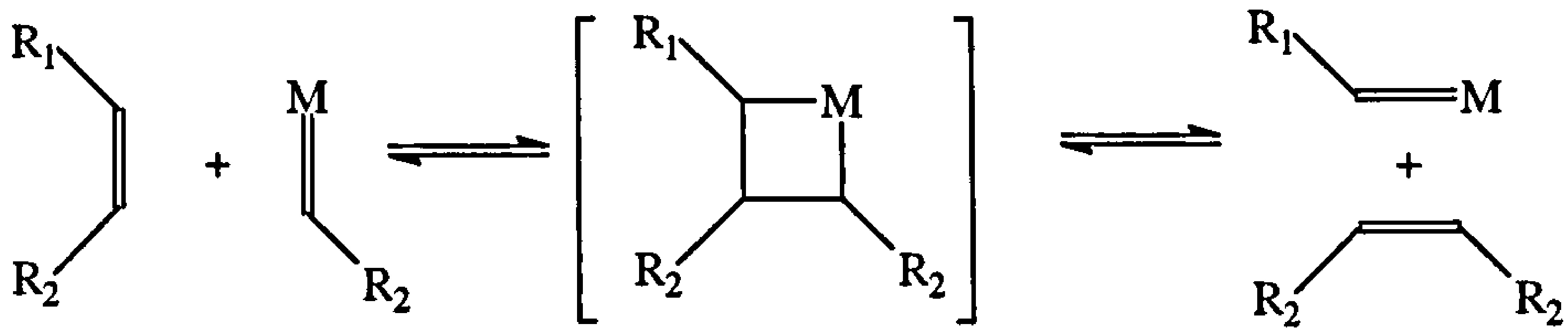


The resulting copolymer was degraded by ozonolysis, reduction of the resulting dialdehyde to diols and analysis of the activity of the diols. The cyclopentene was doubly labelled in the vinylene carbons. Olefin cleavage (route X) leads to a doubly labelled pentanediol and an unlabelled octanediol, whereas cleavage of the allyl single bond (route Y) would give single labelling in both diols. Dall'Asta to concluded that double bond cleavage had occurred.

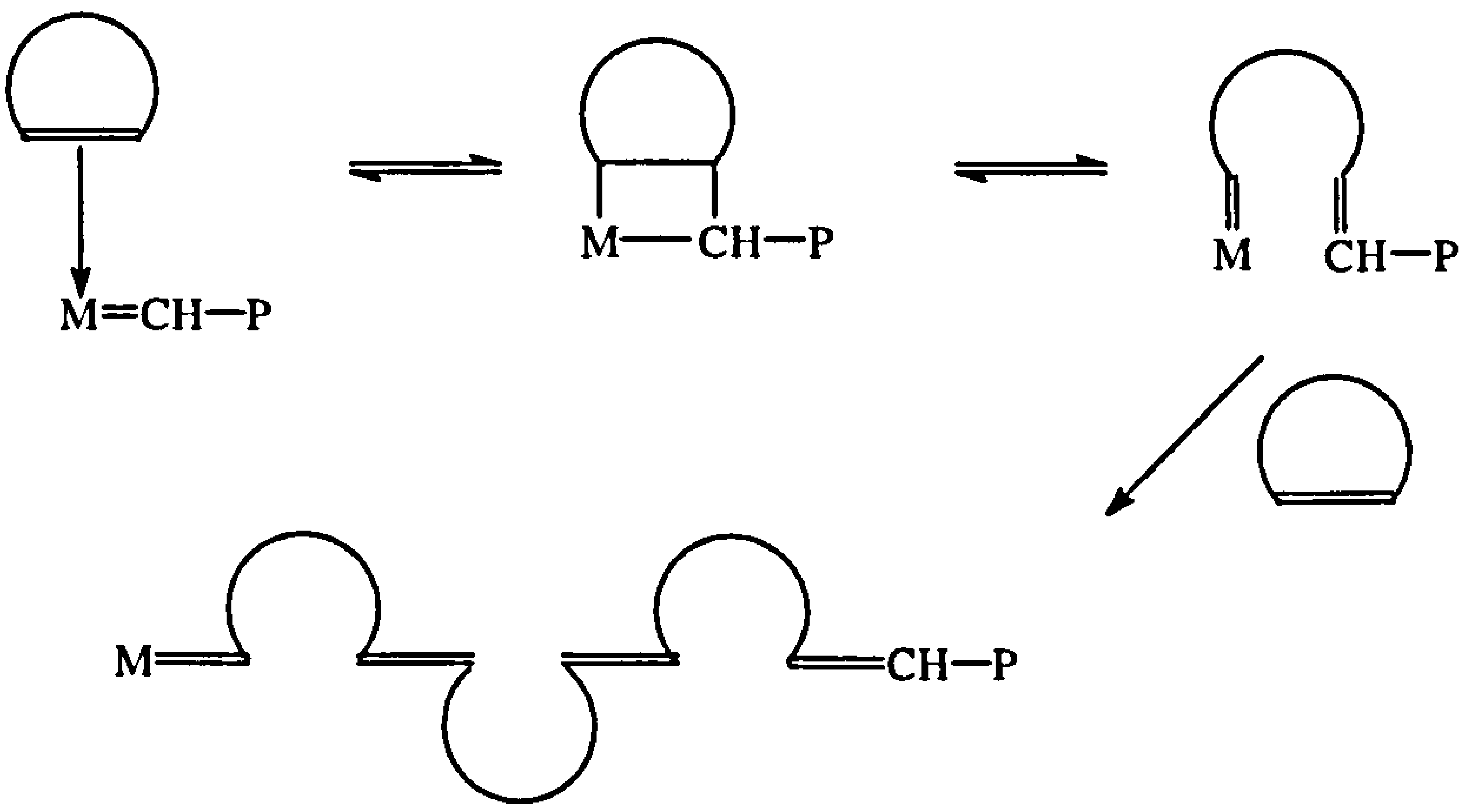
Initially, it was thought that transalkylidenation proceeded via a pairwise mechanism where the double bonds of two alkenes come together at a transition metal centre. It was thought that the π orbitals of the double bonds would overlap with the metal d-orbitals allowing interchange to occur via a weakly bonded cyclobutane complex.



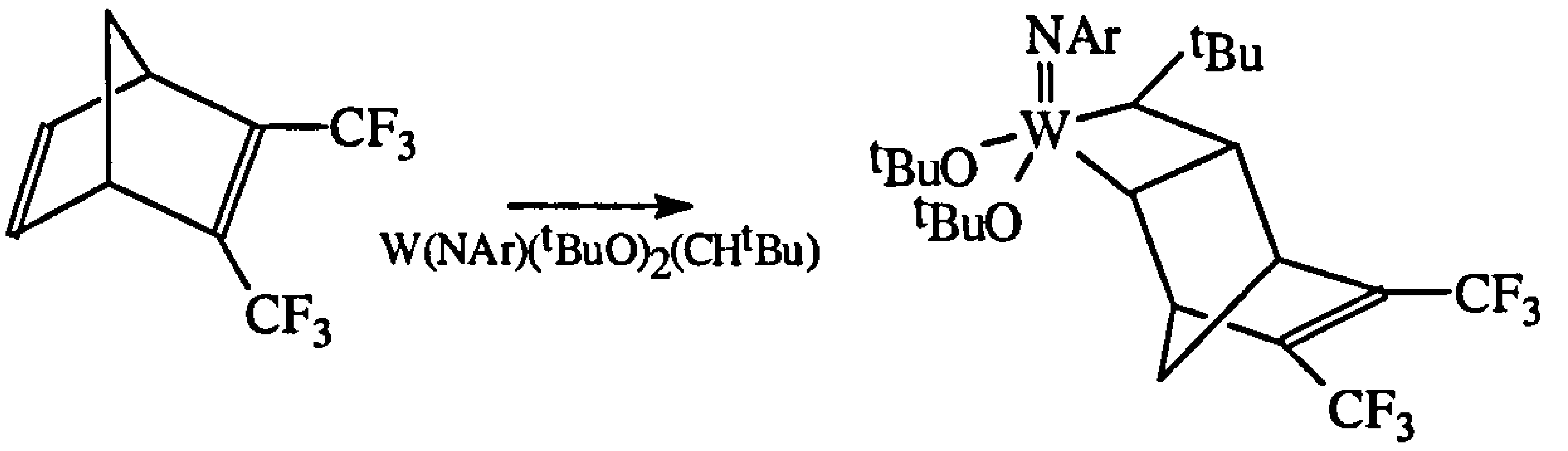
However, the reaction has been shown to proceed via a non-pairwise mechanism involving the formation of a metallocyclobutane intermediate as proposed by Chauvin in 1970.[15] The mechanism, shown below, involves a reversible [2+2] cycloaddition of a carbon-carbon double bond to a metal carbene.



Ring opening polymerisation proceeds via a similar non-pairwise mechanism.

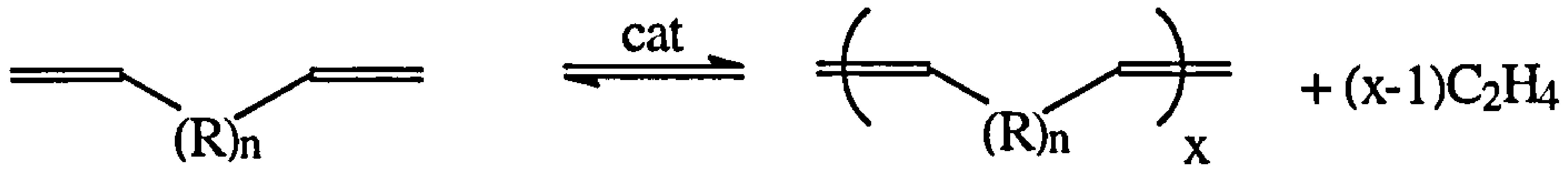


The C=C double bond of the monomer co-ordinates the metal of the carbene complex forming a metal π-complex which converts to the metallocyclobutane intermediate by a [2+2] cycloaddition. The metallocyclobutane cleaves to form a new metal carbene complex and a growing polymer chain. This mechanism has been established in detail for several cases and the intermediates have been isolated and identified. For example Schrock has used detailed NMR spectroscopic analysis to identify the metallocyclobutane formed in the polymerisation shown below using $W(NAr)(^tBuO)_2(CH^tBu)$.[16]



2.4 Acyclic diene metathesis (ADMET)

A second method of using the olefin metathesis reaction to create polymers is acyclic diene metathesis (ADMET) polymerisation. This involves the reaction shown schematically below.



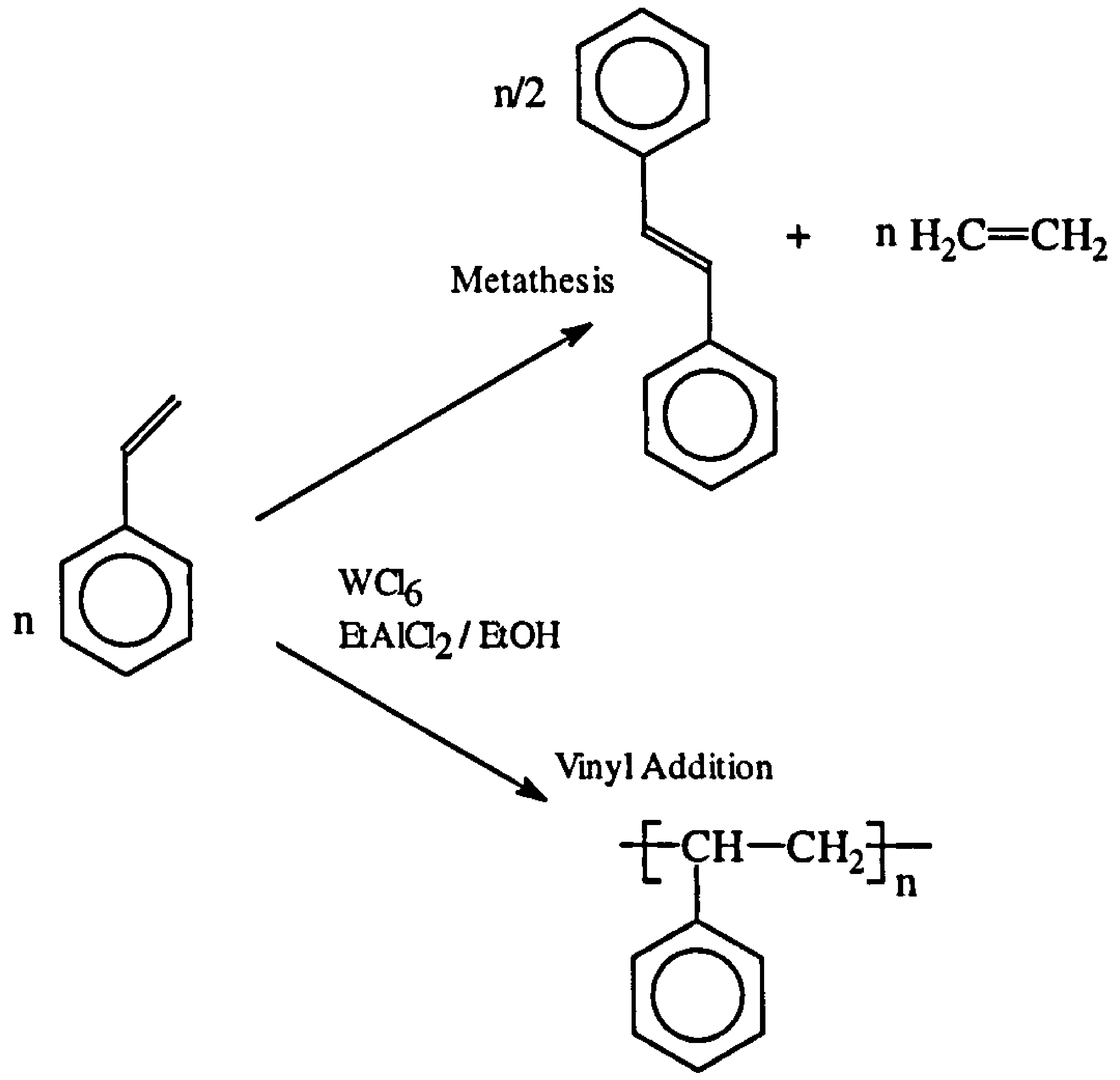
2.4.1 History

In the early 1970s, Dall'Asta studied the metathesis of unconjugated α,ω-dienes.[17] He found that the metathesis of 1,5-hexadiene occurred with pronounced stereospecificity, yielding ethylene and oligomeric polyenes. He investigated various catalysts and found that those possessing even a small amount of Friedel-Crafts activity, such as WCl_6/1,3-dichoro-isopropanol/$Et_3Al_2Cl_3$, led to competing side reactions. Further studies were made by Doyle[18] and Zuech.[19] Doyle found that unconjugated diolefins underwent intra- or inter-molecular metathesis. For example, 1,4-pentadiene gave 1,4,7-octatriene in 100% yield. He also studied 1,5-hexadiene and found that it polymerised to give linear oligomeric products.

These early studies produced complex mixtures of products due to competing processes and no real advances were made until 1987 when Wagener started investigating diene metathesis. He attempted the polymerisation of 1,9-decadiene and 1,5-hexadiene using a $WCl_6/EtAlCl_2$ catalyst system.[20] He found that 1,9-decadiene reacted rapidly evolving large volumes of gas, the main component being ethylene and that both a soluble, highly viscous oil and an intractable solid resulted. Analysis of the oil showed that low number-average molecular weight ($\overline{Mn}$ = 5000) poly(octadiene) had been produced. The intractable solid was presumed to be a cross-linked gel. 1,5-Hexadiene behaved differently, reacting very slowly until a vacuum was applied when ethylene was evolved instantly. Again two products resulted. Analysis showed that low molecular weight poly(butadiene) had been produced.

This work showed that for both monomers, acyclic olefin metathesis was the predominant reaction. However, in order to increase the molecular weight and purity of the polymers produced it was necessary to eliminate the side reactions. Wagener proposed that the competing reactions were alkylation of the olefin by the cocatalyst and the acid catalysed chain vinyl addition of one olefin functional group to another

Wagener believed that the second reaction was the most important as he thought that the intractable fraction formed was the result of vinyl addition reactions. To prove this, he studied the polymerisation of styrene which would lead to stilbene if metathesis predominated or polystyrene if vinyl addition predominated.



He found that polystyrene was the only product and that no ethylene was evolved. It was thought that the $EtAlCl_2$ was initiating cationic polymerisation. On the basis of this evidence Wagener realised the need for Lewis acid free catalysts.

In 1989, he published the first paper containing acyclic metathesis polymerisation using Lewis acid free catalysts.[21] He polymerised 1,9-decadiene using

$W(CH\text{-}t\text{-}Bu)(n\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)[OCMe(CF_3)_2]_2$. Using this Schrock initiator, Wagener was able to completely eliminate all side reactions and produce poly(octadiene) which had a 92% *trans* configuration and an average $\overline{Mn}$ of at least 50,000.

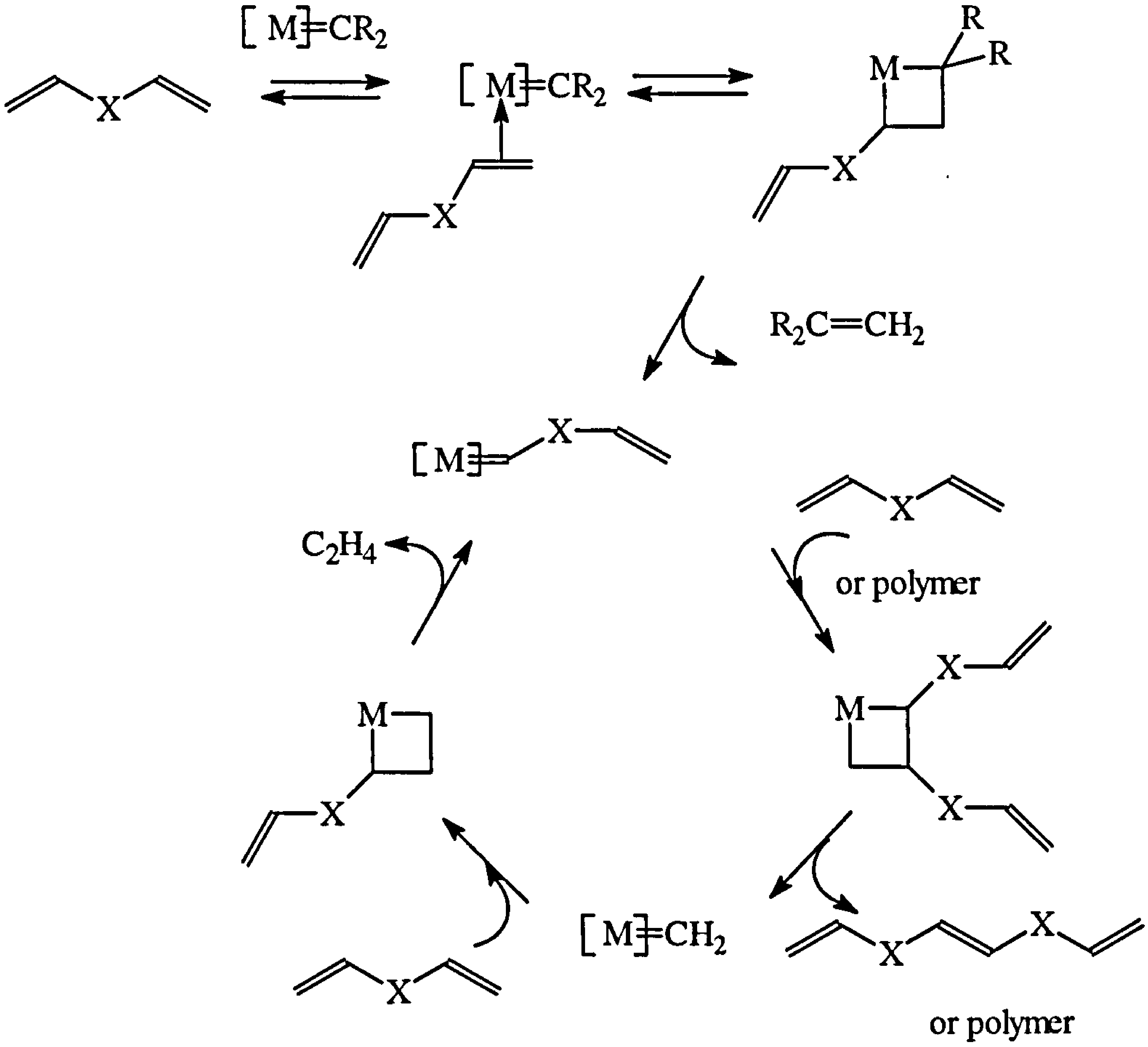
In 1990, Wagener named this type of polymerisation acyclic diene metathesis (ADMET). Since then, he has published numerous papers on the polymerisation of many different monomers yielding a wide range of polymers:- polyesters,[22] polyethers,[23] polyamines[24], polyaromatics,[25] polyketones,[26] polythioethers,[27] polycarbonates,[28] polycarbosiloxanes[29] and poly[carbo(dimethyl)silanes].[30]

He went on to study ADMET polymerisation using Grubbs ruthenium catalyst.[31] He successfully polymerised 2-methyl-1,5-hexadiene, diallyl ether, 1,9-decadiene and 1,5-hexadiene. These polymerisations occurred more slowly than the corresponding polymerisations using Schrock initiators and this was thought to be due to intramolecular π-coordination occurring between the ruthenium metal centre and the dienes.

Work also continued on ADMET polymerisation using classical initiators. Nubel decided to use classical initiators as the Schrock alkylidene complexes were not easily prepared and were not commercially available. He polymerised 1,5-hexadiene using a modified WCl_6-$SnMe_4$ catalyst.[32] He used a weak Lewis base (n-propyl acetate) to reduce undesired side reactions. In 1976, Ichikawa and Fukuzumi reported the highly selective metathesis of 1-octene using WCl_6/Bu_4Sn/n-propyl acetate where the n-propyl acetate was responsible for suppressing bond migration.[33]

2.4.2 Mechanism

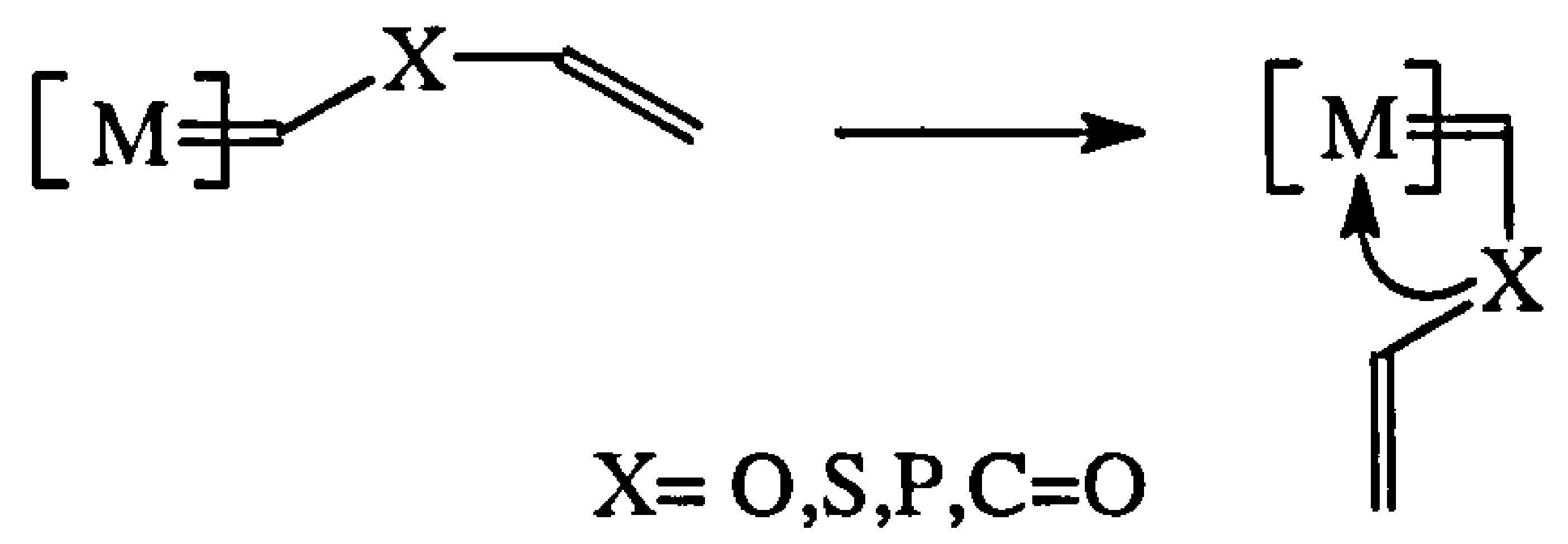
ADMET proceeds by a similar mechanism to ROMP with the formation of metallacycle intermediates.[34]



The mechanism of ADMET differs from the mechanism of ROMP in the following ways;

- Ethylene is produced and this drives the reaction.
- Two metallocyclobutane intermediates are formed in each propagation step
- An intermediate methylene complex is formed as the oligomer dissociates from the metal centre.

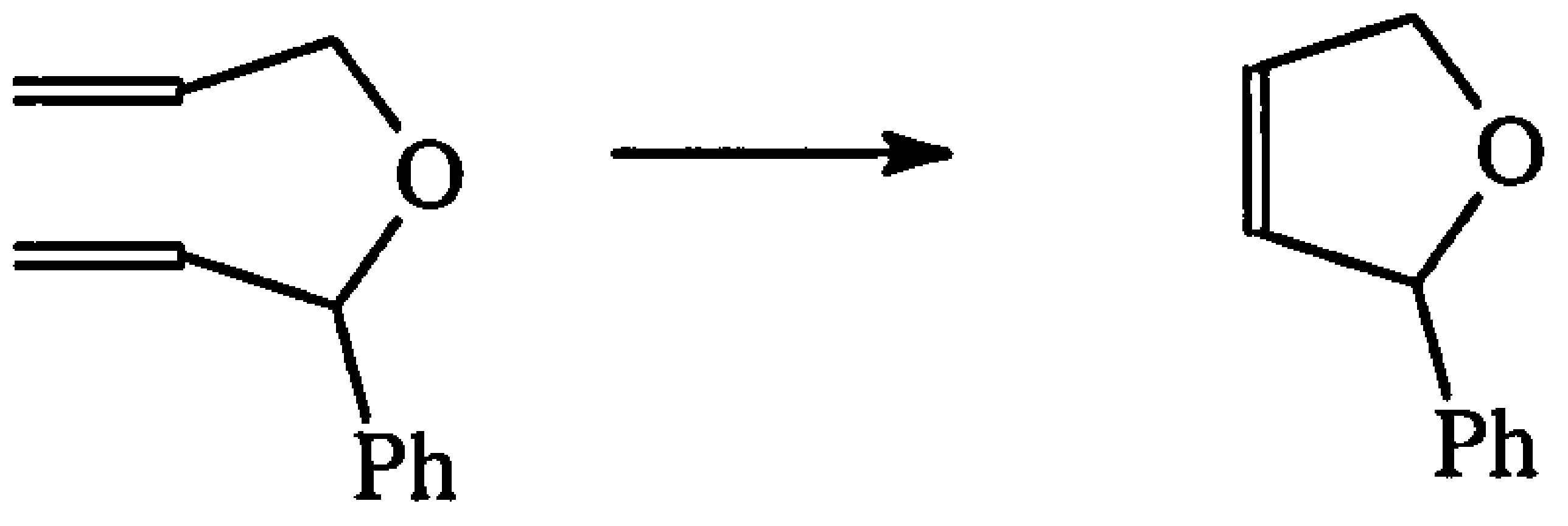
One factor that has to be taken into account with ADMET is the distance between any functional groups and the alkene. It has been demonstrated that the minimum number of methylene spacers required between an ester group and the olefin is two.[35] It is thought that if the ester is closer to the olefin, the ester may polarise the olefin so that the formation of the metallocycle is hindered leading to decreased reactivity. Secondly there is the possibility of co-ordination of the ester carbonyl to the metal centre.

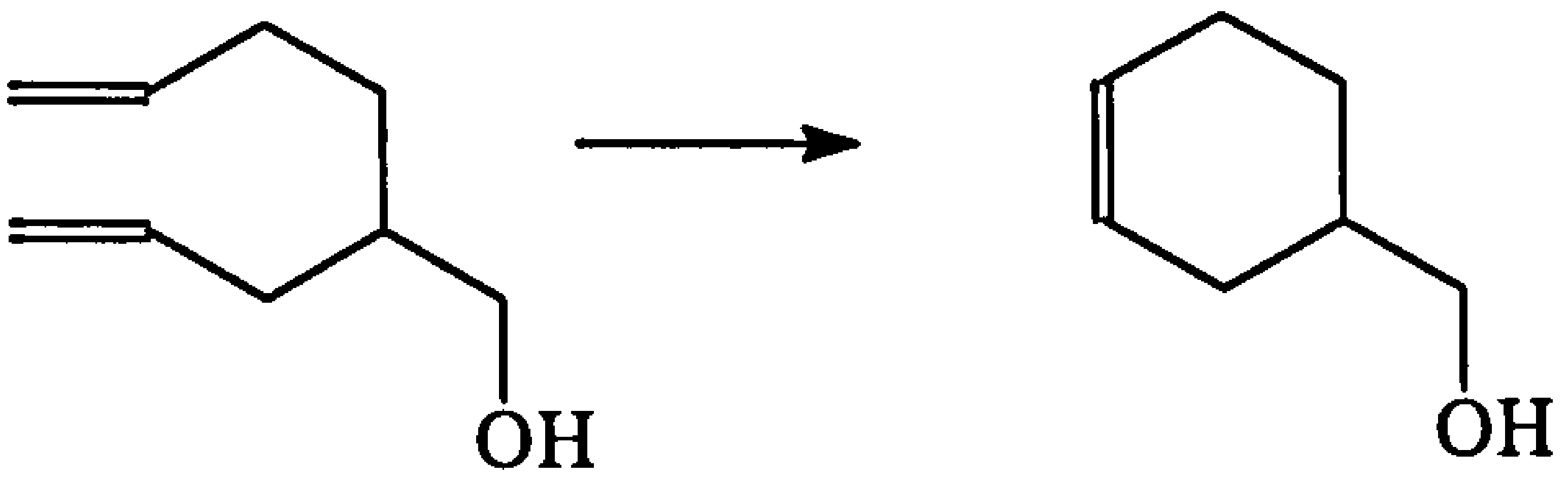


Wagner called these effects 'the negative neighbouring group effect'. This effect has also been observed for ether containing dienes.[23]

2.4.3 Ring closing

A variation on ADMET polymerisation is ring closing. This is undesirable if polymers are required but the process has been used specifically to generate small ring structures. Ring closure is generally achieved when the ring formed is stable for example six- and five-membered rings. Examples are shown below.[36]



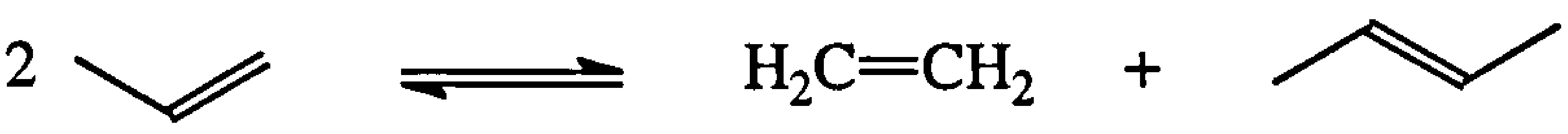


Another factor which determines whether the ring or the polymer is formed is the free energy of polymerisation of the cyclic compound. When the free energy of the compound is close to zero, a high concentration of substrate will favour polymerisation whereas a dilute solution will favour the formation of the cyclic compound.

2.5 Applications

An enormous research effort was directed towards the synthesis of new polymeric materials using ROMP and there have been commercial successes, for example Vestenamer formed by the ROMP of cyclooctene has been produced by Chemische Werke Hüls. It is a resilient elastomer and is used in blends.

The Philips triolefin process also used the metathesis reaction commercially to produced high purity ethene and but-2-ene from propene.



Another example of the commercial success of the olefin metathesis reaction is the Shell Higher Olefin Process (SHOP) which converts ethene to larger, detergent range alkenes ($C_{11\text{-}14}$) as shown schematically below.[37]

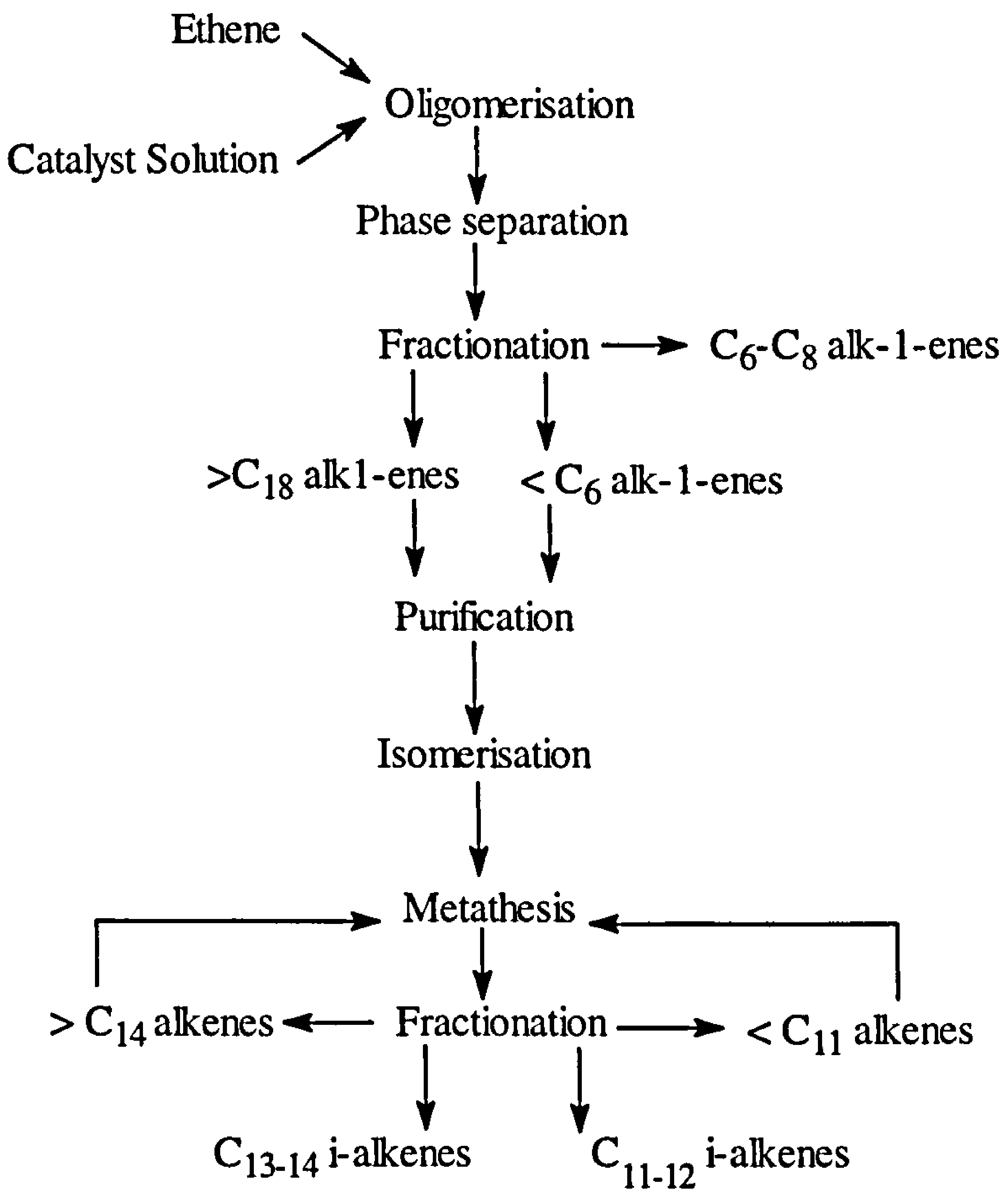
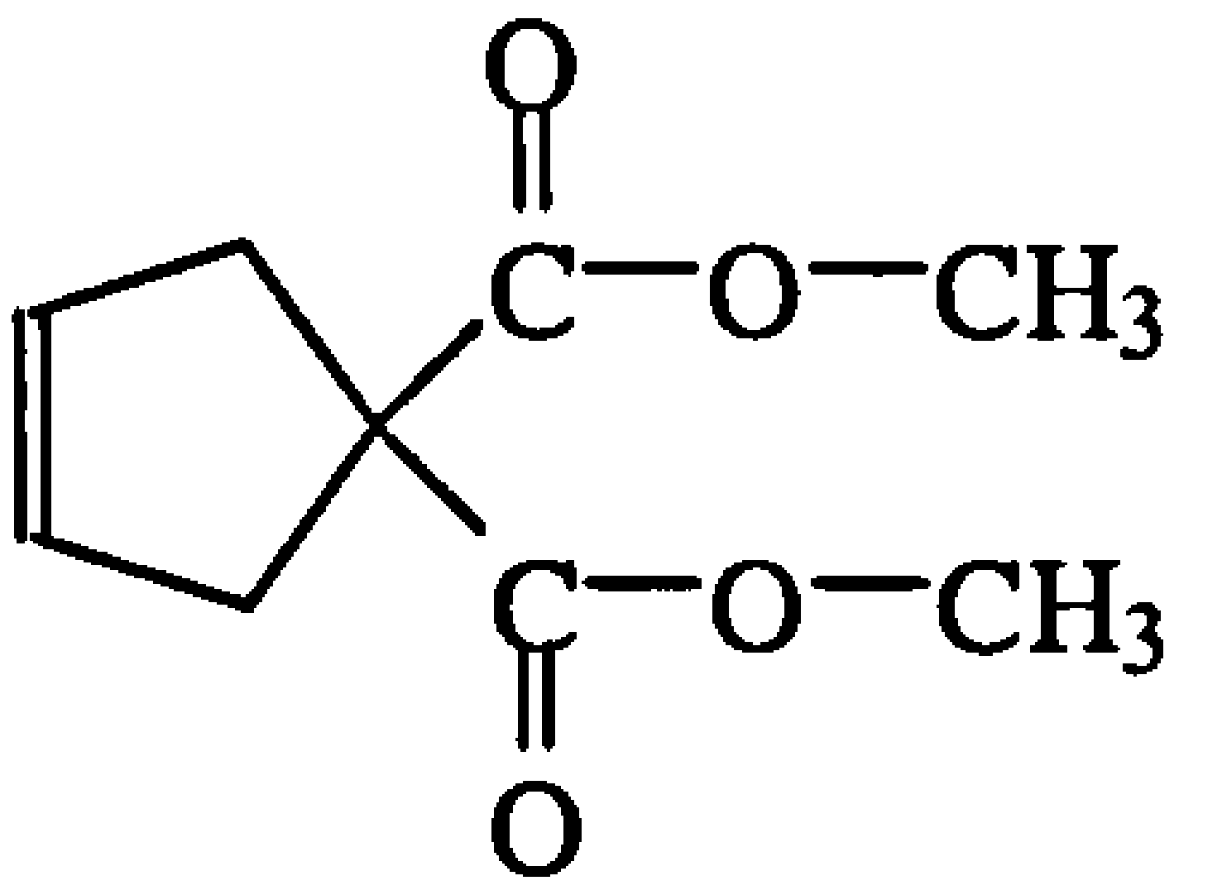
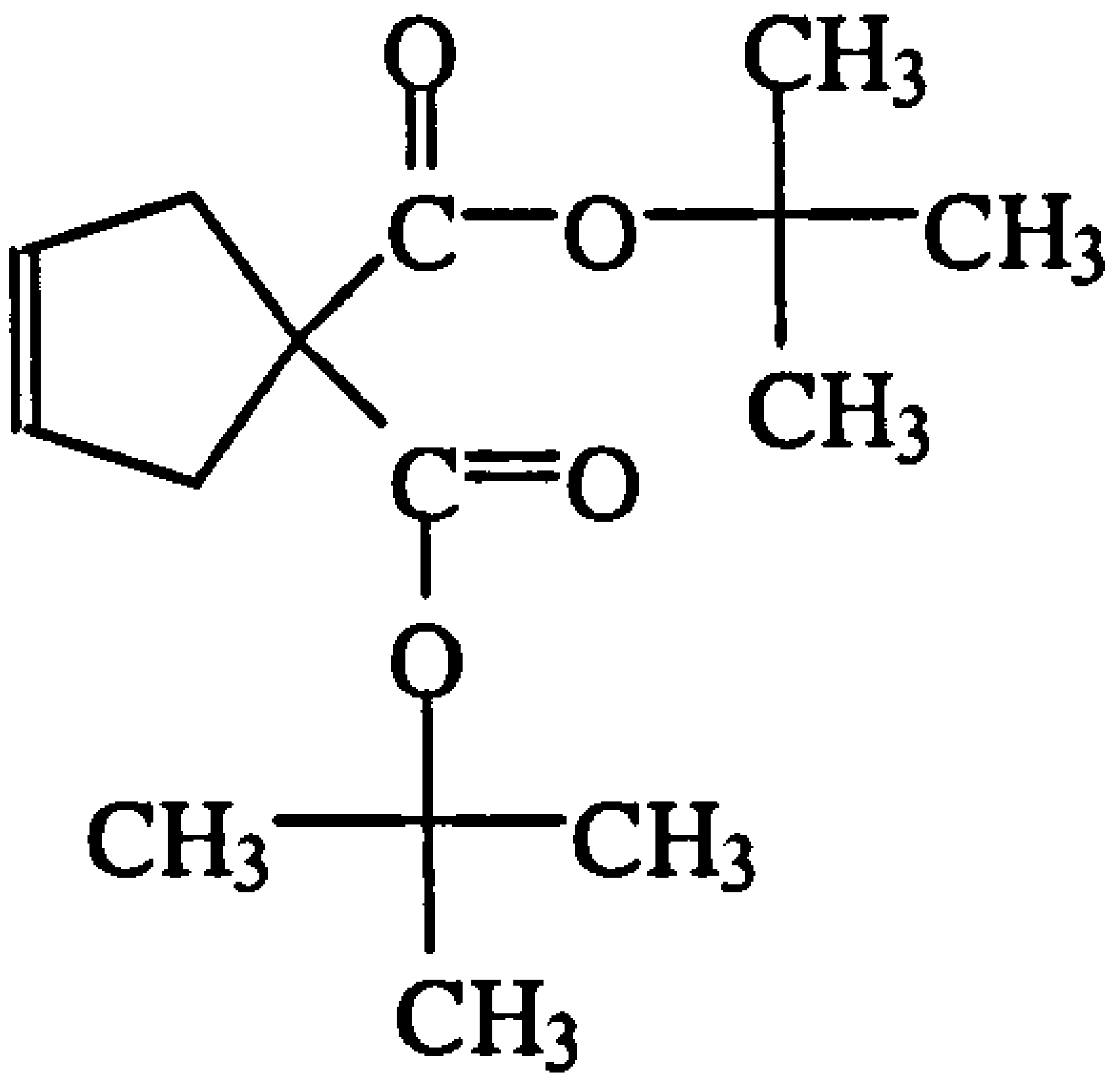


Figure 2-1 Schematic for the SHOP process

2.6 Synthesis of 3-cyclopentene-1,1-dicarboxylate monomers

Initial attempts to produce polar elastomeric polymers were based on the ring opening metathesis polymerisation of cyclopentenes. The two monomers studied are shown below.

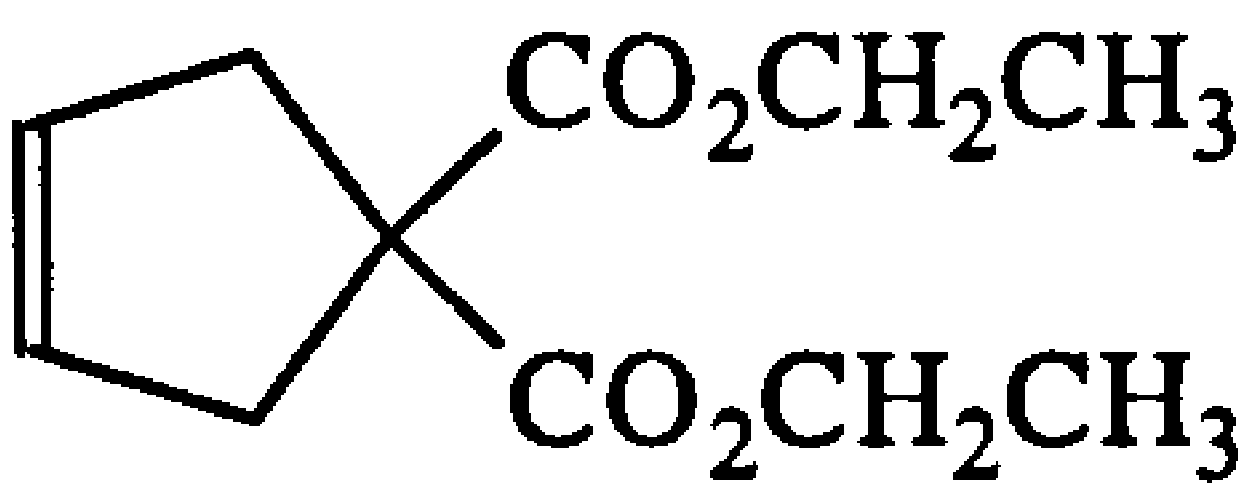




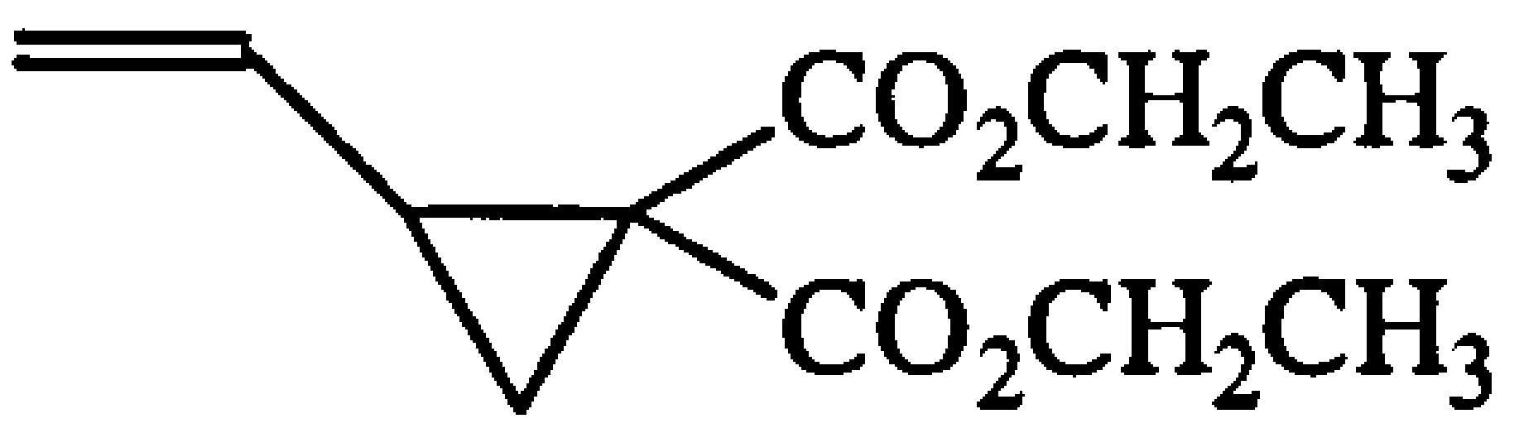
In theory, these monomers could undergo ROMP to produced a polymer with an unsaturated, five-carbon repeat unit bearing two polar, ester groups.

2.6.1 Background

The first recorded attempt to produce a 3-cyclopentene-1,1-dicarboxylate was published in 1950 by Skinner et *al.*.[38]

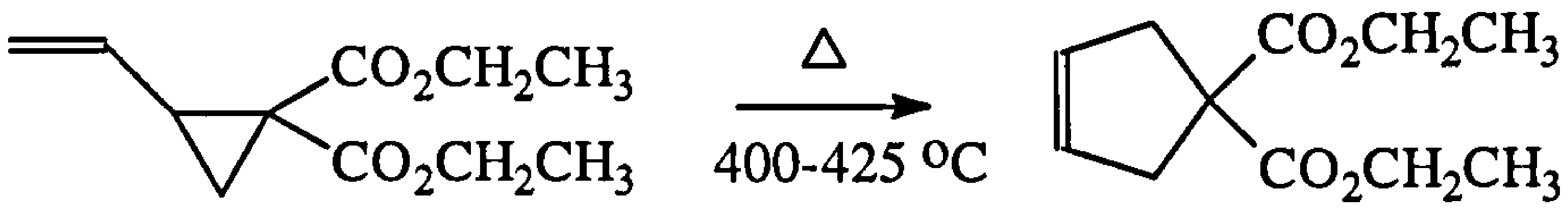


They claimed to have formed the ester, shown above, in good yields by the condensation of 1,4-dibromo-2-butene with malonic ester but no physical data was presented. Later papers[39, 40, 41, 42] showed that Skinner had used the *trans* isomer of dibromobutene and had formed a vinylcyclopropane derivative instead of the desired ester. The product of that work is shown below.



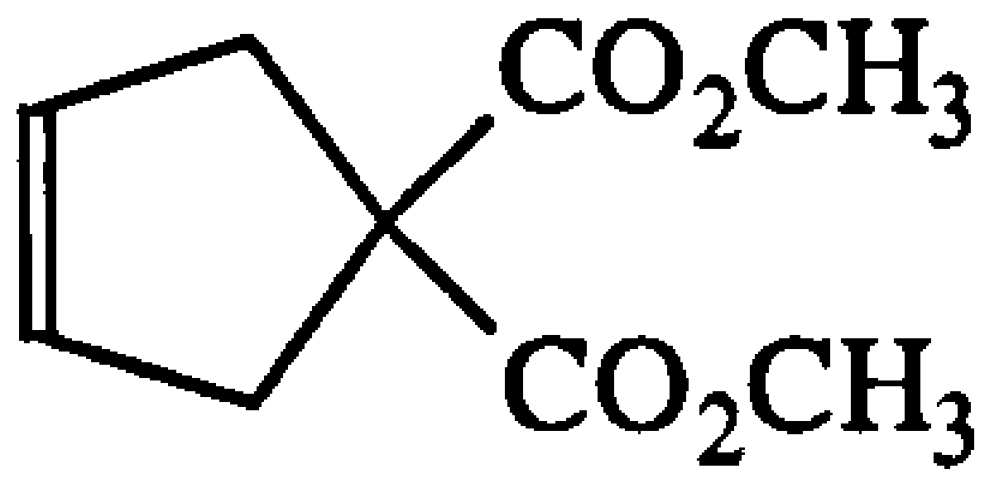
In order to form the desired ester, it is necessary to use the *cis* isomer of the butene, and in 1962 Murdock and Angier published a procedure for the condensation of *cis*-1,4-dibromo-2-butene with malonic ester.[41] They used sodium in ethanol to deprotonate the diethylmalonate and obtained the cyclopentene derivative in a ~1:1 mixture with the vinyl cyclopropane derivative.

In 1966 Schmid and Wolkoff published a modification to Murdock and Angiers' method which improved the yield of the cyclopentene derivative by means of the thermal vinylcyclopropane rearrangement.[43]



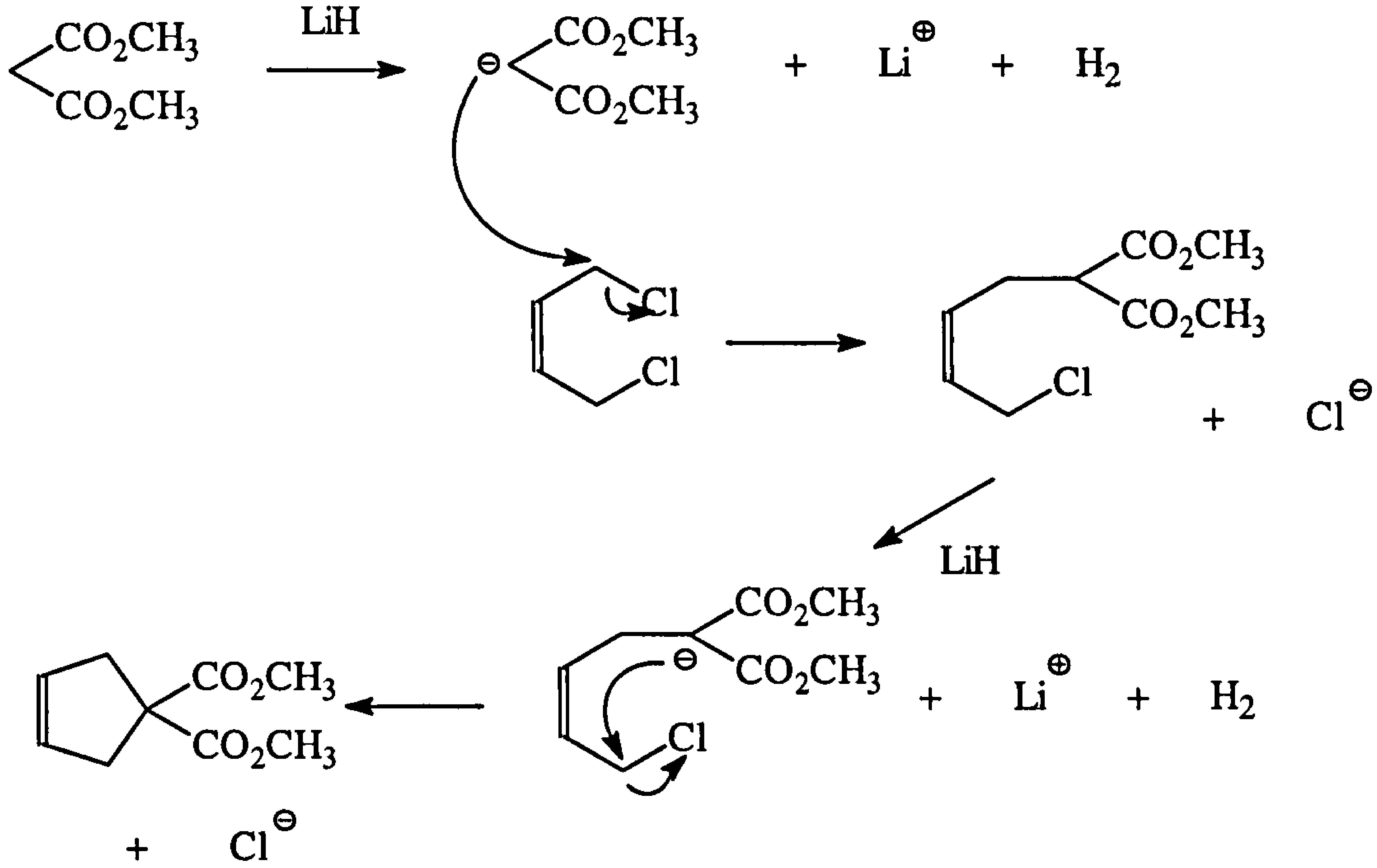
Schmid used Murdock and Angiers' method and produced a mixture containing 58% cyclopentene and 42% vinylcyclopropane. The mixture was then pyrolysed to form the desired cyclopentene derivative in 72% yield.

In 1984, Dèpres and Greene published an alternative procedure for improving the yield of difunctionalised 3-cyclopentenes.[44] They found that the ratio of the cyclopentene to vinylcyclopropane derivatives was highly sensitive to changes in the base, solvent and to some extent, the alkyl group on the malonic ester. They found that using lithium hydride as the base, dimethylformamide (DMF) as the solvent and dimethyl malonate, the yield of the cyclopentene shown below (without pyrolysis) was 70%.



2.6.2 Synthesis of dimethyl-3-cyclopentene-1,1-dicarboxylate

Dèpres and Greenes' method was used in this work to produce the dimethylester. The proposed reaction mechanism is shown schematically below.



In the synthesis, a 25% excess of LiH was used to ensure that complete deprotonation of the dimethyl malonate occurred. Dichlorobutene was used in a 14% excess with respect to dimethyl malonate. The reaction lead to the production of white, oily crystals. This oiliness was found to be due to residual DMF, the reaction solvent. Sublimation under vacuum produced DMF-free crystals in a 25% yield.

2.6.3 Synthesis of di-*tert*-butyl-3-cyclopentene-1,1-dicarboxylate

Di-*tert*-butyl-3-cyclopentene-1,1-dicarboxylate was synthesised using the method reported by Dèpres and Greene.[44] The synthesis proceeded as expected and gave 53% yield of white crystals which, after a single recrystallisation, were found to be free of impurities. The mother liquor from recrystallisation yielded large crystals suitable for X-ray crystallography.

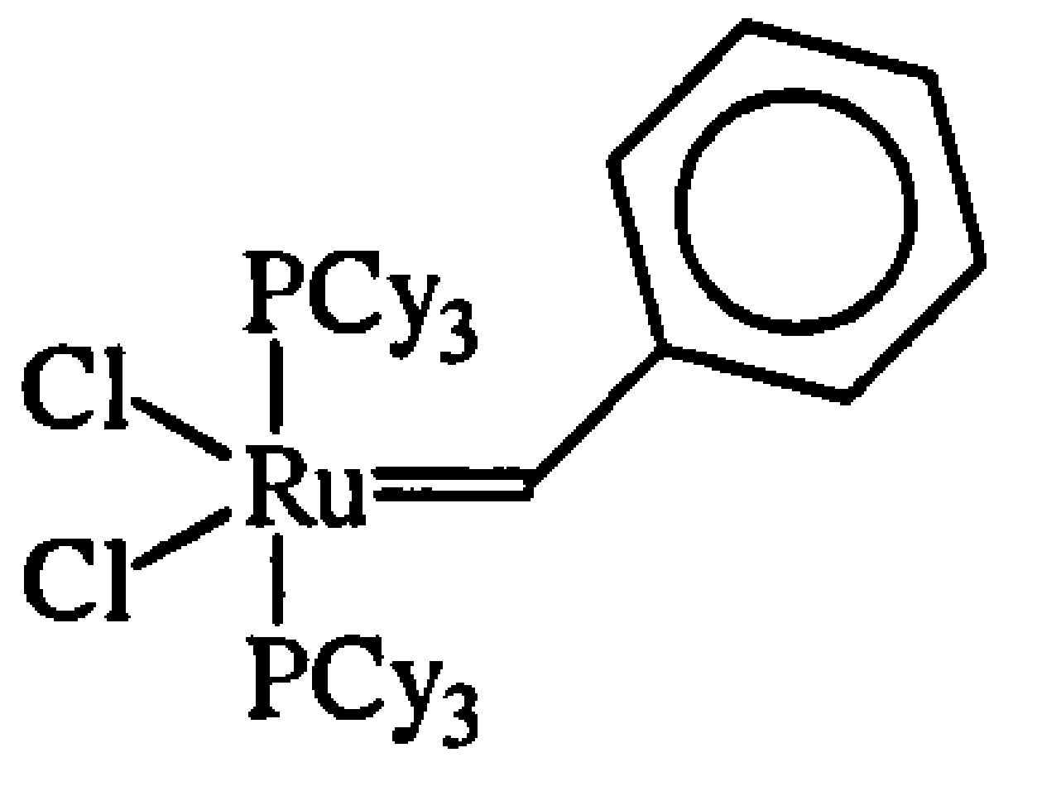
2.7 Attempted polymerisation of 3-cyclopentene-dicarboxylate monomers

Attempts were made to polymerise the cyclopentene dicarboxylate monomers using two initiators as shown in the following table.

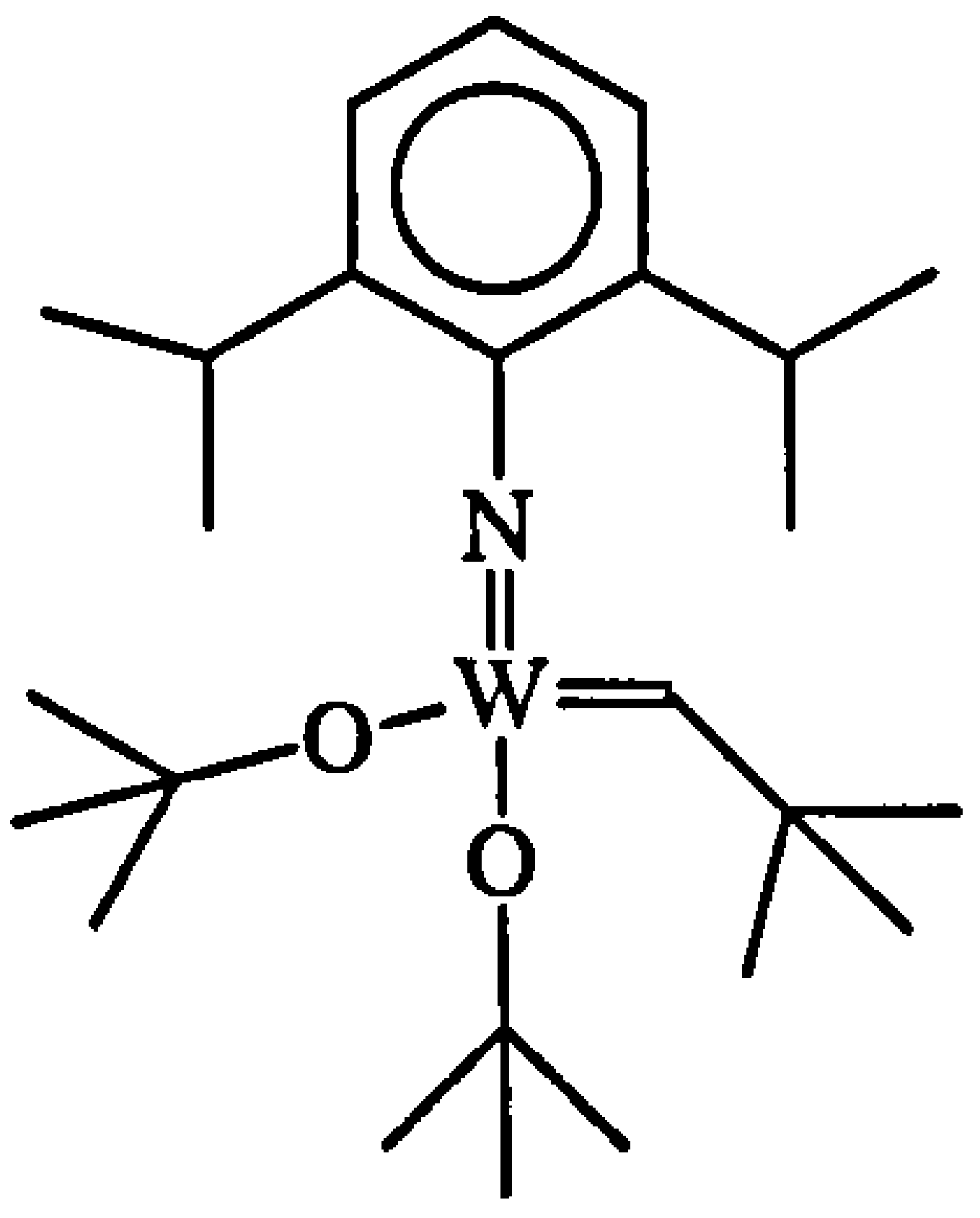
Monomer	Initiator	Mon:init ratio	Solvent	Temperature
Methyl	Ru catalyst	200:1	DCM	Room temp
Methyl	W catalyst	400:1	Benzene	-78°C
Butyl	Ru catalyst	100:1	DCM	Room temp
Butyl	W catalyst	400:1	Benzene	-78°C

Table 2-2 Summary of the polymerisation conditions for the 4,4disubstituted cyclopentene monomers. See experimental section for details.

The structures of the two catalysts used are shown below.



$C_9H_{12}O_4$
mw 184.19



$C_{25}H_{45}NO_2W$
mw 1047.48

In all cases of attempted polymerisation, no colour or consistency change was observed suggesting no reaction. For a successful polymerisation reaction in the case of the ruthenium catalyst, a colour change from purple to red occurs and with the tungsten initiator a change from yellow to orange is observed. ^1H NMR analysis of the reaction mixture indicated that the alkylidene hydrogens of the initiators were still present suggesting that the monomers do not destroy the initiator. The monomers do not, however, undergo polymerisation.

This was a disappointing, although not altogether surprising result. The ring opening metathesis of 5-membered rings is a process sensitive to a number of physical factors such as monomer concentration and temperature, and to chemical factors such as the nature of substituents. These factors affect the Gibbs free energy (ΔG) which in turn determines whether the reaction will proceed. ΔG must be negative in order for polymerisation (or any other reaction) to occur.

The following graph shows the effect of ring size and substituents on ΔG for the ring-opening of methylated cycloalkanes with ethylene, propene and isobutene as reference points.[45] It can be assumed that cycloalkenes will show a similar pattern.

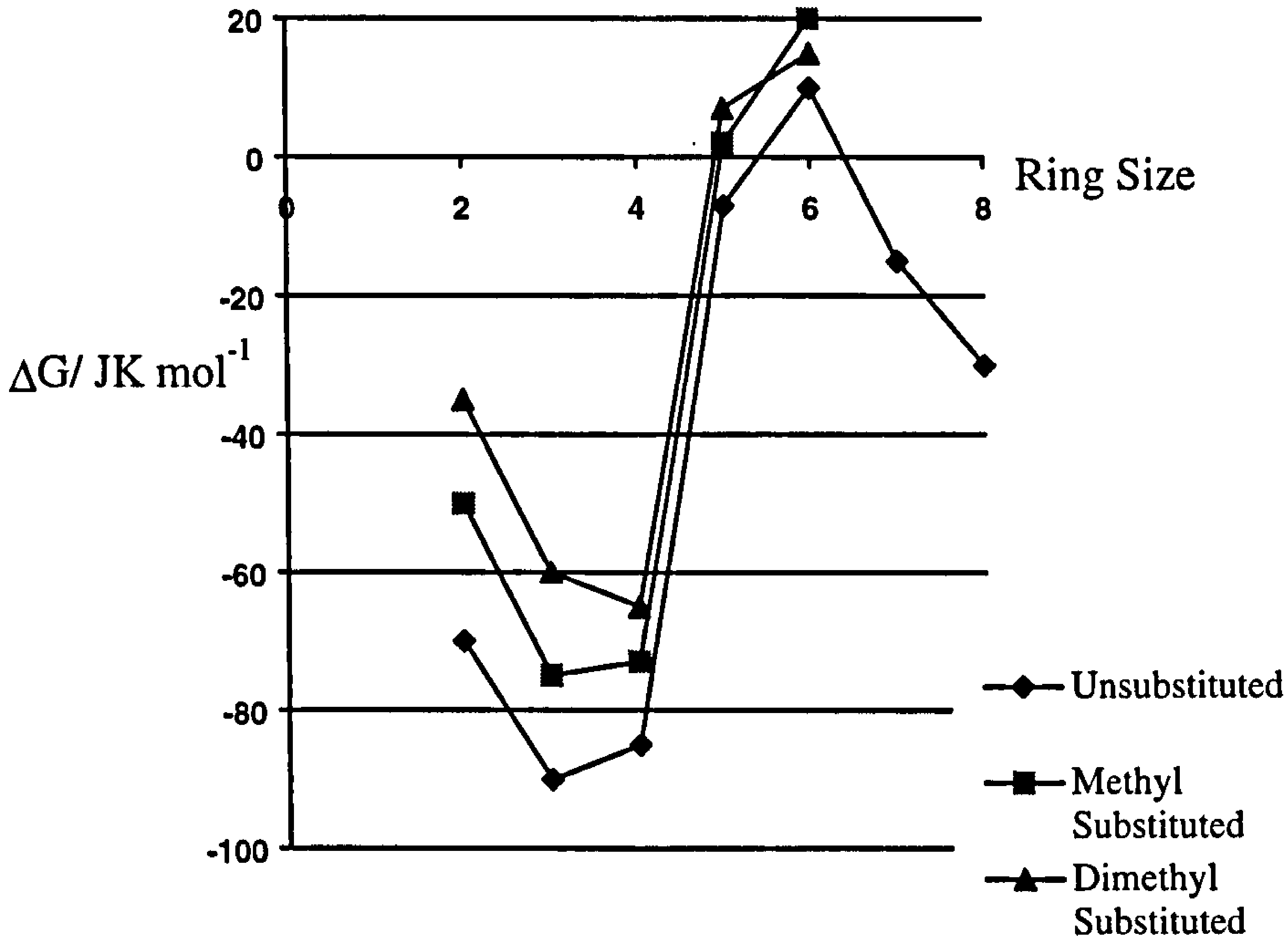


Figure 2-2 Graph showing the effect of ring size and substituents on the ΔG of ring opening for cycloalkanes

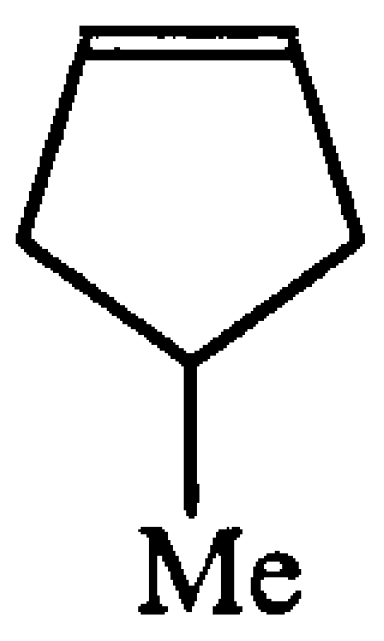
It can be assumed that unsubstituted cyclopentene has a small negative ΔG value. This ΔG value is made up of two parts; an enthalpy term and an entropy term.

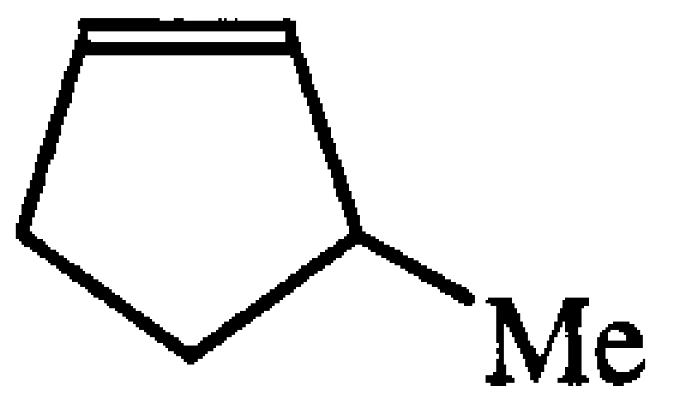
$$\Delta G = \Delta H - T\Delta S$$

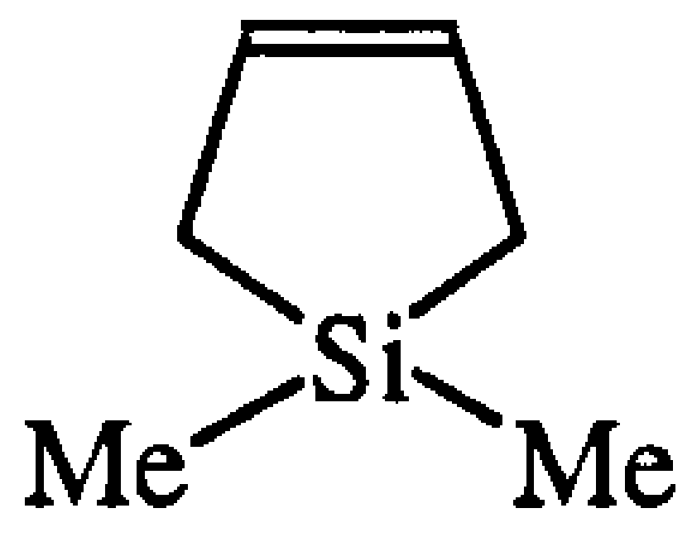
In favourable cases, ΔH is large and negative, however, in cyclopentene it is relatively small. This is due to the fact that the bond lengths and angles in the ring are such that they induce little strain. Entropy changes for ring-opening polymerisation are negative, owing to the loss of the translational energy of the monomer as they are ‘tied down’ in the polymer chain. This decrease in entropy and small ΔH value of cyclopentene mean that polymerisation is not thermodynamically very favourable.

One method of inducing polymerisation is to decrease the temperature. This reduces the TΔS term of the equation and (since ΔS is negative) therefore reduces ΔG. In the attempted polymerisation of the two substituted cyclopentenes using the Schrock tungsten initiator, the temperature was lowered in an attempt to make the polymerisation favourable. This, however, was unsuccessful. This lack of success is probably due to the substituents present on the ring.

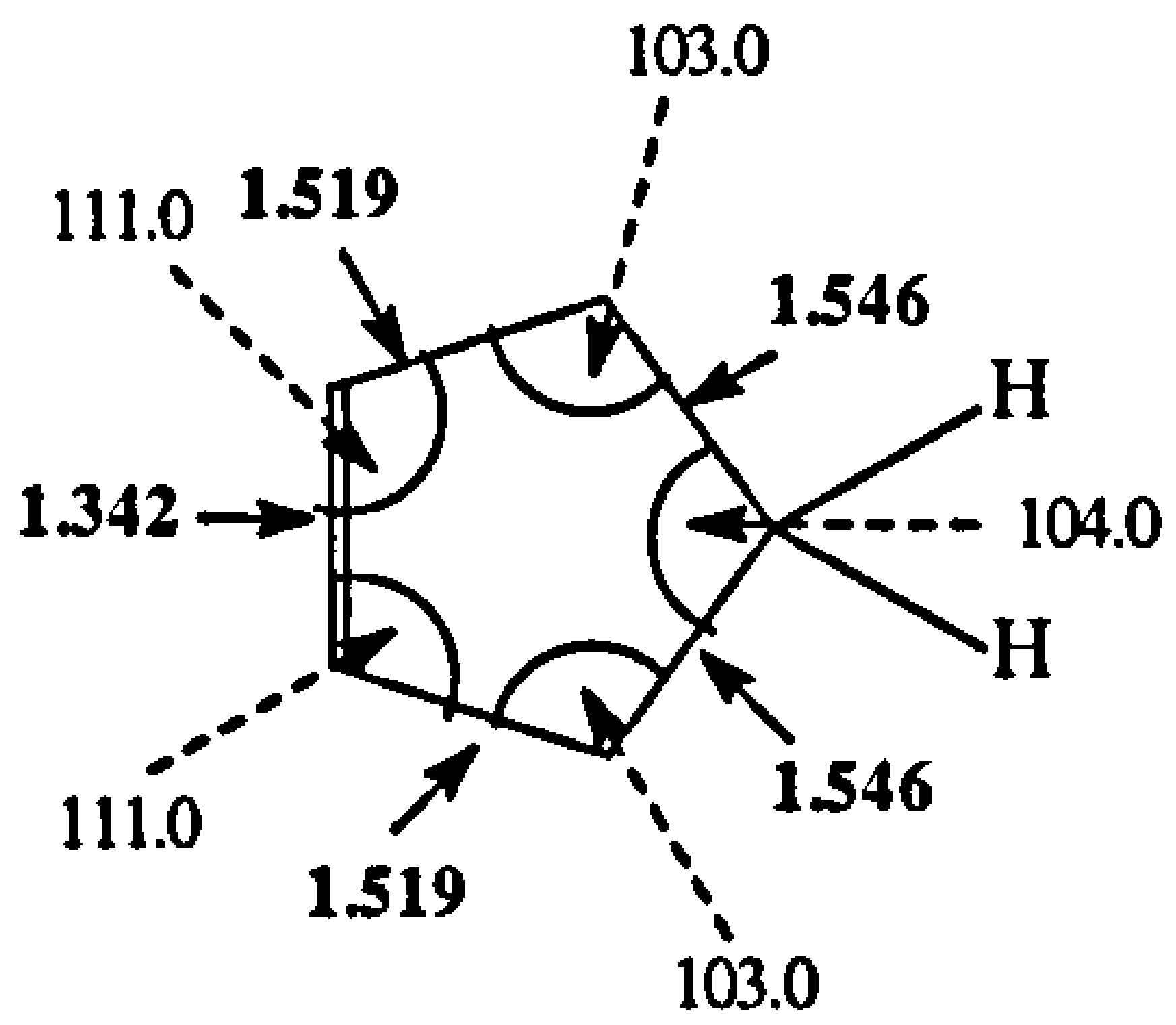
It can be seen in the graph (Figure 2-2) above that substituents have an unfavourable effect on ΔG. In the case of cyclopentane, they tend to change the sign of ΔG from negative to positive. This is a generalisation and several cases of the polymerisation of substituted cyclopentenes have been reported. For example, the monomers shown below were found to undergo polymerisation.[46, 47, 48]

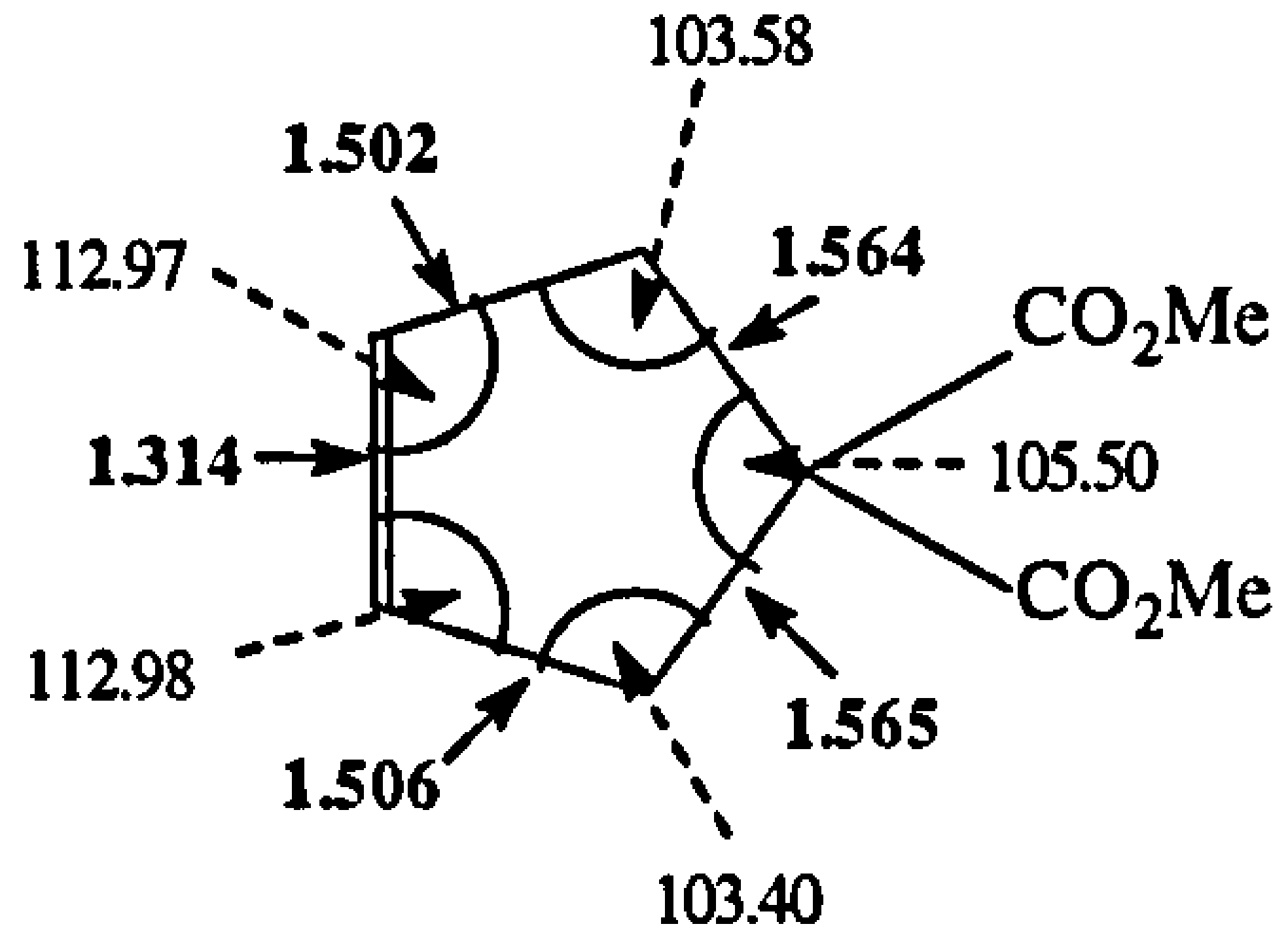


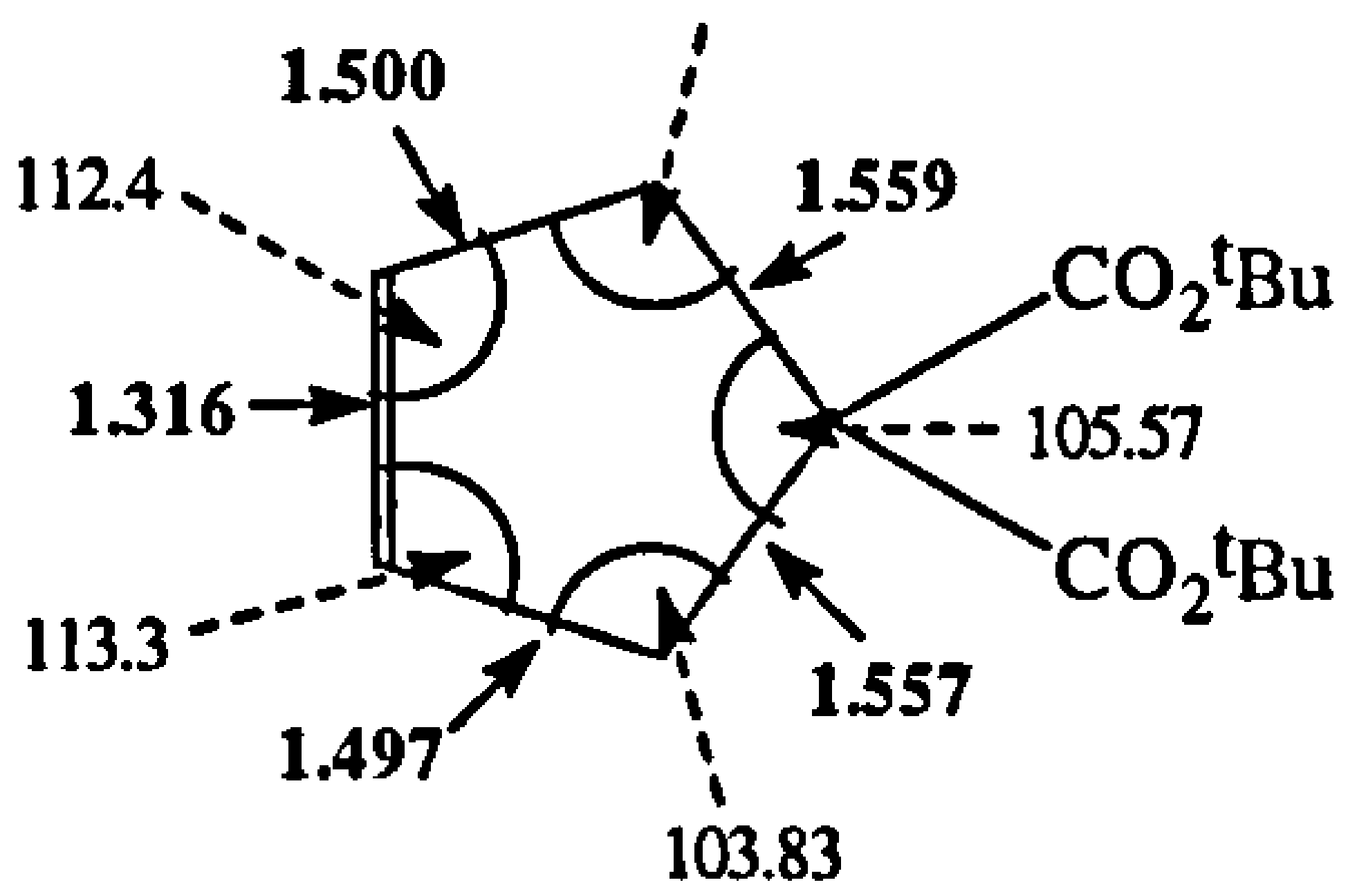




It was hoped that by using a cyclopentene substituted with two bulky ester groups, that the ring system would be distorted and the ring strain would increase. This would lead to a larger, negative ΔH value which would make the polymerisation more favourable. However, X-ray crystallographic studies showed that the angles and bond lengths in the ring are not significantly changed by the substitution.[49]



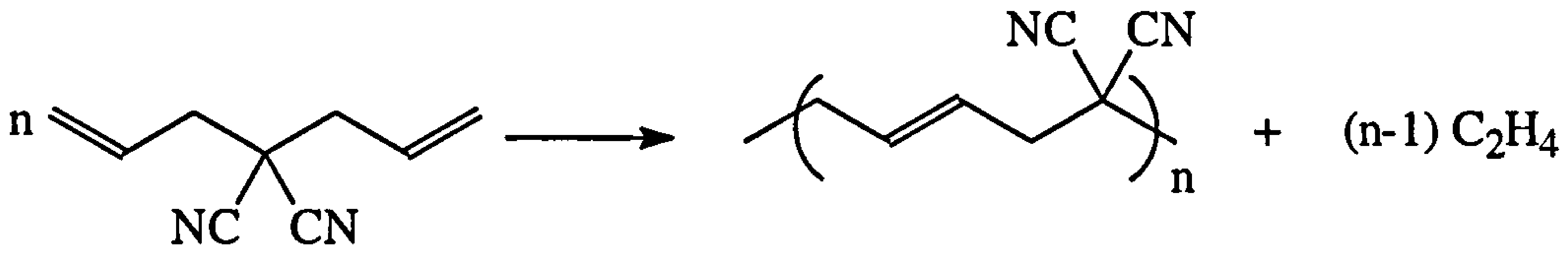




These observations and results lead to the conclusion that polymerisation of these monomers by ROMP cannot be achieved.

2.8 Synthesis of 1,1-diallyl malononitrile

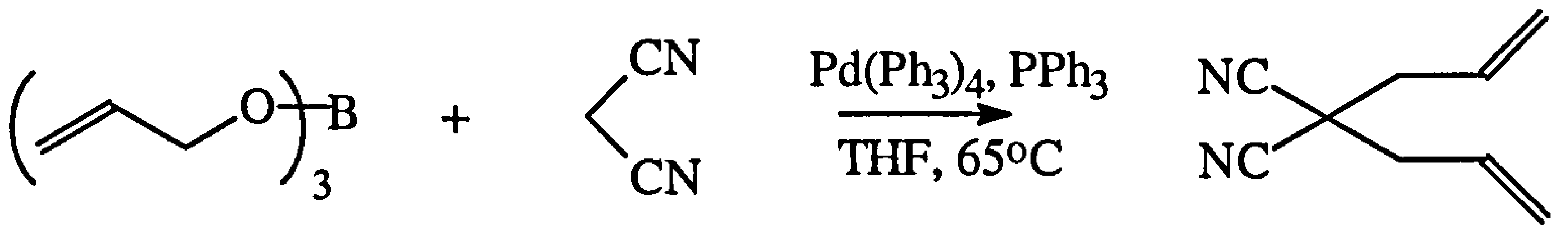
In an attempt to produce polar, elastomeric polymers, the ADMET polymerisation of 1,1-diallyl malononitrile was studied. 1,1-Diallyl malononitrile could potentially undergo ADMET to produce a polymer with an unsaturated, five-carbon repeat unit bearing two polar cyano groups. The potential route is shown below.



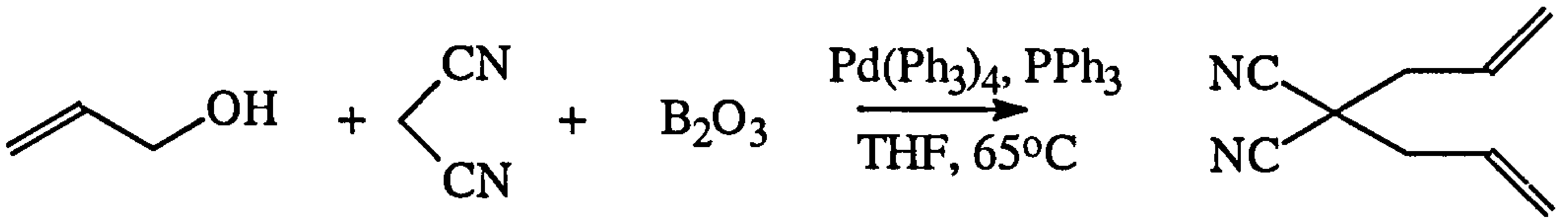
2.8.1 Background

The first published synthesis of 1,1-diallyl malononitrile was in 1961 when Shimo *et al.* claimed to have produced it in 91% yield by the reaction of malononitrile with allyl bromide in liquid ammonia at -50°C.[50]

In 1988, Lu *et al.* used a palladium catalyst, $Pd(PPh_3)_4$, to react allylic borates or allylic alcohols with malononitrile.[51] Using triallyl borate, 1,1-diallyl malononitrile was formed in 4.5 hours in a yield of 83%.



The allylic alcohol afforded an 80% yield in the same reaction time.



Later, in 1991, Diez-Barra *et al.* prepared 1,1-diallyl malononitrile in a 68% yield by the reaction of malononitrile with allylbromide using potassium *tert*-butoxide as a base and tetra-butyl-ammonium bromide (TBAB) as a phase transfer catalyst without solvent.[52]

In 1992, Curran and Seong used lithium hydride as a base to deprotonate malononitrile in THF. This active species then went on to react with diallyl bromide to produce 1,1-diallyl malononitrile in a 40% yield.[53]

2.8.2 Synthesis

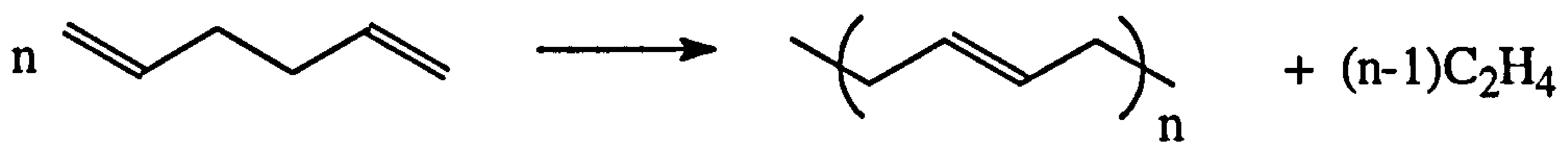
Shimo's and Lu's methods gave higher yields of the desired product but both methods have some experimental problems. Shimo's method requires the use of liquid ammonia and Lu's method involves the preparation of a palladium catalyst. It was therefore decided to combine the methods reported by Diez-Barra and Curran in the hope that the advantages of the two methods could be gained. It was decided to use potassium tert-butoxide as the base but to use this in dry THF rather than use no solvent and a phase transfer catalyst. It was hoped that this would lead to the higher yields quoted by Diez-Barra along with the greater ease of handling the base as a suspension rather than adding it as a solid.

1,1-Diallyl malononitrile was prepared using potassium tert-butoxide as a base in THF in a 53% yield and was characterised using ^1H NMR, ^{13}C NMR, infra-red spectroscopy and elemental analysis.

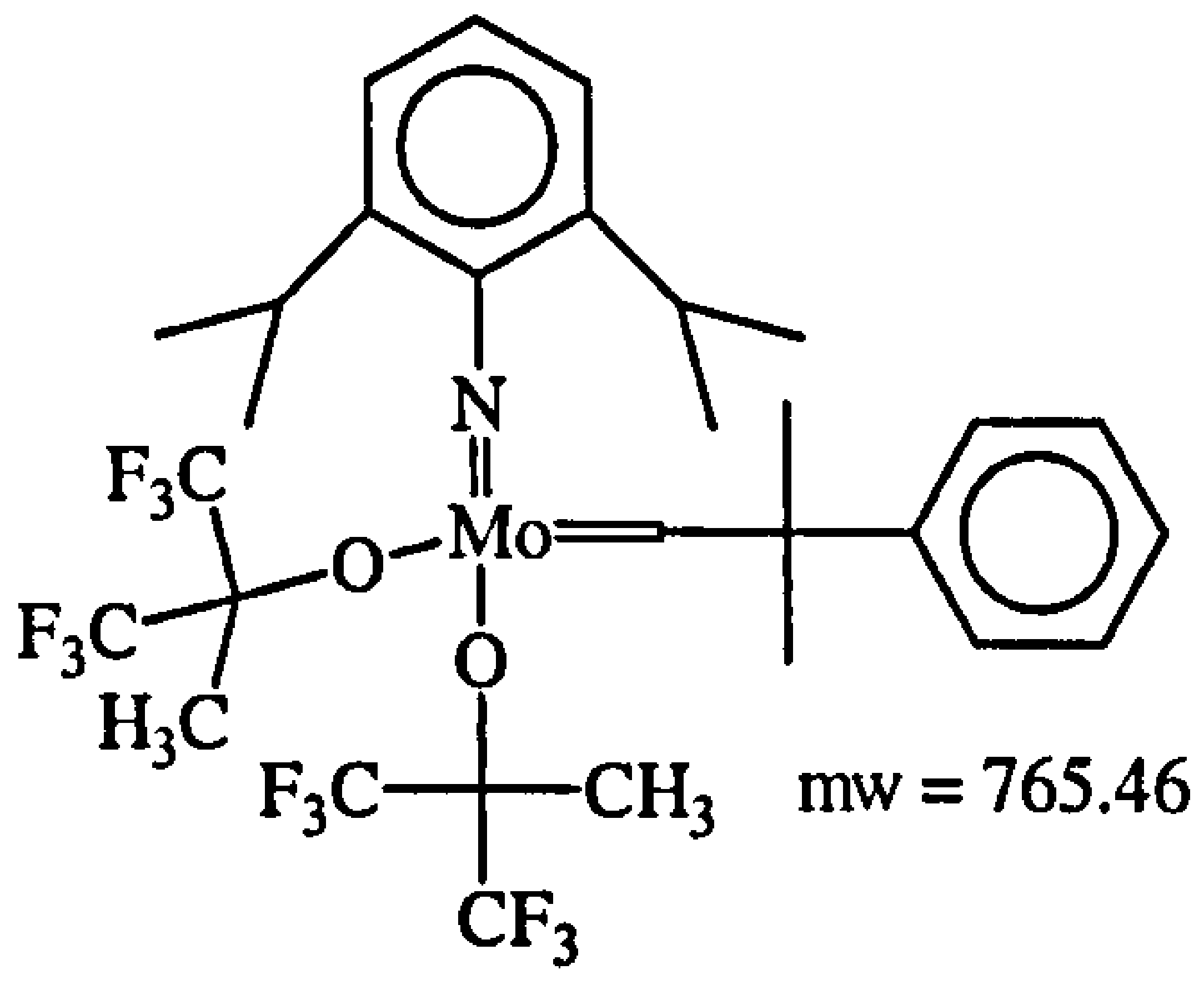
2.9 Attempted polymerisation of 1,1-diallyl malononitrile

It has been shown on several occasions that hexadiene polymerises by ADMET to give poly(butadiene). Wagner used hexadiene in his initial studies[20] and later used Schrock initiators as the catalyst.[21] Nubel has also polymerised hexadiene using a modified WCl_6-$SnMe_4$ catalyst.[32] Hexadiene is a useful test for ADMET polymerisation because the polymerisation has been extensively studied and also because there is no possibility for ring-closing as this would lead to a highly strained four-membered ring.

It was decided to repeat the polymerisation of 1,5-hexadiene using both Nubel's initiating system and using a Schrock initiator to test the validity of the methods. The possible route of reaction is shown below.



Hexadiene was polymerised using a classical initiator system WCl_6/n-propyl acetate/Me_4Sn and the Schrock initiator shown below.

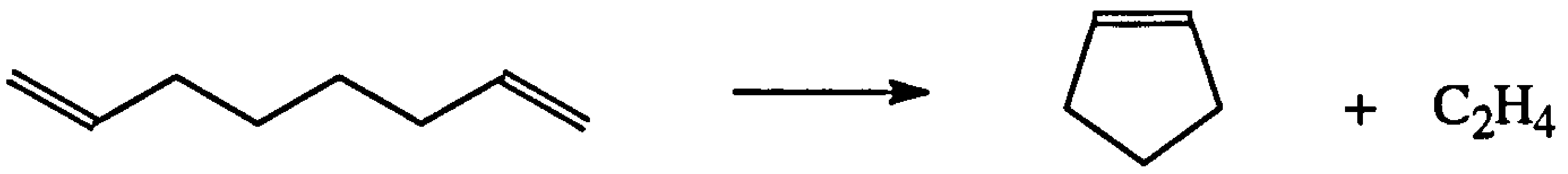


The initiator : monomer ratios were 1:100 for the classical system and 1:1500 for the well-defined system. See experimental section for further details. In both cases, rapid gas evolution was observed on the addition of the initiator to the monomer and this was believed to be ethylene. Poly(butadiene) was produced in both experiments; a brown oil in the first case and a beige solid in the second. This physical difference is due to the difference in molecular weights. The different initiator : monomer ratios gave the expected differences in molecular weight i.e. the polymer produced with the Schrock initiator has a higher molecular weight.

This work was continued to attempt to polymerise heptadiene using the same catalysts used for hexadiene. Heptadiene is the unsubstituted analogue of 1,1-diallyl malononitrile and therefore its polymerisation is of interest as an indicator of the polymerisability of diallyl malononitrile.

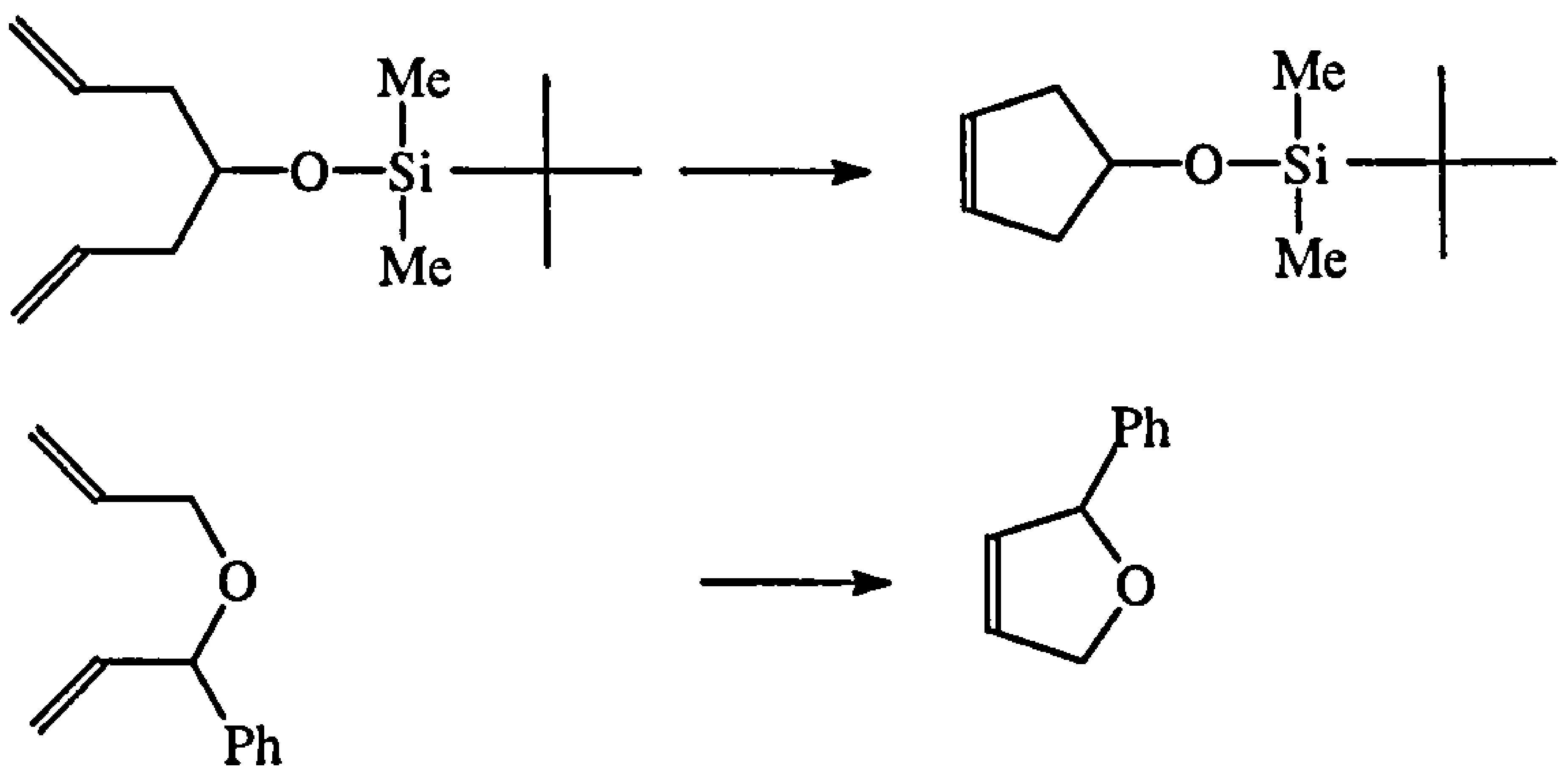
Attempts were made to polymerise heptadiene using the classical initiator in a initiator : monomer ratio of 1:100 and using the well-defined initiator in a ratio of 1:2000. See experimental section for further details.

In both cases, no polymer was produced although some evolution of gas was observed. The most likely explanation is that heptadiene is undergoing ring closure to form cyclopentene.



Attempts were made to trap the gas evolved to check for the presence of cyclopentene. However, owing to the very small scale of the reaction necessitated by the cost of the initiator, it was not possible to isolate any evolved gas.

Cyclopentene is a very stable ring structure and therefore it seems likely that its formation is favoured. Examples of ring formation from seven membered dienes have been previously observed.[36]



Although these results were not encouraging, having made the monomer, it was decided to try and polymerise 1,1-diallyl malononitrile using the Schrock initiator in an initiator : monomer ratio of 1:2000. No polymer was produced and no gas evolution was observed in all of several attempts.

This lack of reaction is probably due to the intolerance of the Schrock initiator to the functional groups which bind to the metal centre making the catalyst inactive.

2.10 Summary

ROMP and ADMET are not suitable methods for the production of the desired polymers. ROMP of cyclopentene monomers is extremely difficult owing to the unfavourable Gibbs free energy, as explained earlier.

ADMET of 1,1-diallyl malononitrile is unsuccessful for two reasons. Firstly, the metathesis catalysts have a poor tolerance of cyano groups. Secondly, even in the absence of cyano groups, seven membered dienes exhibit limited polymerisability owing to the stability of the cyclopentene ring which can be formed by ring closing metathesis. Diene monomers with a different number of carbon atoms was not considered to be a viable option. Using a longer diene would decrease the chance of ring formation as rings larger than seven membered are not favoured entropically. However, having a longer diene would decrease the concentration of polar groups on the polymer backbone and this would not produce a sufficiently polar polymer.

A shorter diene is also not a possibility owing to the negative neighbouring group effect described earlier in the chapter which dictates that the minimum number of methylene spacer units required between the functional group and the alkene is two.

2.11 Experimental

2.11.1 General methods

Dimethylformamide (DMF) and benzene were dried over calcium hydride. Dichloromethane (DCM) and chlorobenzene were dried by refluxing over phosphorous pentoxide. Deuterated benzene (C_6D_6) was dried by stirring over phosphorous pentoxide and then vacuum transfered. Tetrahydrofuran (THF) was dried by refluxing with sodium/benzophenone and storing over sodium wire.

Malononitrile was distilled under vacuum prior to use. Hexadiene was distilled under nitrogen, passed through a silica column, stored over molecular sieves and degassed prior to use. All other reagents were used as supplied.

A stock solution of WCl_6 was prepared by dissolving 0.3 g of catalyst in 30 cm^3 of dry chlorobenzene.

Infra red spectra were recorded on a Perkin Elmer 1600 series FTIR. The spectra were recorded as KBr discs or between sodium chloride discs. ^1H and ^{13}C NMR were recorded on a Varian VXR 400 NMR spectrometer and a Varian Gemini 200 NMR spectrometer. The solvent used was deuterated chloroform with TMS as internal reference. Gel permeation chromatography was carried out in chloroform using a Knauer HPLC pump (model 64), Waters model R401 differential refractometer detector and 3 PLgel columns with pore sizes of 10^2, 10^3 and 10^5 Å (column packing PLgel 5μm mixed styrene-divinyl benzene beads). The sample solutions were filtered through a Whatman WTP type 0.2μm filter to remove any particules before injection. The columns were calibrated using Polymer Laboratories polystyrene standards (162-770 000amu).

2.11.2 Synthesis of dimethyl-3-cyclopentene-1,1-dicarboxylate

Dimethyl malonate (17.03 g, 0.129 mol) was dissolved in DMF (190 cm^3) and the solution was stirred in a flask under nitrogen in an ice/water bath. Lithium hydride (2.78 g, 0.35 mol) was added in one portion and the mixture was left stirring for three hours. *Cis*-1,4-dichlorobutene (18.90 g, 0.151 mol) was added and the mixture was allowed to warm to room temperature. The reaction mixture was left stirring under nitrogen for 72 hours. The mixture was then diluted with 20% ether in hexane and poured into cold water. The organic layer was washed with water, brine, dried with magnesium sulphate and then filtered to remove the solid. The solvent was removed in vacuuo to give a solid which was recrystallised from hexane three times and then sublimed under vacuum to produce dimethyl-3-cyclopentene-1,1-dicarboxylate (5.83 g , 25%) as white crystals (m.p. = 57-58°C). Calculated for $C_9H_{12}O_4$: C, 58.7%; H, 6.6%; Found : C, 58.3%; H, 6.5%.

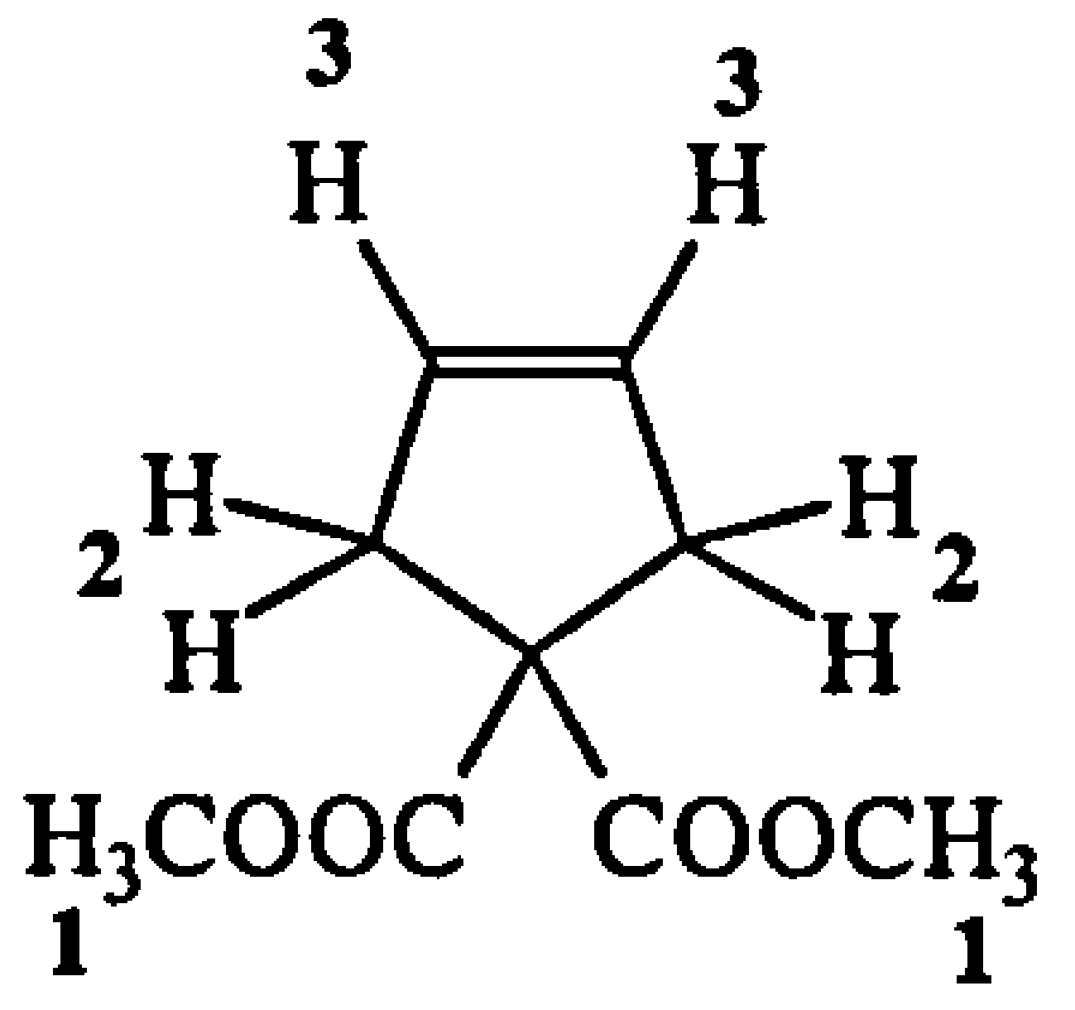
2.11.2.1 Characterisation

The monomer was analysed by several techniques. Assignments were made by comparison with data in K. Sugawara's thesis.[48]

Infra-Red Spectroscopy - See appendix 1.1

3020 cm^{-1} (vinylic C-H stretch), 2963 cm^{-1} (aliphatic C-H stretch), 1728 cm^{-1} (C=O stretch of ester), 1438 cm^{-1} (C-H deformation), 1276 cm^{-1} (C-O ester stretch)

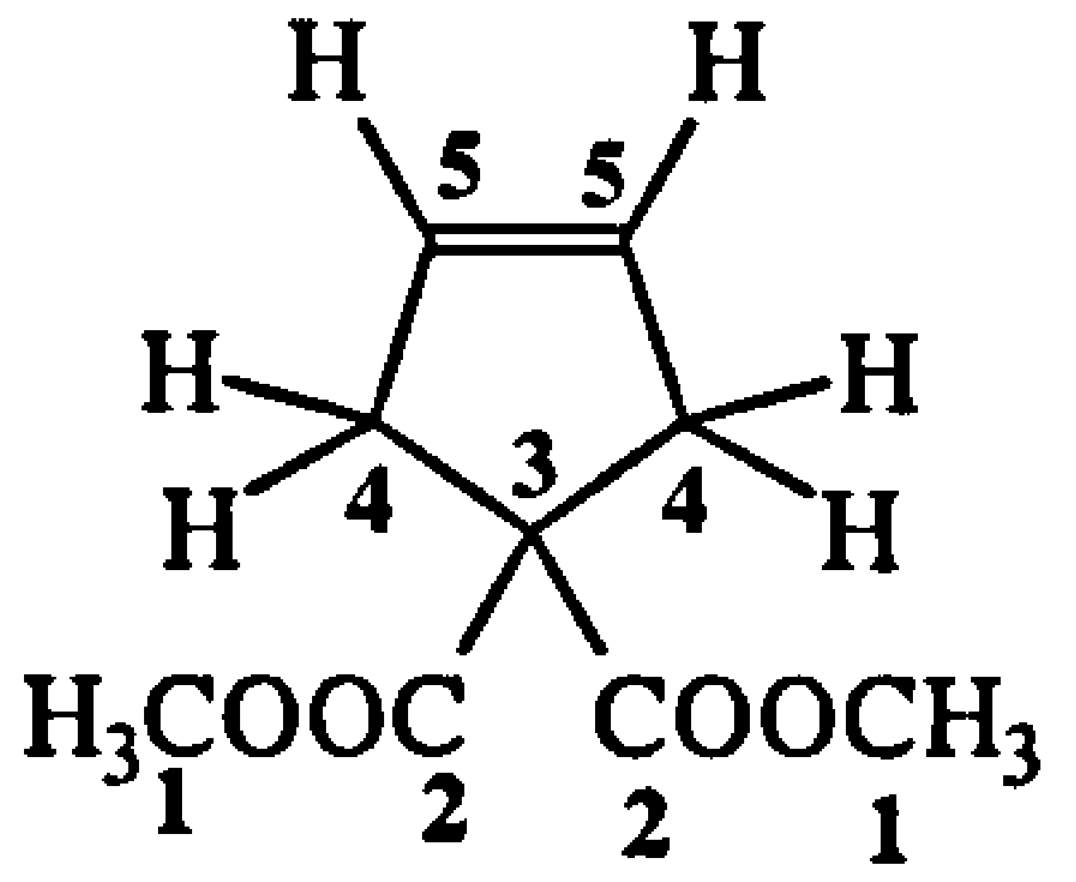
^1H NMR -See appendix1.2



δ / ppm = 5.61 (s,3), 3.74 (s,1) 3.03 (s,2)

Intensity ratio 1:3:2

^{13}C NMR - See appendix 1.3



δ = 172.64 (2), 128.77 (5), 58.73 (3), 52.81 (1), 40.91 (4)

X-ray Crystal Structure - See appendix 1.4 for crystal structure

2.11.3 Synthesis of ditertiarybutyl-3-cyclopentene-1,1-dicarboxylate

Di-*tert*-butyl malonate (19.0 g, 0.088 mol) was dissolved in DMF (190 cm^3) and the solution was stirred in a flask under nitrogen in an ice/water bath. Lithium hydride (1.69 g, 0.21 mol) was added in one portion and the mixture was left stirring for three hours. *Cis*-1,4-dichlorobutene (12.66 g, 0.101 mol) was added and the mixture was allowed to warm to room temperature. The reaction mixture was left stirring under nitrogen for 72 hours. The mixture was then diluted with 20% ether in hexane and poured into cold water. The organic layer was washed with water, brine, dried with magnesium sulphate and then filtered to remove the solid. The solvent was removed in vacuuo and the remaining solid was recrystallised from hexane to give ditertbutyl-3-cyclopentene-1,1-dicarboxylate (12.38 g , 53%) as white crystals (m.p. = 82.5-83°C). Calculated for $C_{15}H_{24}O_4$: C, 67.1%; H, 9.0%; Found : C, 66.7%; H, 8.9%.

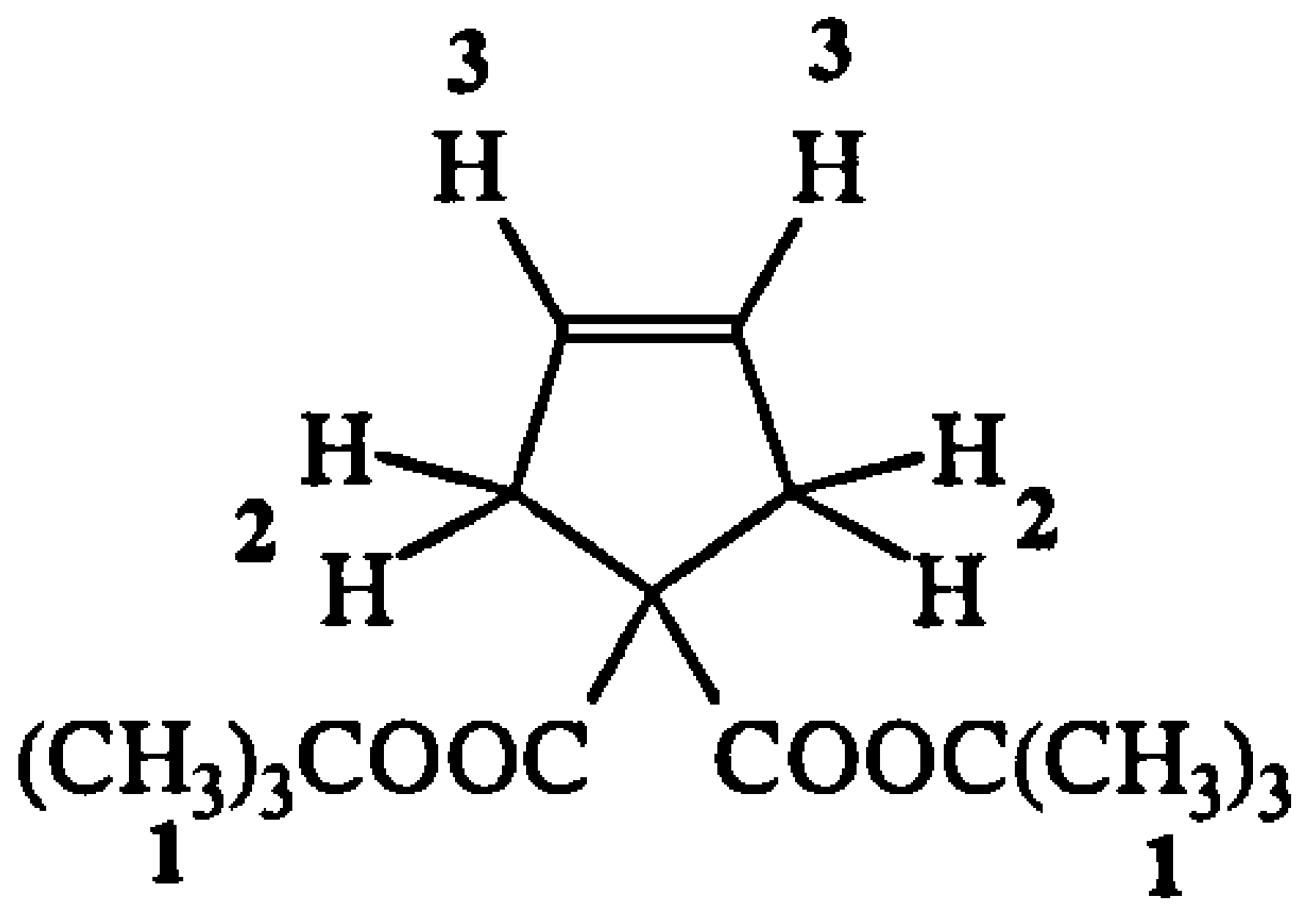
2.11.3.1 Characterisation

The monomer was analysed by several techniques.

Infra-Red Spectroscopy - See appendix 1.5

2983 cm^{-1} (vinylic C-H stretch), 2938 cm^{-1} (aliphatic C-H stretch), 1717 cm^{-1} (aliphatic stretch of ester), 1455 cm^{-1} (C-H deformation), 1258 cm^{-1} (C-O ester stretch)

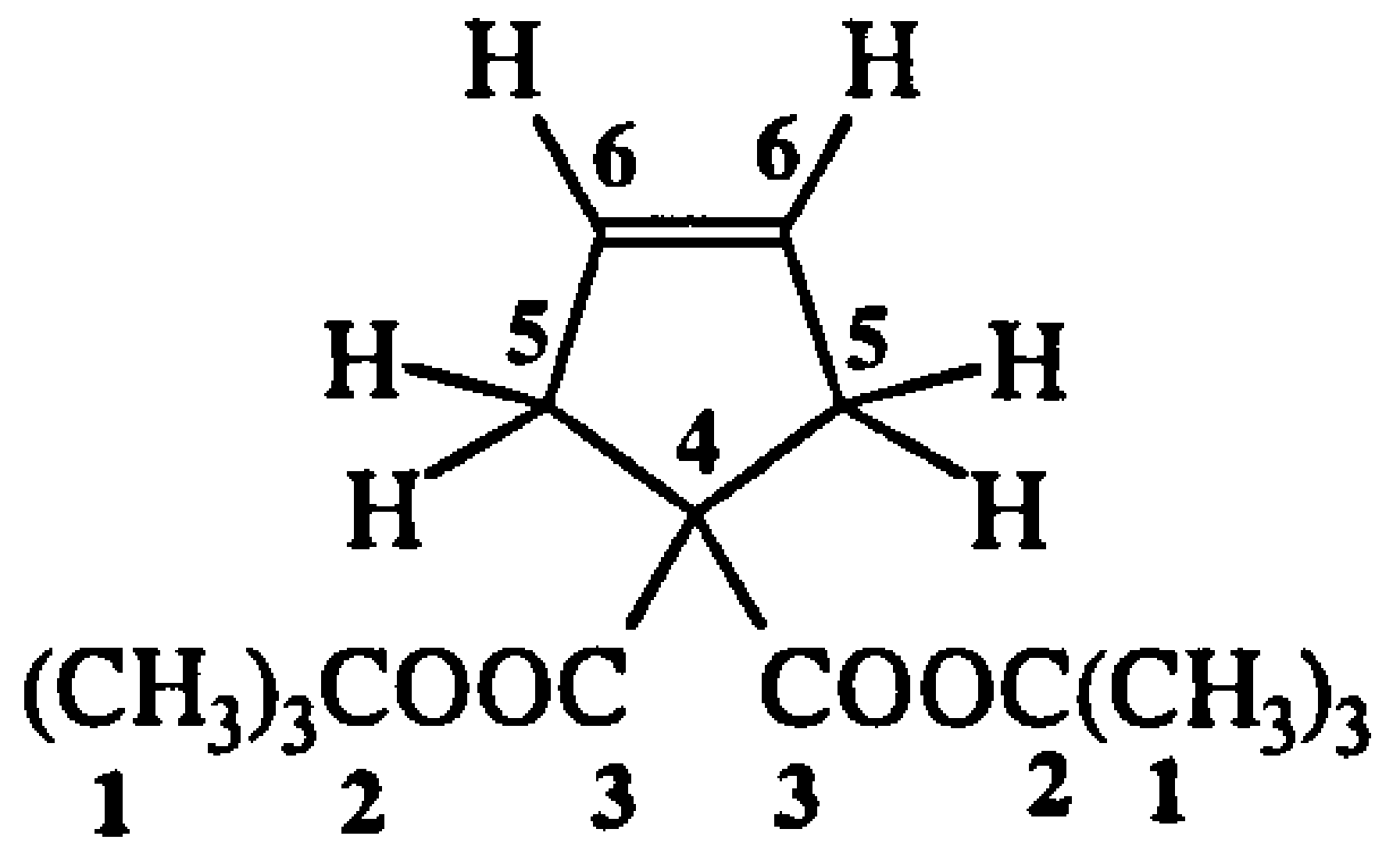
^{1}H NMR - See appendix 1.6



δ / ppm = 5.58 (s,**3**), 2.91 (s,**1**) 1.45 (s,**2**)

Intensity ratio 1:2:9

^{13}C NMR - See appendix 1.7



δ / ppm = 171.49 (**3**), 127.82 (**6**), 81.07 (**2**), 59.97 (**4**), 40.64 (**5**), 27.85 (**1**)

X-ray Crystal Structure - See appendix 1.8 for crystal structure

2.11.4 Attempted polymerisation of dicarboxylate monomers

2.11.4.1 Typical polymerisation of cyclopentene monomers using ruthenium catalyst

In an oxygen and moisture free environment, dimethyl cyclopentene dicarboxylate (0.978 g, 5.3 mmol) was dissolved in 2 cm^3 of dry DCM. The ruthenium catalyst (21.85 mg ,0.0265 mmol) was dissolved in 1 cm^3 of dry DCM. The monomer solution was quickly added to the stirred initiator solution and the mixture was stirred for 3 hours. No attempt was made to recover any polymer since the absence of any colour or consistency change indicated that no reaction had occurred.

2.11.4.2 Typical polymerisation of cyclopentene monomers using a well-defined tungsten catalyst

In an oxygen and moisture free environment, dimethyl cyclopentene dicarboxylate (0.919 g, 5.0 mmol) was dissolved in 2.5 cm^3 of dry, deuterated benzene. The tungsten catalyst (0.013 g, 0.0125 mmol) was dissolved in 1 cm^3 of dry, deuterated benzene. The two solutions were cooled in a freezer at -38°C for 30 minutes. The monomer solution was quickly added to the stirred initiator solution and the mixture was transferred to an ampoule, brought out from the glove box and placed in dry ice overnight. The ampoule was then returned to the glove box and the contents transferred to an NMR tube. NMR spectroscopic analysis showed that no reaction had occurred and therefore no attempt was made to precipitate any polymer.

2.11.5 Synthesis of 1,1-diallyl malononitrile

A two-necked, one litre, round-bottomed flask was fitted with a dropping funnel with a nitrogen inlet and a cooling jacket. Dry THF (200 cm^3) was transferred into the flask using a cannular. Malononitrile (3.30 g, 0.05 mol) and allyl bromide (13.31 g, 0.11 mol) were added under nitrogen. The flask was fitted with a condenser. Dry THF (150 cm^3) was transferred into the dropping funnel and potassium *tert*-butoxide (12.34 g, 0.11 mol) was added to the dropping funnel under nitrogen. The cooling jacket was filled with ice. The flask was placed in an acetone/dry ice bath at -

15°C and the contents were stirred for one hour. The suspension of base was slowly added to the flask and the mixture was stirred overnight. The reaction mixture was poured into dichloromethane and the product extracted into the DCM. The solvent was removed in vacuuo to yield an orange sludge. Distillation of this lead to a clear, colourless liquid (b.p. = 60.5°C at 0.35mm/Hg). On standing this oil solidified to form clear, colourless crystals. Recrystallisation of these crystals in DCM/hexane yielded 1,1-diallyl malononitrile (3.88 g, 53%) as a white solid (m.p. = 32-33°C). Calculated for $C_9H_{10}N_2$: C, 73.9%; H, 6.9%; N, 19.2%; Found : C, 74.1%; H, 7.1%; N, 19.1%.

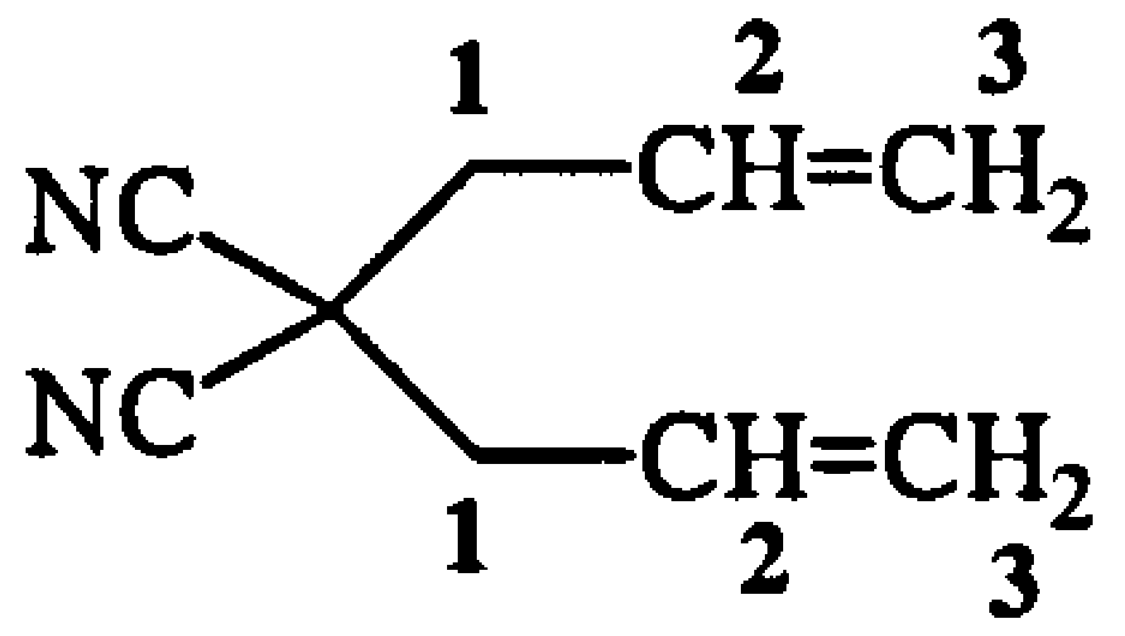
2.11.5.1 Characterisation

The monomer was analysed by several techniques.

Infra-Red Spectroscopy - See appendix 1.9

2987 cm^{-1} (vinylic C-H stretch), 2251 cm^{-1} (C-N stretch),1644 cm^{-1} (C=C stretch), 1452 cm^{-1} (C-H bend), 990 cm^{-1} (C-H out of plane bend), 934 cm^{-1} (C=C absorption)

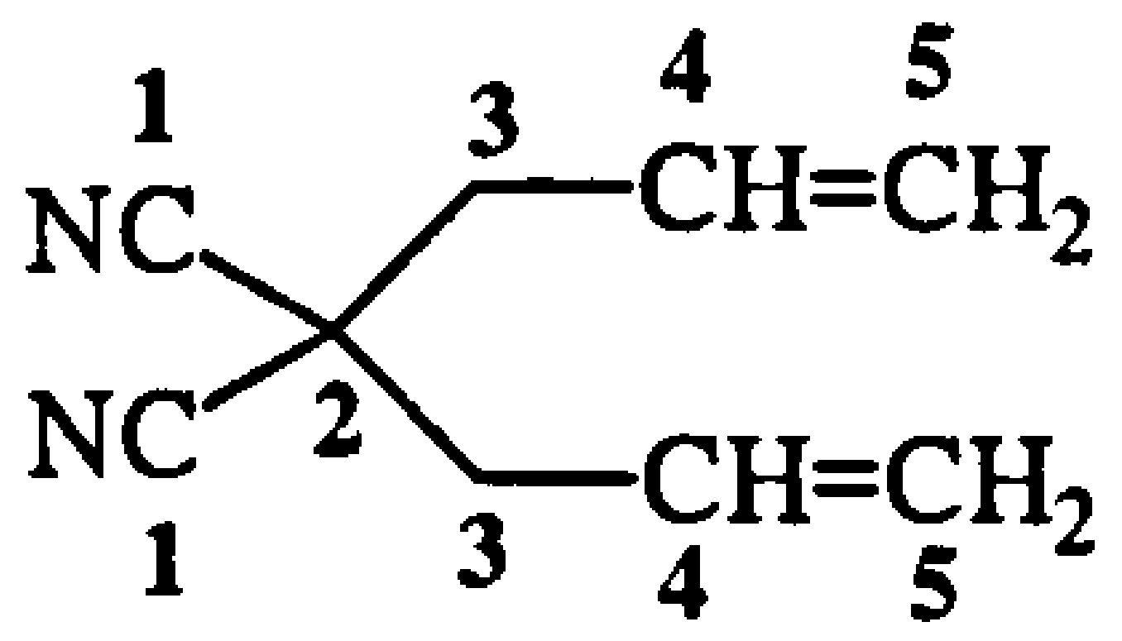
^{1}H NMR - See appendix 1.10



δ / ppm = 5.89 (m, 2), 5.43 (m,3), 2.68 (m,1)

Intensity ratio = 1:2:2

^{13}C NMR - See appendix 1.11



δ / ppm= 128.40 (5), 123.39 (4), 114.83 (1), 40.83 (3), 37.25 (2)

2.11.6 ADMET polymerisation

2.11.6.1 Polymerisation of hexadiene using WCl_6 initiator

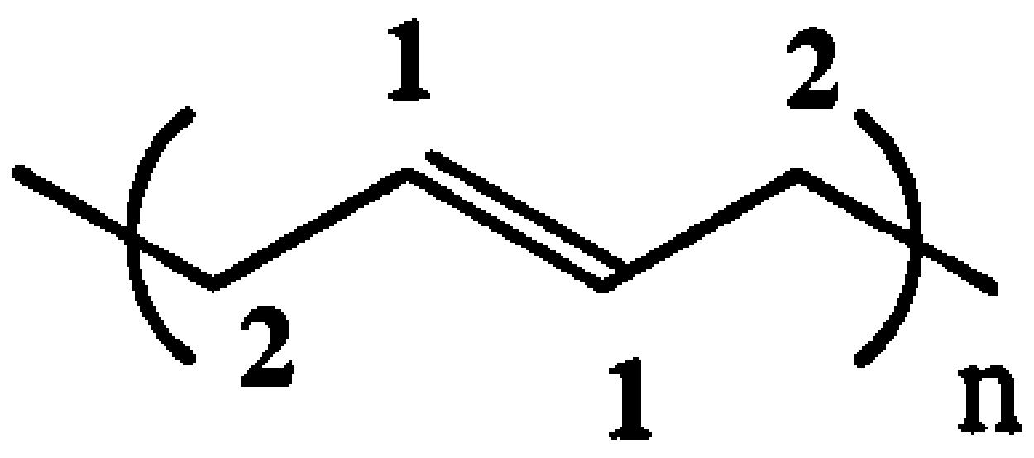
Hexadiene (1.0 g, 12.17 mmol) was syringed under nitrogen into an ampoule. Into a second ampoule was syringed 4.83 cm^3 of the catalyst stock solution, propyl acetate (0.056 cm^3, 0.49 mmol) and tetramethyl tin (0.033 cm^3, 0.25 mmol). This mixture was transferred using a syringe into the ampoule containing the monomer. The mixture was stirred overnight at 85°C. After the reaction time the mixture was dark brown in colour with a black precipitate. On the addition of methanol to the reaction mixture, a brown oily precipitate was formed. This precipitate was dissolved in dichloromethane and passed through an alumina column to remove the catalyst. The solvent was removed in vacuuo to yield poly(hexadiene), a brown coloured oil.

2.11.6.1.1 Characterisation

Assignments were made by comparison to reference to the literature.[32]

It should be noted that it was difficult to purify the polymeric product owing to its low molecular weight which lead to the product being an oil. After, precipitation in methanol, it was not possible to decant off all the solvent and this residual solvent will have contained some residual monomer and other impurities. These can be seen especially in the ^{13}C NMR where the peaks at 136.36, 114.33 and 33.95 ppm correspond to unreacted hexadiene.

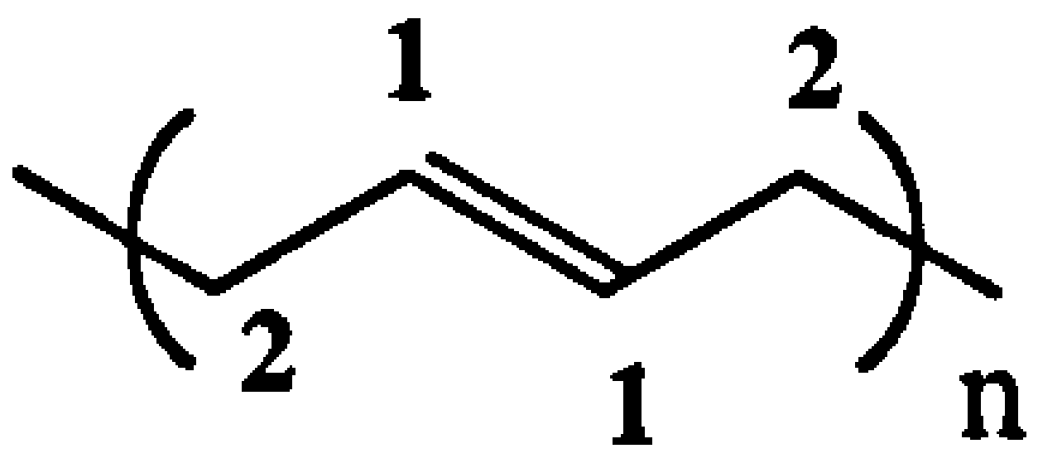
^1H NMR - See appendix 1.12



δ = 5.39 (1,m), 2.03 (2,m) - Peak splittings are due to *cis/trans* isomerism.

Intensity ratio = 1:2

^{13}C NMR - see appendix 1.13



δ / ppm = 130.00 (**1**,*trans*), 129.42 (**1**,*cis*), 32.71 (**2**,*trans*), 27.39 (**2**,*cis*)

Gel Permeation Chromatography - See appendix 1.14

$\overline{Mn} = 1002 \quad \overline{Mw} = 1198 \quad \text{Pdi} = 1.20$

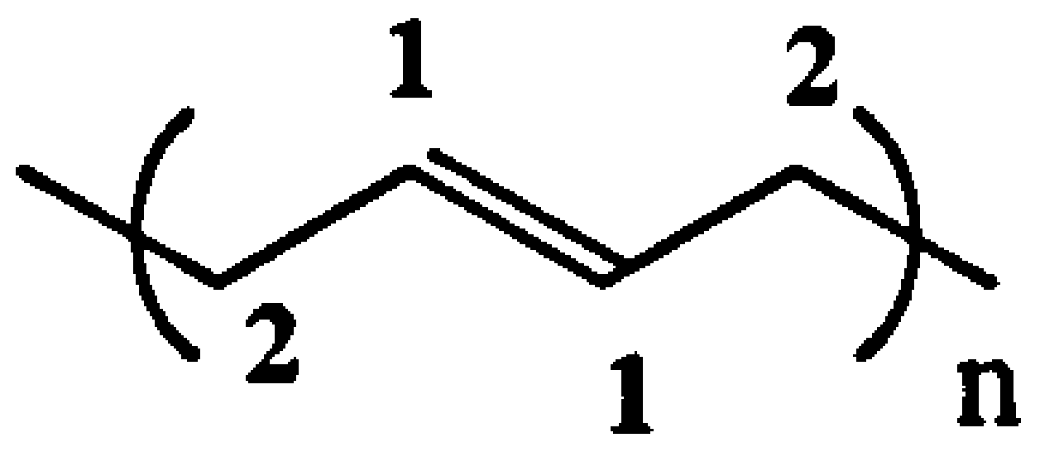
2.11.6.2 Polymerisation of hexadiene using Schrock initiator

Hexadiene (0.5 g, 6.08 mmol) and the initiator (0.0031 mg, 0.005 mmol) were measured into two separate vials. The solids were dissolved in the minimum volume of dry benzene. The monomer solution was transferred to an ampoule and was stirred as the initiator solution was added. Rapid gas evolution was observed. The mixture was left to stir overnight. After the reaction period, dichloromethane was added to the reaction mixture and then the solution was added dropwise to methanol to yield poly(hexadiene), a beige solid. The polymer was washed with methanol and dried overnight in a vacuum oven.

2.11.6.2.1 Characterisation

Analytical data was compared to that in the literature.[32]

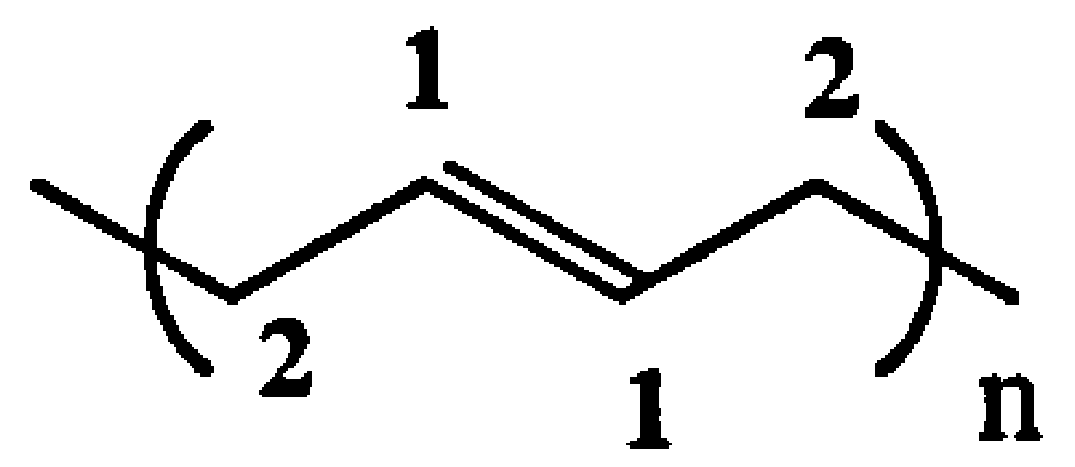
^{1}H NMR - See appendix 1.15



δ / ppm = 5.41 (1,m), 2.03 (2,m)

Intensity ratio = 1:2

^{13}C NMR - See appendix 1.16



δ / ppm = 130.02 (1,*trans*), 129.44 (1,*cis*), 32.73 (2,*trans*), 27.41 (2,*cis*)

Gel Permeation Chromatography - See appendix 1.17

$\overline{Mn} = 5295 \quad \overline{Mw} = 13849 \quad \text{Pdi} = 2.61$

2.11.7 Attempted polymerisation of heptadiene using WCl_6 initiator

Heptadiene (1.0 g, 10.4 mmol) was syringed under nitrogen into an ampoule. Into a second ampoule was syringed 4.12 cm^3 of the catalyst stock solution, propyl acetate (0.048 cm^3, 0.42 mmol) and tetramethyl tin (0.029 cm^3, 0.21 mmol). This mixture was then transferred using a syringe into the ampoule containing the monomer. The mixture was stirred overnight at 80°C. After the reaction time the mixture was clear with a black precipitate. On the addition of the reaction mixture to the methanol, no precipitate was formed.

2.11.8 Attempted polymerisation of heptadiene using Schrock initiator

Heptadiene (1.0 g, 10.4 mmol) and the initiator (0.0080 mg, 0.01 mmol) were measured into two separate vials. The solids were dissolved in the minimum volume of dry benzene. The monomer solution was transferred to an ampoule and was stirred as the initiator solution was added. The mixture was left to stir overnight. After the reaction period, dichloromethane was added to the reaction mixture and then methanol was used in an attempt to precipitate the product. No polymer was precipitated.

2.11.9 Attempted polymerisation of 1,1-diallyl malononitrile using Schrock initiator

1,1-Diallyl malononitrile (0.481 g, 3.3 mmol) and the initiator (0.0036 mg, 0.002 mmol) were measured into two separate vials. The solids were dissolved in the minimum volume of dry benzene. The monomer solution was transferred to an ampoule and was stirred as the initiator solution was added. The mixture was heated at 50°C and stirred overnight. After the reaction period, dichloromethane was added to the reaction mixture and then methanol was used in an attempt to precipitate the product. No polymer was produced.

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Chapter 3

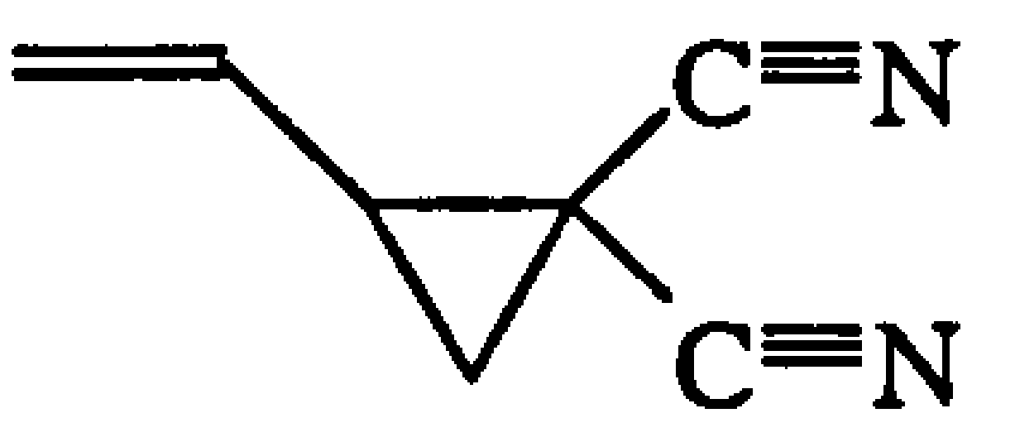
Free-radical polymerisation of dicyano-vinylcyclopropane monomers

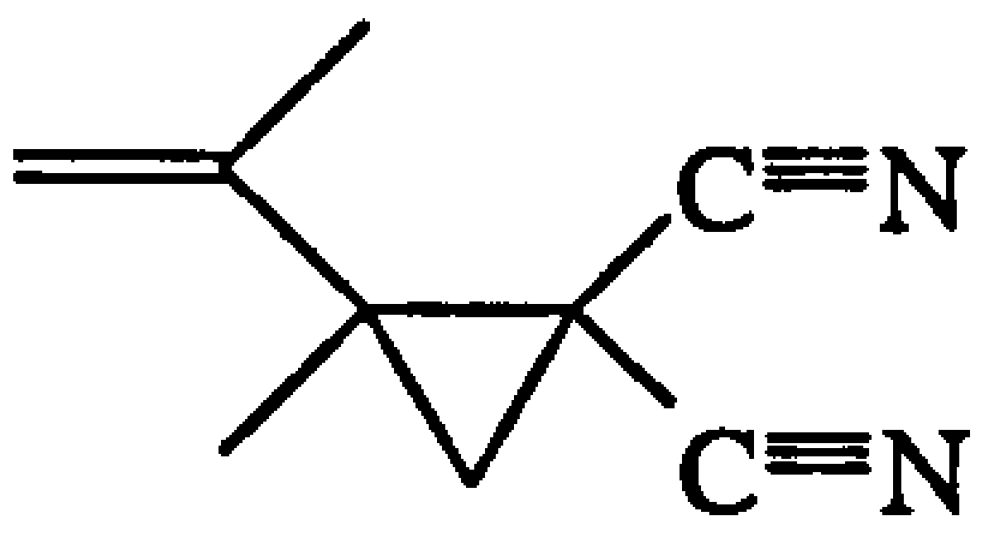
3. Free-radical polymerisation of 1,1-dicyano-vinylcyclopropane monomers

3.1 Introduction

The aim of the work described in this thesis was to produce polar elastomeric polymers. Attempts described in chapter 2, to produce such a material using the olefin metathesis reaction proved unsuccessful. It was therefore decided to focus the work on the free-radical polymerisation of vinylcyclopropane monomers which, it was hoped, would lead to a material with the desired properties.

The work reported in this chapter describes the synthesis and free-radical polymerisation of two vinylcyclopropane monomers containing cyano functional groups. The monomers considered were 1,1-dicyano-2-vinylcyclopropane and 1,1-dicyano-2-methyl-2-isopropenylcyclopropane shown below.

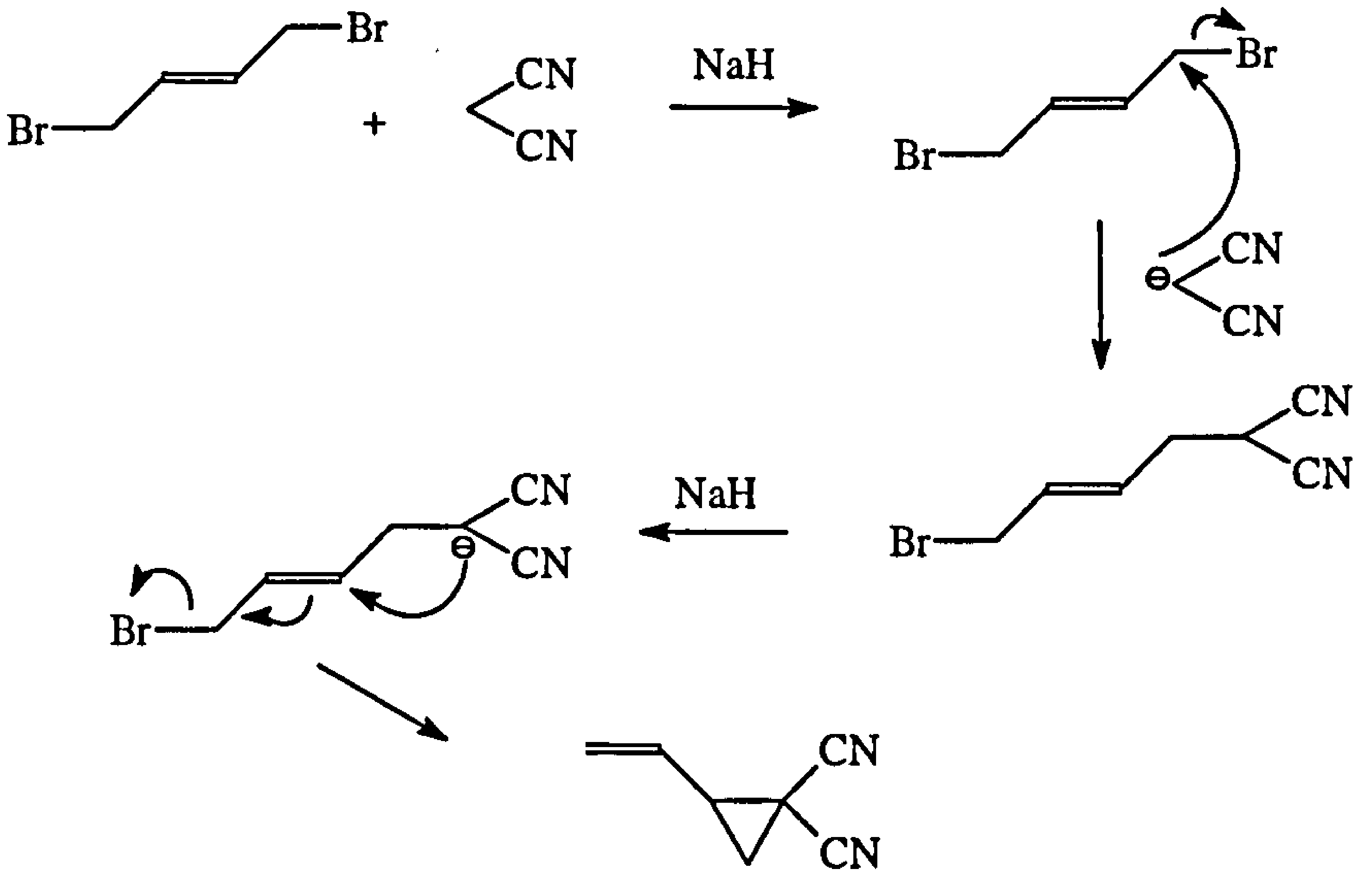




3.2 Synthesis of 1,1-dicyano-2-vinylcyclopropane

The synthesis of 1,1-dicyano-2-vinylcyclopropane has been reported previously by Saicic.[1] It was prepared in yields up to 50% by the reaction of malononitrile with *trans*-1,4-dibromobutene.

The mechanism of the reaction is shown schematically below.



The monomer, 1,1-dicyano-2-vinylcyclopropane, was prepared in 42% yield following the literature method.[1] The product was a clear, colourless liquid with a boiling point of 67°C/1mmHg.

The product was found to be extremely difficult to purify, the main impurities being the starting materials, malononitrile and dibromobutene. Longer reaction times did not effect full conversion of starting materials. There was also possibly some 4,4-dicyano-cyclopentene in the product, formed from small amounts of *cis*-dibromobutene present in the starting material. Purification of the monomer was attempted by both distillation and column chromatography. The boiling points of the starting materials are extremely close to the boiling point of the product hence distillation was not completely successful. The product appeared to decompose on the neutral silica column used for chromatography.

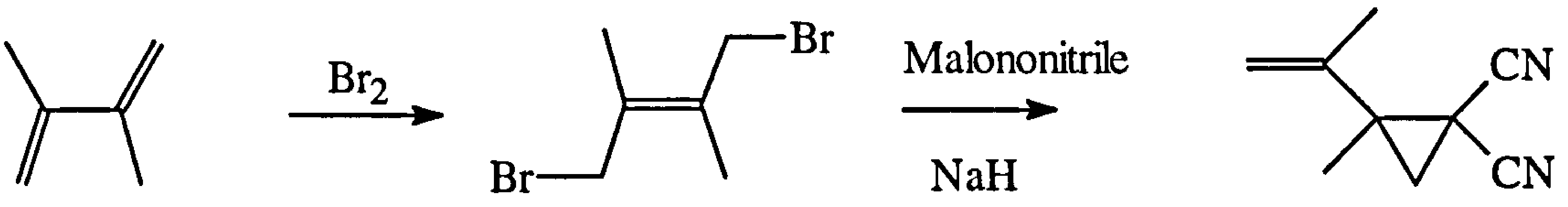
3.2.1 Analysis

It can be seen from the ^1H NMR spectrum of the monomer (appendix 2.2) that these impurities are only present in small amounts (less than 5%); the peak at ~3.6ppm being due to the malononitrile and the peak at ~3.95ppm being due to the 1,1-dibromobutene. The integration for the peak at 5.6 ppm in the ^1H NMR spectrum corresponding to the vinyl hydrogens is slightly high and this is probably due to the hydrogens of the alkene in the dicyano-cyclopentene impurity being under the multiplet. The elemental analysis for this product (see experimental) showed a misleadingly low carbon content and this is due to the low carbon content of the malononitrile and 1,4-dibromobutene impurities.

3.3 Synthesis of 1,1-dicyano-2-methyl-2-isopropenylcyclopropane

There are several reports in the literature of the synthesis of 1,1-dicyano-2-methyl-2-isopropenylcyclopropane. In 1971, it was synthesised by the irradiation of bromomalononitrile and 2,3-dimethylbutadiene in dry dichloromethane.[2] Bromomalononitrile is not readily available and is produced by reacting bromine and malononitrile in water. 1,1-Dicyano-2-methyl-2-isopropenylcyclopropane has also been produced by a multi-step reaction via a cyclic dicyano-thioether.[3]

It was decided to attempt the synthesis of the monomer via a two step reaction not previously reported in the literature. The first step was the bromination of 2,3-dimethylbutadiene[4] and the second step involved the addition of malononitrile, using the method described for the synthesis of 1,1-dicyano-2-vinylcyclopropane.



The first step was achieved in 58% yield to give *trans*-1,4-dibromo-2,3-dimethyl-2-butene as a pale yellow lachrymatory solid. The second step proceeded in 54% yield to give a clear, colourless oil boiling at 74°C/0.6mmHg. The structure of the product was confirmed using spectroscopic analysis (see experimental).

3.4 Polymerisation of cyano monomers

3.4.1 History

The polymerisation of cyano containing monomers has been studied previously by several groups. In the late 1970's, Cho and Ahn polymerised 1,1-dicyano-2-vinylcyclopropane using AIBN as the free-radical initiator.[5,6] They claimed to have formed high molecular weight polymer which was found to be soluble only in hot solvents such as dimethylformamide (DMF) and dimethyl sulphoxide (DMSO). Infra-red spectroscopic analysis of the polymer lead them to suggest that the polymer backbone contained exclusively *trans* double bonds. They also recorded a ^{1}H NMR spectrum at 90 MHz which showed two broad peaks. They claimed that the simplicity of the spectrum proved that the monomer had polymerised exclusively by 1,5-addition. They observed a broad transition at about 25°C in the DSC trace which they ascribed to the Tg.

In 1989, Endo studied the polymerisation of 1,1-dicyano-2-vinylcyclopropane in various solvents.[7] He obtained a low yield (4-13%) of an insoluble polymer when benzene was the solvent but he was unable to produce any polymer using DMF as the solvent. He analysed the polymer formed in benzene and confirmed Ahn and Cho's conclusions about the structure of the polymer

Endo extended this work to the bulk radical polymerisation of 1,1-dicyano-2-vinylcyclopropane.[8] He produced a pale yellow, opaque solid in a high yield but was unable to characterise it because it was insoluble in common organic solvents.

The analytical data presented by these workers is somewhat ambiguous and the fine structure of the polymer produced from the polymerisation of 1,1-dicyano-2-vinylcyclopropane is yet to be established.

There are no references in the literature to the polymerisation of 1,1-dicyano, 2-methyl-2-isopropenylcyclopropane.

3.4.2 Polymerisation of 1,1-dicyano-2-vinylcyclopropane

The polymerisation of 1,1-dicyano-2-vinylcyclopropane was carried out in sealed ampoules using AIBN as initiator in benzene under the various conditions shown in the table below and the polymers produced were characterised by ^{1}H and ^{13}C NMR, infra-red spectroscopy, DSC, GPC and elemental analysis.

	Temperature / °C	Time / hours	Initiator (% mol)	Yield %	Appearance
A	60	20	0.1	29	White powder
B	room temp	20	0.4	No polymer produced	
C	60	20	0.4	42	White powder
D	120	20	0.4	33	White powder
E	60	20	1.5	50	White powder
F	60	20	3.0	45	White powder
G	60	5	0.4	34	White powder
H	60	48	0.4	36	White powder
I*	60	20	0.4	67	Pale yellow powder

*- neat monomer

Table 3-1 Summary of polymerisation conditions for the polymerisation of 1,1-dicyano-2-vinylcyclopropane (See experimental)

After the required reaction time, the product polymers were found to have precipitated as fine pale yellow solids. These powders were recovered by filtration, washed with methanol and dried in a vacuum oven for several days. In the bulk polymerisation (sample I), the whole mass set as a solid lump in the ampoule. This solid was ground to a fine powder, washed with methanol and dried in a vacuum oven.

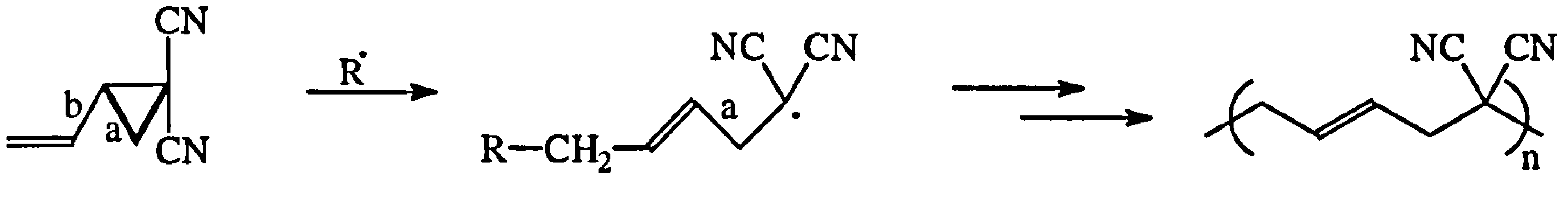
The yields produced are in agreement with those reported previously. This work shows that when using benzene as a solvent, the yields are low even after 48 hours reaction time. In the literature the yields when using benzene as a solvent range from 4 to 45%.[5-7] Literature yields for the bulk polymerisation range from 86 to 99%[5,8] and it can be seen that in this work the highest yield was obtained for sample I where no solvent was used. However, bulk polymerisation of this monomer is not ideal because, at the end of the reaction, the polymer is set solid into the bottom of the ampoule and can only be extracted by smashing the ampoule and grinding the product.

The polymers were found to be insoluble in all common organic solvents except hot (80°C) dimethylsulphoxide (DMSO). This led to some difficulties in the characterisation of the polymers.

3.4.2.1 Analysis

Infra-red spectroscopy of the polymers gave almost identical spectra. A sharp band at 973 cm^{-1} indicates the presence of *trans* double bonds and the lack of a band between 730-665 cm^{-1} (corresponding to *cis* double bonds) suggests that the polymer is predominantly *trans* as proposed by Cho and Ahn.

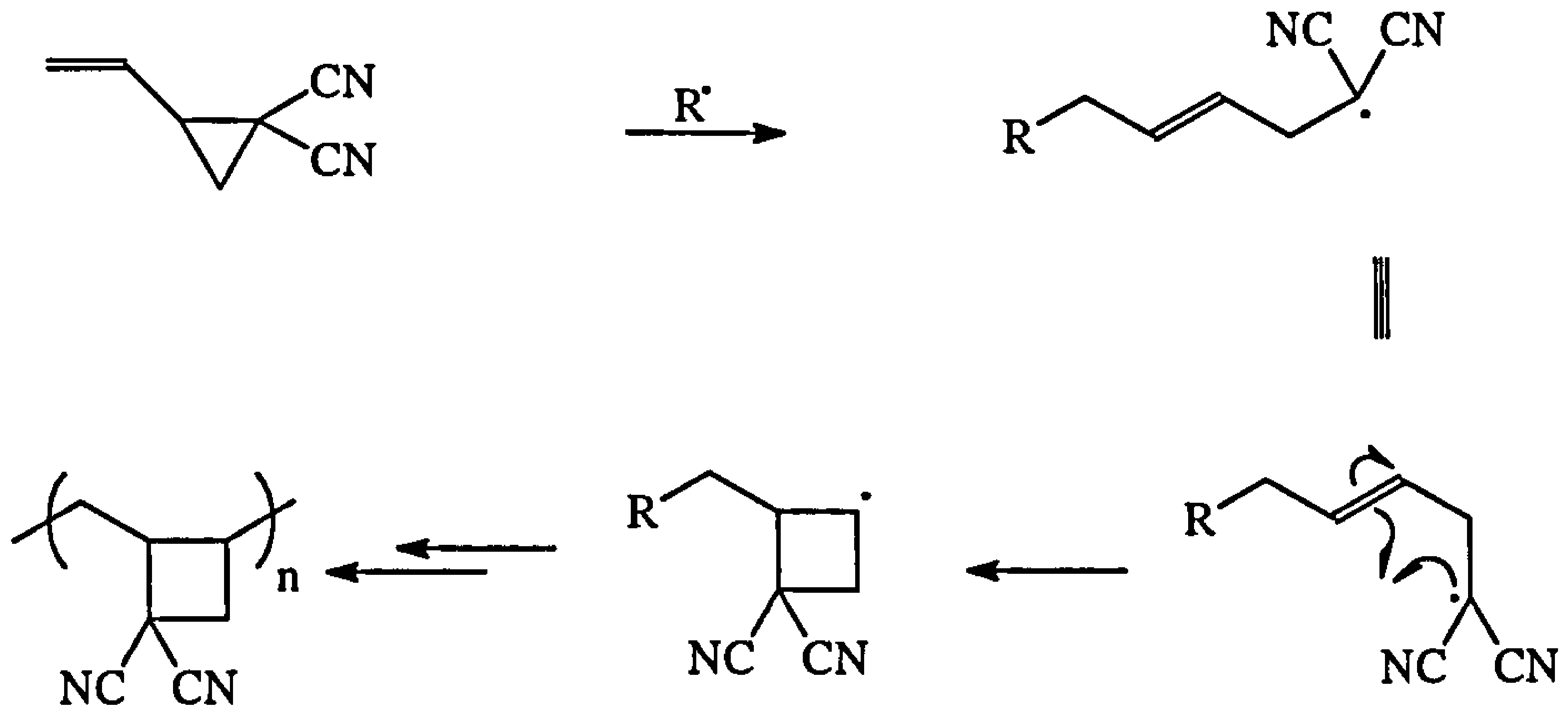
This predominance of *trans* double bonds is possibly due to the conformation adopted by the monomer during polymerisation. The plane of the vinyl group is orthogonal to the plane of the cyclopropyl ring and the most likely conformation is with the double bond pointing away from the ring as shown below.



This places the vinyl group in an anti configuration relative to the bond in the ring that remains intact during the polymerisation (a) and hence the double bond formed at (b) will be in a *trans* configuration. Ideal repetition of this process leads to an all *trans* 1,5-incorporation of the monomer.

However, an IR band at 1062 cm^{-1} is present in the product, particularly easily seen in sample E and this could correspond to residual cyclopropyl rings; in the monomer a similar band appears at 1072 cm^{-1}.

The ^1H NMR spectra show two main peaks at 5.90 and 2.92 ppm corresponding to the olefinic and methylene hydrogens of the 1,5-ring-opened product respectively. There is another peak which occurs in all of the polymer samples at 1.30 ppm which could be due to the ring hydrogens of a cyclobutane structure formed as shown below.



All samples display a small doublet at 2.95 ppm which corresponds to the methylene hydrogens of the polymer unit containing a cyclobutane ring. The integrated intensity of these peaks correspond to about 3 mole% of cyclobutane units.

In polymer samples D, E ,F and H, an extra peak is observed at -0.13 ppm and this could be due to ring methylene hydrogens on a cyclopropyl unit incorporated in the polymer by 1,2-addition of the radical. It is not clear why this is only observed in four of the polymer samples. The relative integrated intensity of this peak in samples D, E, F and H also varies reaching a maximum corresponding to about 5 mole% of such units in sample E. The backbone methylene hydrogens of this unit are not distinguishable in the spectra and are probably hidden under another peak.

In the ^{13}C NMR only the four peaks corresponding to carbons in the 1,5-ring-opened repeat unit are observed confirming that the cyclobutane and cyclopropane defects detected in the ^1H NMR spectra are present only in low concentrations and the polymer is predominantly the 1,5-ring-opened product.

In both the ^1H and ^{13}C NMR spectra, sample I was found to contain a considerable amount of unreacted monomer.

The glass transition temperatures of these polymers detected as weak transitions in DSC (appendix 2.15) were found to range from 68°C to 88°C. This range may reflect the somewhat ill-characterised nature of the products; however, they are certainly not elastomeric at room temperature and are therefore not suitable for the study of electrostriction.

Gel permeation chromatography was carried out and the values obtained are shown below.

Sample	Mw	Mn	Polydispersity
A	213 000	77 000	2.8
C	180 000	44 000	4.1
D	189 000	54 000	3.5
E	58 000	23 000	2.5
F	35 000	15 000	2.4
H	284 000	93 000	3.1
I	179 000	69 000	2.6

Table 3-2 Gel permeation chromatography results for the polymerisation of 1,1-dicyano-2-vinylcyclopropane (see appendix 2.14 for traces)

These values were obtained by RAPRA Technology by running the samples dissolved in DMSO at 80°C. In this GPC analysis a broad molecular weight Dextran calibrant is used and the molecular weights gained are expressed as the "Dextran equivalent" molecular weights. There could be considerable difference between these "Dextran equivalents" and the actual molecular weights of the polymers. However, the results can be used in a simple comparative manner. It should also be noted that there was a lack of reproducibility in these measurements which again suggests that these molecular weight values may not be reliable.

Sample C was produced using the standard polymerisation conditions of 20 hours at 60 °C using a 0.4 mole% of initiator. By comparing the molecular weights of the other samples with the value obtained for sample C it is possible to see the effect that the various changes in the polymerisation conditions had on the molecular weight.

An increase in temperature (sample D) and absence of solvent (sample I) did not appear to effect the molecular weight of the sample produced significantly. An increase in the reaction time (sample H) led to an increase in the polymer's molecular weight. This was unexpected and may indicate some side reaction leading to chain coupling, possibly via a reaction at the defect sites identified by ^{1}H NMR analysis. Some product of these polymerisations was insoluble consistent with such inter-chain reactions leading to a cross-linked product. Changing the mole% of initiator had the expected effects on the molecular weight; a decrease in the amount of initiator (sample A) led to a higher molecular weight whilst an increase in the amount of initiator (samples E and F) led to a decrease in molecular weights.

High molecular weight shoulders are seen on several of the samples particularly samples D, E, H and C. This is also consistent with chain coupling and shows that there are several processes occurring in this polymerisation which is not a simple clean reaction. It is to be noted that the largest shoulder appears on sample E which showed the highest amount of cyclopropyl units present.

For free-radical polymerisation, a polydispersity of 2 is expected for ideal reactions with disproportionation termination. It can be seen that the data obtained gives polydispersities between 2.6 and 4.1 and this is a further indication that this radical polymerisation is not ideal.

Elemental analysis of the polymers showed good agreement with the calculated values, which suggests that the impurities present in the monomer are not incorporated into the polymer chain.

3.4.2.2 Conclusion

The polymerisation of 1,1-dicyano-2-vinylcyclopropane has been carried out producing polymers in typical yields of 45%. The polymers were found to be predominantly the 1,5-ring-opened product although all samples showed evidence of a cyclobutane unit and several samples showed evidence of a 1,2-addition product. The polymers were shown to contain predominantly *trans* double bonds.

The glass transition temperatures of the polymers ranged between 68-88°C. This is too high for these polymers to be of interest as polar, elastomeric polymers.

It was hoped that the incorporation of two methyl groups into the monomer would induce more disorder within the polymer structure which would lower the glass transition temperature; work directed to this end is described in the following section.

3.4.3 Attempted polymerisation of 1,1-dicyano-2-methyl-2-isopropenylcyclopropane

Following the protocol which was successful for the polymerisation of 1,1-dicyano-2-vinylcyclopropane, attempts were made to polymerise 1,1-dicyano-2-methyl-2-isopropenylcyclopropane using the various conditions shown below.

	Temperature / °C	Time / hours	Solvent	Initiator (% mol)
A	60	20	C_6H_6	0.1
B	room temp	20	C_6H_6	0.4
C	60	20	C_6H_6	0.4
D	120	20	C_6H_6	0.4
E	60	20	C_6H_6	1.5
F	60	20	C_6H_6	3.0
G	60	5	C_6H_6	0.4
H	60	48	C_6H_6	0.4
I*	60	20	none	0.4

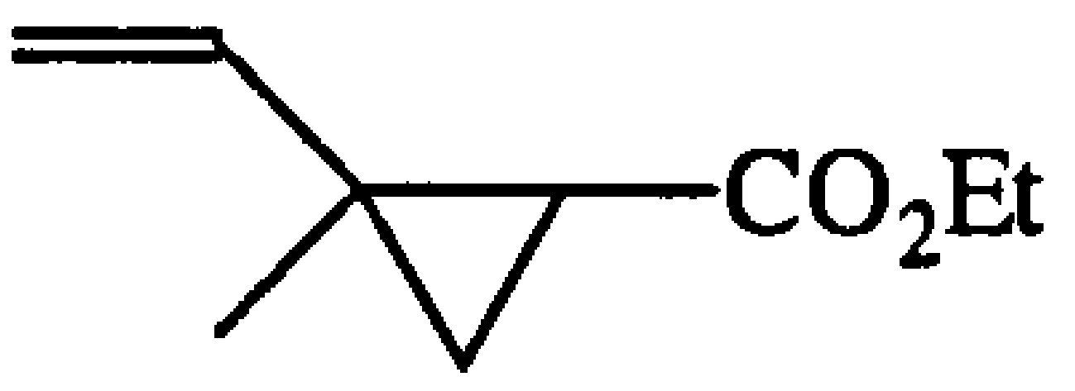
* - neat monomer

Table 3-3 Summary of polymerisation conditions for the attempted polymerisation of 1,1-dicyano-2-methyl-2-isopropenylcyclopropane (See experimental)

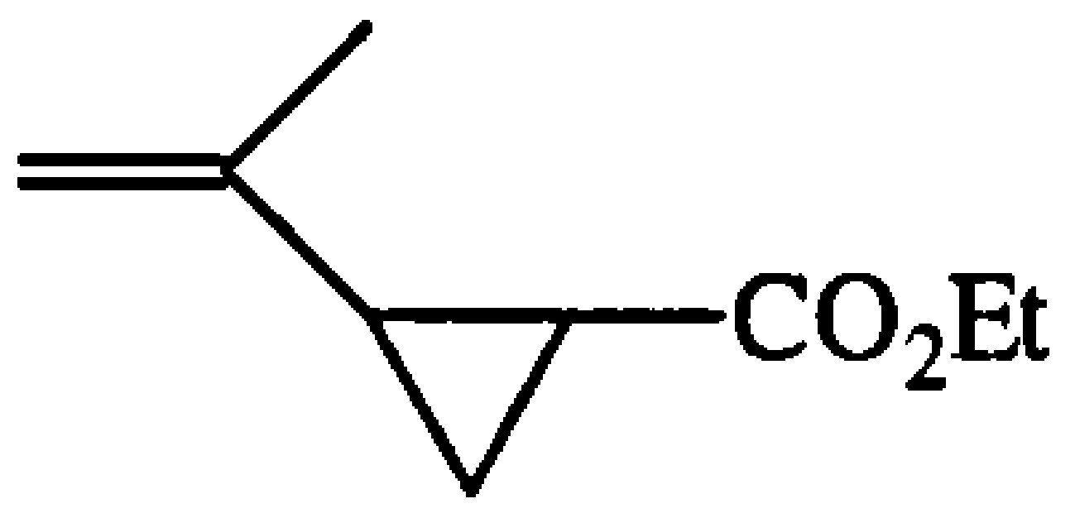
After the required reaction time, the contents of the ampoule were added drop-wise to methanol. In all cases no product precipitated. The methanol was removed in vacuuo to yield a clear, colourless liquid. Analysis of this liquid revealed that it was unreacted monomer. This suggests that under the conditions used 1,1-dicyano-2-methyl-2-isopropenylcyclopropane is not polymerisable.

Early studies by Takahashi on the polymerisation of vinylcyclopropane monomers had shown that although isopropenylcyclopropane underwent free-radical ring-opening polymerisation, 1-methyl-1-vinylcyclopropane did not polymerise.[9]

In 1987, Endo studied the polymerisation of a mixture of 1-ethoxycarbonyl-2-vinyl-2-methylcyclopropane (**A**) and 1-ethoxycarbonyl-2-isopropenylcyclopropane (**B**).[10]



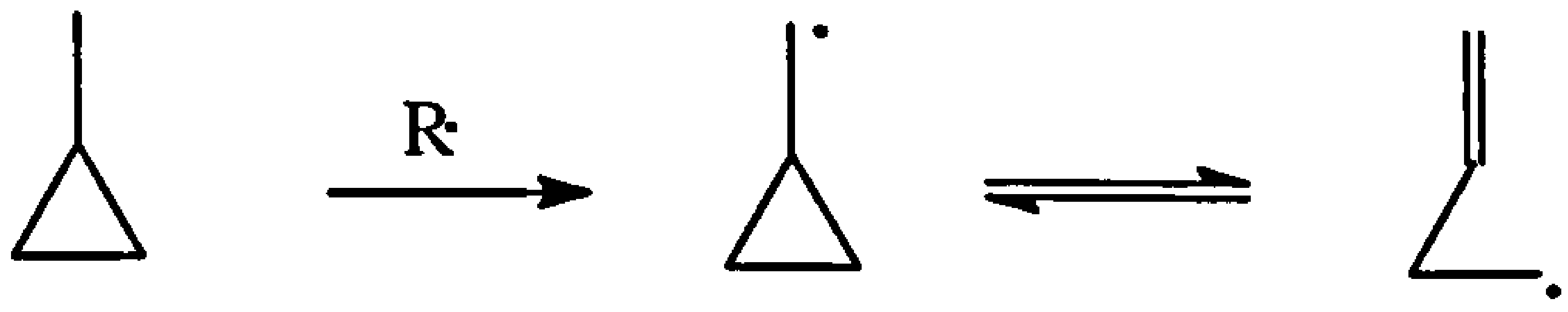
A



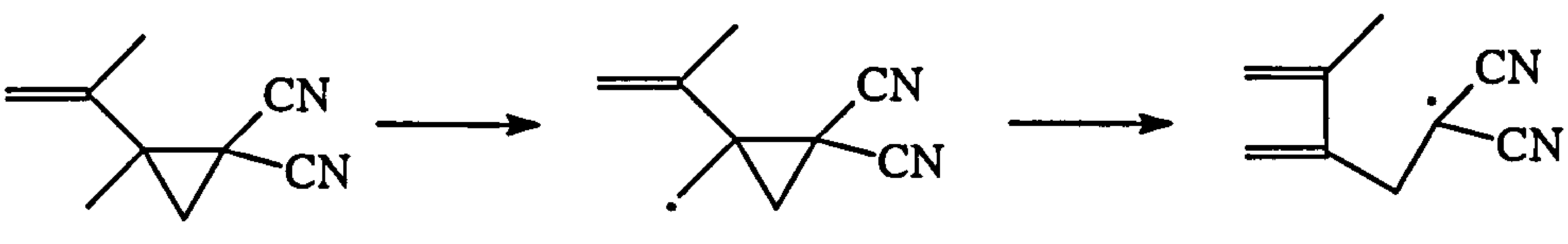
B

He found that monomer B polymerised at a significantly faster rate than monomer A. However, he drew no conclusions concerning the reasons for this observation.

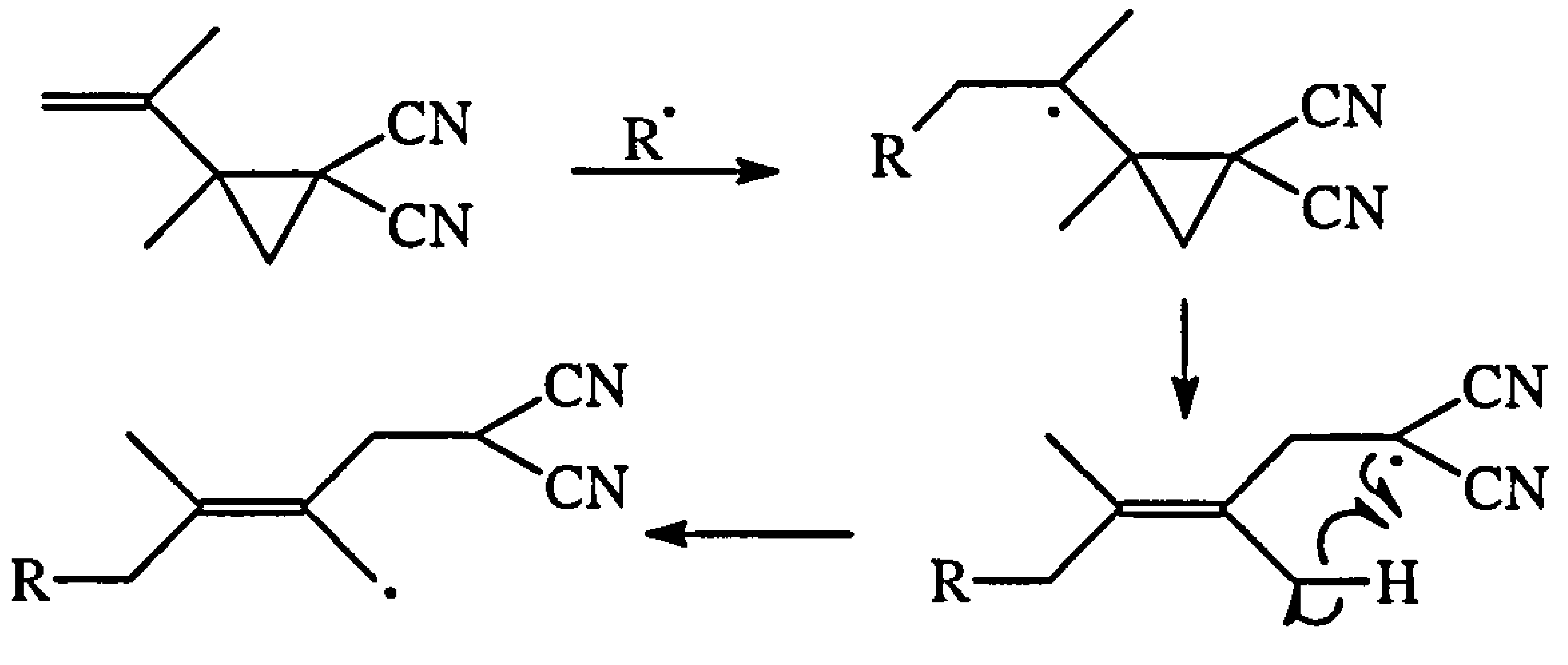
It seems likely that in 1,1-dicyano-2-methyl-2-isopropenylcyclopropane, it is the presence of the methyl group on the ring which inhibits polymerisation. There is the possibility that hydrogen abstraction occurs at this methyl group. It has been previously reported that methyl-cyclopropane undergoes hydrogen abstraction in the presence of radicals to give an unstable cyclopropylcarbinyl radical which rapidly isomerises to an allylcarbinyl radical.[11]



1,1-Dicyano-2-methyl-2-isopropenylcyclopropane could undergo a similar reaction as shown schematically below;



This scheme is, however, only a very tentative suggestion for why polymerisation does not proceed as expected. There is no experimental data to support this hypothesis since it was possible to recover the unreacted monomer and no other species were detected by NMR spectroscopy and, had the diene been formed, it might be expected to polymerise under these conditions. An alternative explanation for this failure could be transfer to monomer by the scheme shown below.



Stabilised allyl radical

Whatever the explanation it was shown that no evidence for polymerisation of this monomer was found in any of a total of more than twenty attempts.

3.4.3.1 Conclusion

This work has shown that it is not possible polymerise 1,1-dicyano-2-methyl-2-isopropenylcyclopropane using the conditions described and the reason for this failure is unclear.

3.5 Summary

Bulk and solution free radical polymerisation of the cyano-containing vinylcyclopropane monomers investigated in the work described in this chapter are not suitable methods for producing polymers with the desired characteristics. The polymer produced from 1,1-dicyano-2-vinylcyclopropane is formed only in low yields and its poor solubility and high glass transition temperature make it unsuitable for our purposes.

Attempts will be made to copolymerise 1,1-dicyano-2-vinylcyclopropane with a plasticising monomer in an attempt to retain the desirable polar characteristics expected from the VCP monomer and obtain an elastomeric copolymer. This work will be reported in chapter 4.

3.6 Experimental

3.6.1 General

Tetrahydrofuran (THF) and benzene was dried prior to use by refluxing over sodium/benzophenone and chloroform over calcium chloride. Malononitrile was purified by distillation under vacuum. AIBN was recrystallised from acetone. All other reagents were used as supplied

Infra-red spectra were recorded on a Perkin Elmer 1600 series FTIR. The spectra were recorded between NaCl discs or as a KBr disc. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR 400 MHz spectrometer. The solvent used was deuterated chloroform with TMS as internal reference or deuterated DMSO. Gel permeation chromatography was carried out by RAPRA Technology using a PL210 instrument with PLgel 2 x mixed bed-B, 30cm, 10 microns columns. The polymers were dissolved in DMSO with 100ppm LiBr and the samples were run at 80°C at a flow rate of 1.0 ml/min. Calibration of the system was performed using a broad molecular weight Dextran calibrant and a refractive index detector was used. Thermogravimetry (TG) was carried out using a Stanton Redcroft TG 760 series and differential scanning calorimetry (DSC) using either a Perkin Elmer DSC 7 or a Pyris 1.

3.6.2 Synthesis of 1,1-dicyano-2-vinylcyclopropane

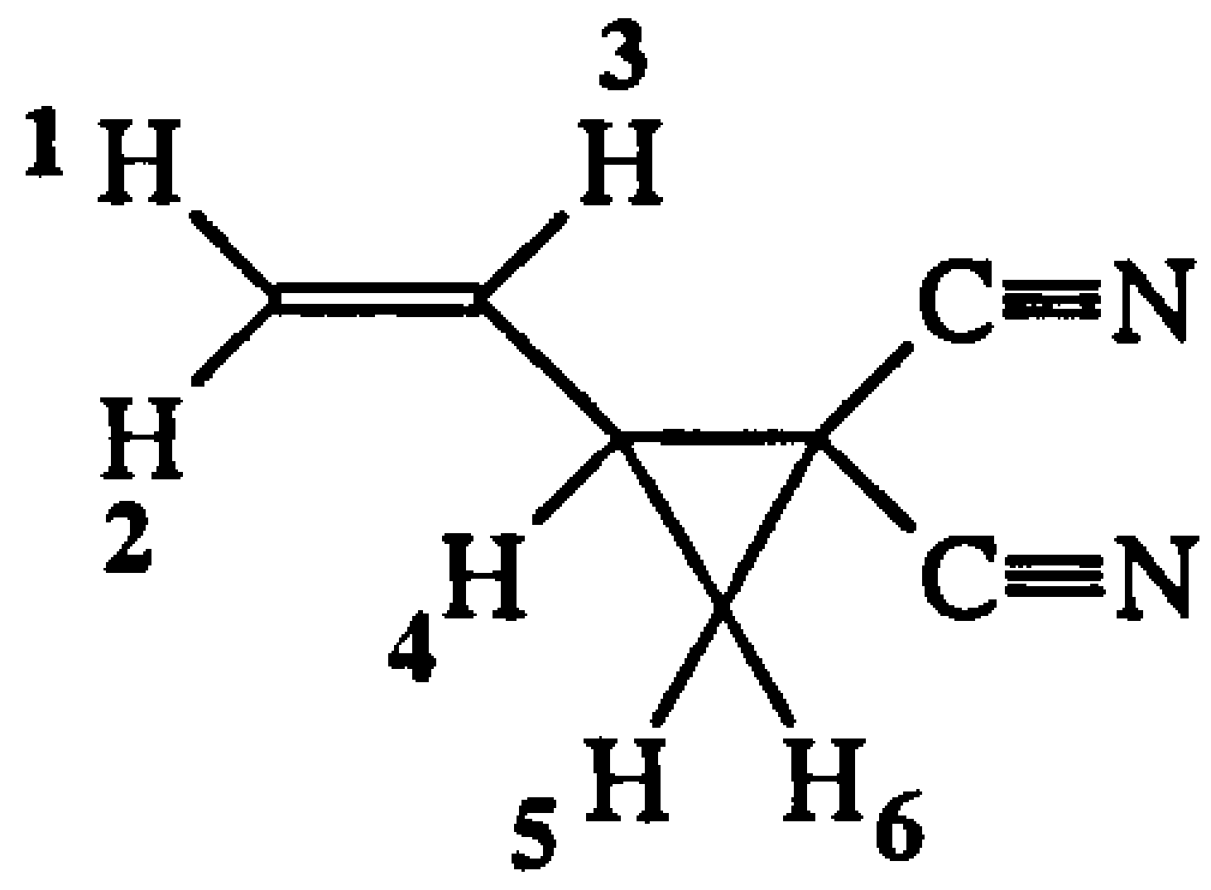
To a suspension of sodium hydride (5.0 g, 0.21 mol) in dry THF (200 cm^3), a mixture of malononitrile (4.37 cm^3, 0.069 mol) and *trans*-1,4-dibromo-2-butene (15.42 g, 0.072 mol) in dry THF (150 cm^3), was added dropwise at room temperature and under nitrogen. The reaction mixture was stirred overnight at room temperature, poured into cold 10% HCl and extracted with diethyl ether. The etheral layer was washed twice with saturated sodium hydrogen carbonate, once with saturated sodium chloride solution and then dried using magnesium sulphate. The mixture was filtered and the solvent removed in vacuuo yielding a clear dark orange oil which was distilled under vacuum to give 1,1-dicyano-2-vinylcyclopropane (2.96 g, 36 %) as a clear colourless oil (b.p. = 67°C 1mm/Hg). Calculated for $C_7H_6N_2$: C, 71.2%; H, 5.3%; N, 23.8%; Found : C, 64.7%; H, 4.7%; N, 20.3%.

3.6.2.1 Characterisation

Infra-Red Spectroscopy -See appendix 2.1

3103 and 3022 cm^{-1} (vinylic C-H stretch), 2248 cm^{-1} (CN stretch), 1642cm^{-1} (C=C stretch), 1444 cm^{-1} (C-H bending in ring), 987 and 933 cm^{-1} (out of plane terminal vinylic C-H), 707 cm^{-1} (out of plane vinylic C-H deformation)

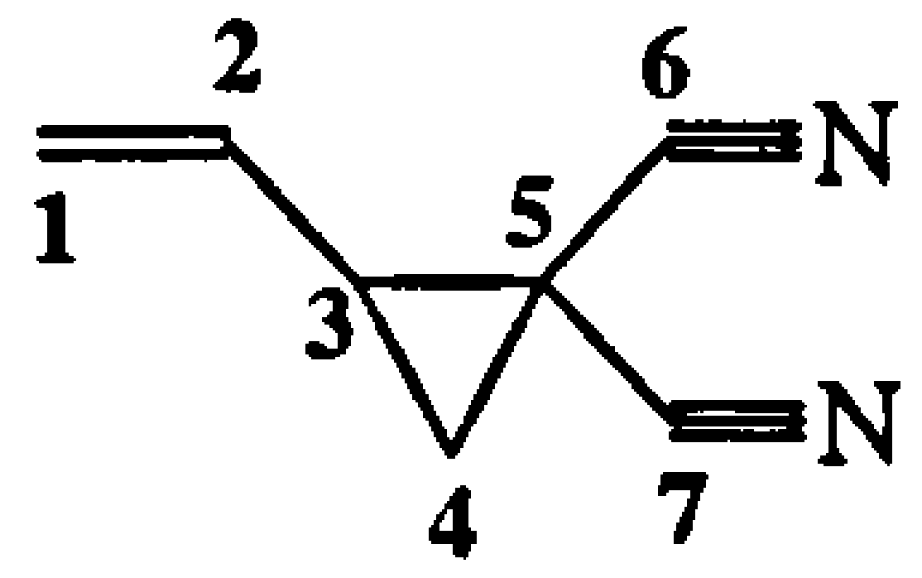
^{1}H NMR - See appendix 2.2



δ / ppm = 5.55 (m,**1**,**2**&**3**), 2.68 (m,**4**), 2.07 (m,**5** or **6**), 1.83 (m,**5** or **6**)

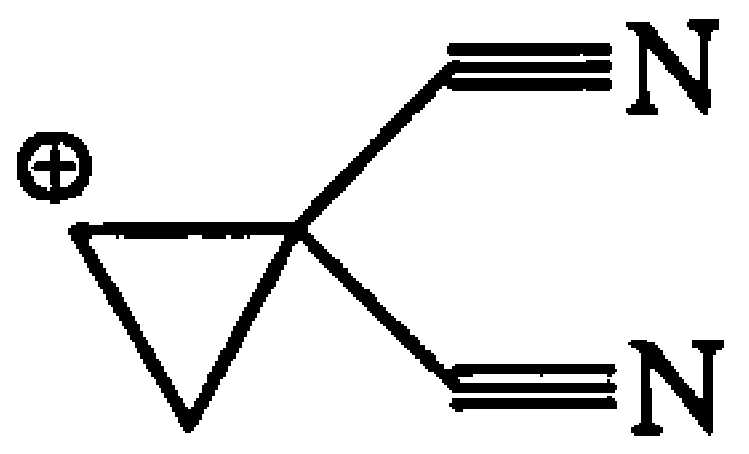
Intensity ratio = 3:1:1:1

^{13}C NMR - See appendix 2.3



δ / ppm = 131.0 (**1**), 124.5 (**2**), 116.2 (**6** or **7**), 113.6 (**6** or **7**), 34.6 (**3**), 24.7 (**4**), 7.1 (**5**)

Mass Spectrometry - See appendix 2.4

M/Z	Assignment
118	$M^{+\cdot}$
91	
39	$H_2C{=}C{=}\overset{\oplus}{C}H$
27	$[HC{\equiv}N]^{+\cdot}$

3.6.3 Synthesis of 1,1-dicyano-2-methyl-2-isopropenylcyclopropane

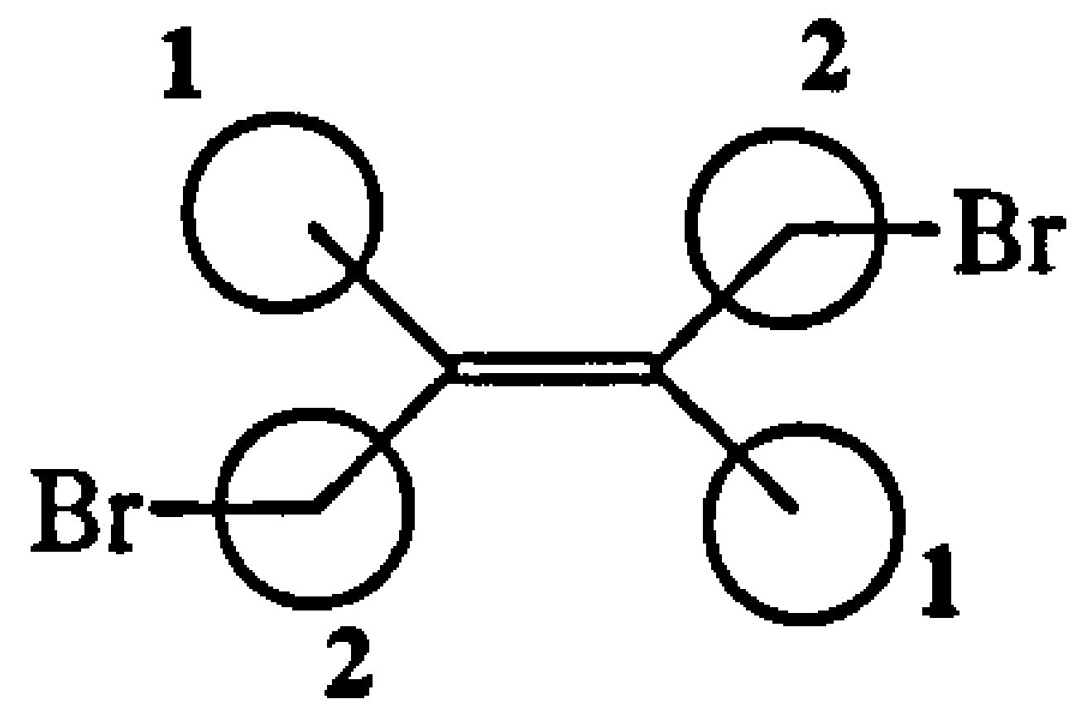
The bromination of 2,3-dimethylbutadiene was carried out as in the literature.[4] 2,3-Dimethylbutadiene (15.0 g, 0.182 mol) was dissolved in dry chloroform (210 cm^3)

at 0°C. Bromine (28.06 g, 0.176 mol) in dry chloroform (175 cm^3) was added drop-wise over 5 hours with efficient stirring. The solvent was removed in vacuuo to yield a yellow sludge. This was filtered to give a pale yellow solid which was then recrystallised from petroleum spirit yielding *trans*-1,4-dibromo-2,3-dimethyl-2-butene (24.7 g, 58%) as pale yellow crystals (m.p. 46.9 - 47.2°C). Calculated for $C_6H_{10}Br_2$: C, 29.8%; H, 4.2%; Found : C, 29.3%; H, 4.0%.

To a suspension of sodium hydride (5.0 g, 0.21 mol) in THF (200 cm^3), a mixture of malononitrile (4.37 cm^3, 0.069 mol) and *trans*-1,4-dibromo-2,3-dimethyl-2-butene (17.44 g, 0.072 mol) in THF (150 cm^3), was added drop-wise at room temperature and under nitrogen. The reaction mixture was stirred overnight at room temperature, poured into cold 10% hydrochloric acid and extracted with diethyl ether. The organic layer was washed twice with saturated sodium hydrogen carbonate, once with saturated sodium chloride solution, dried using magnesium sulphate, filtered and the solvent removed in vacuuo. This yielded a clear dark orange oil which was distilled under vacuum to give 1,1-dicyano-2-methyl-2-isopropenylcyclopropane (5.39g, 54%) as a clear colourless oil (b.p. = 74°C 0.6mm/Hg). Calculated for $C_9H_{10}N_2$: C, 73.9%; H, 6.9%; N, 19.2%; Found : C, 73.2%; H, 6.9%; N, 19.1%.

3.6.3.1 Characterisation of *trans*-1,4-dibromo-2,3-dimethyl-2-butene

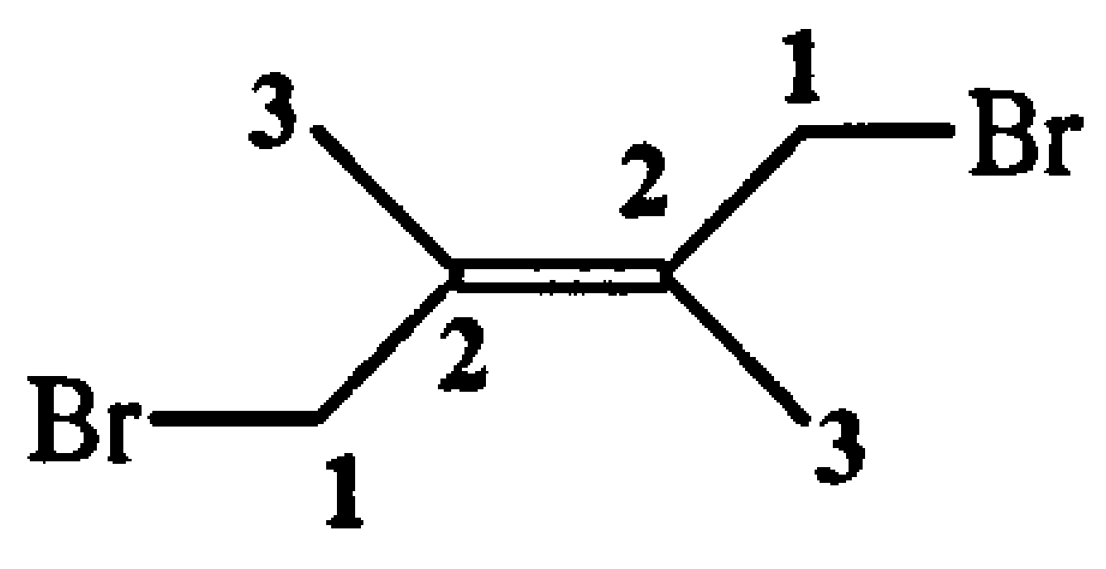
^{1}H NMR - See appendix 2.5



δ / ppm = 4.00 (s,**2**), 1.88 (s,**1**)

Intensity ratio = 2:3

^{13}C NMR - See appendix 2.6



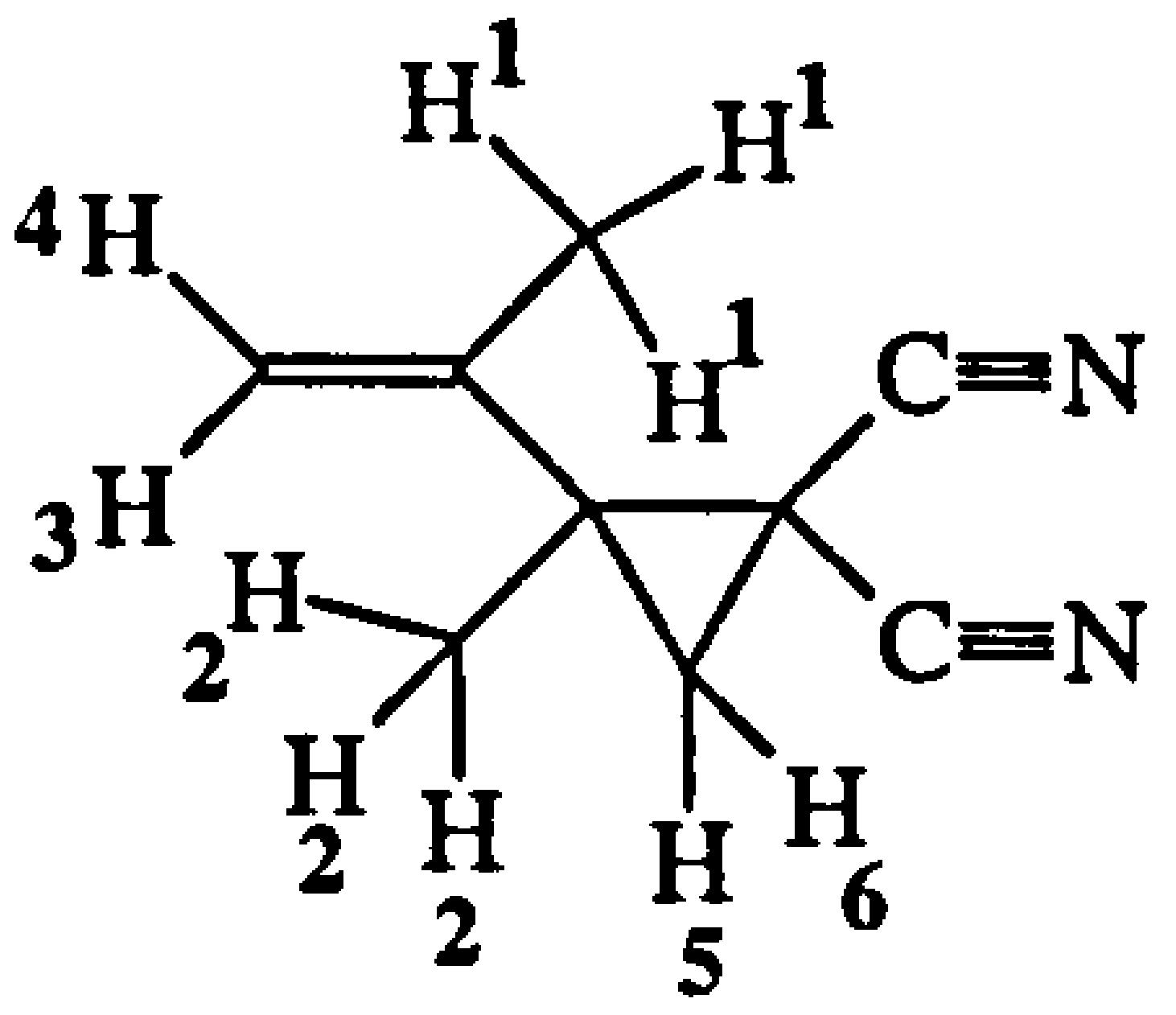
δ /ppm = 131.8 (2), 34.2 (1), 17.1 (3)

3.6.3.2 Characterisation of 1,1-dicyano-2-methyl-2-isopropenylcyclopropane

Infra-Red Spectroscopy - See appendix 2.7

3096 cm^{-1} (vinylic C-H stretch), 2245 cm^{-1} (CN stretch), 1647 cm^{-1} (C=C stretch), 1443 cm^{-1} (C-H bending in ring), 1069 cm^{-1} (C-C bending in ring), 917 cm^{-1} (out of plane terminal vinylic C-H deformation)

^{1}H NMR - See appendix 2.8

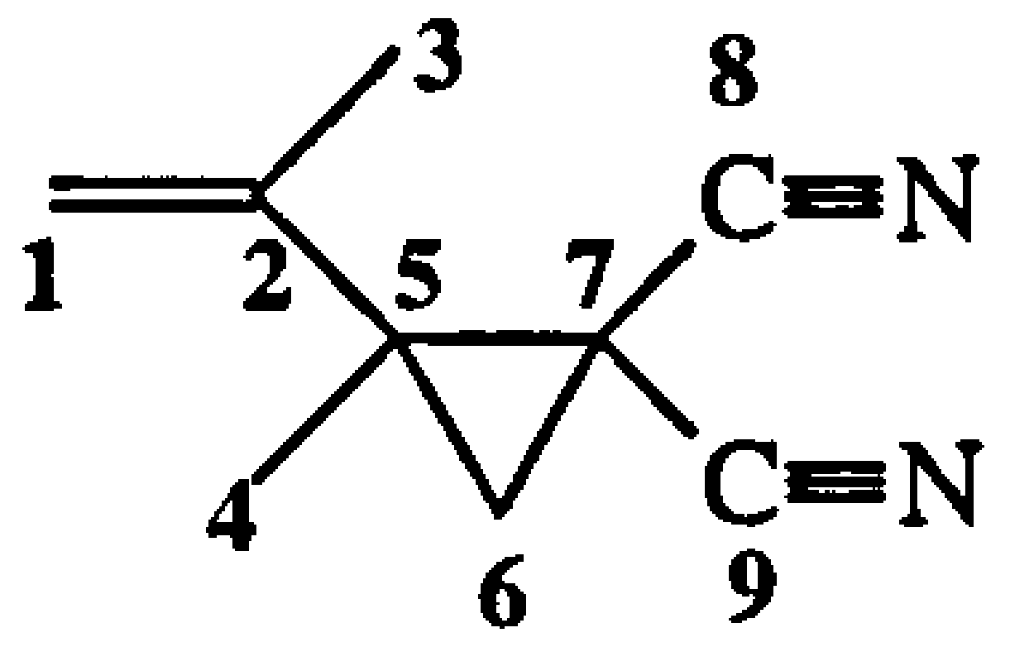


δ /ppm = 5.13 (t,3), 5.00 (s,4), 2.12 (d,5 or 6), 1.93 (t,1), 1.76 (d,5 or 6), 1.56 (s,2)

Intensity ratio = 1:1:1:3:1:3

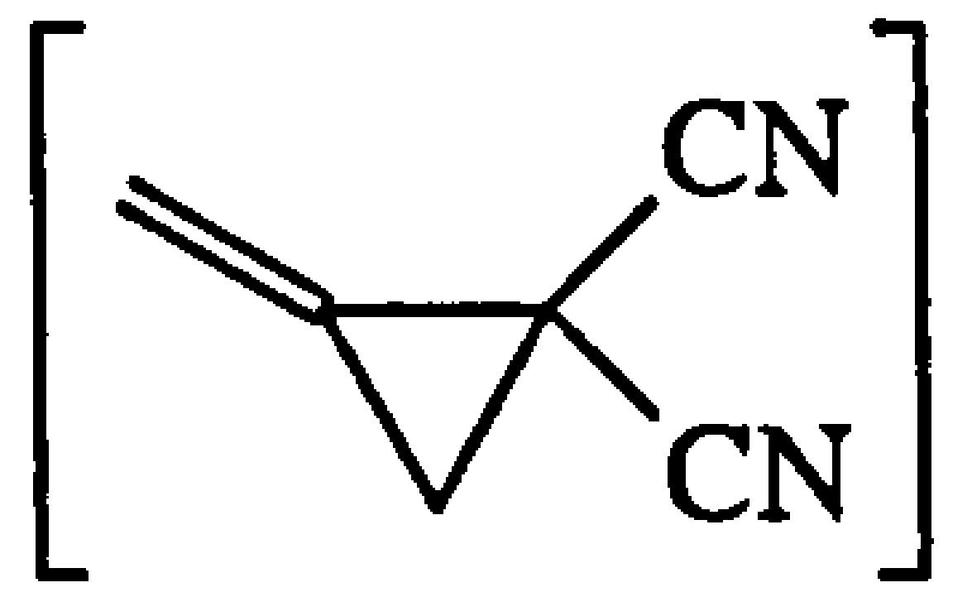
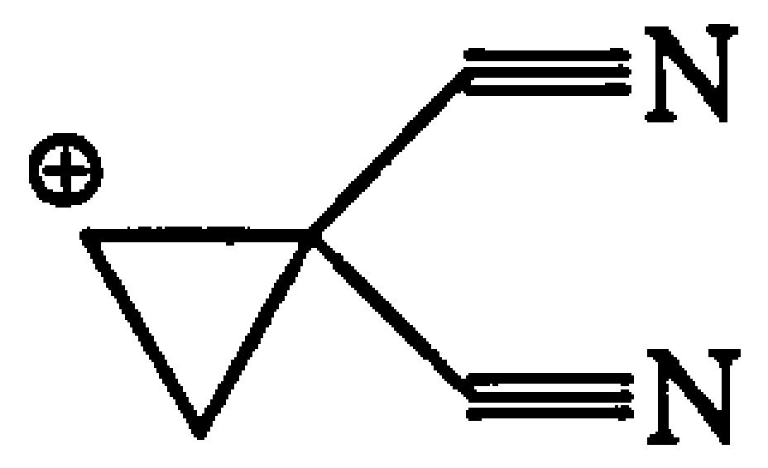
The peaks corresponding to H(1) and H(3) are triplets split by each other as well as by H(2) and H(4) respectively

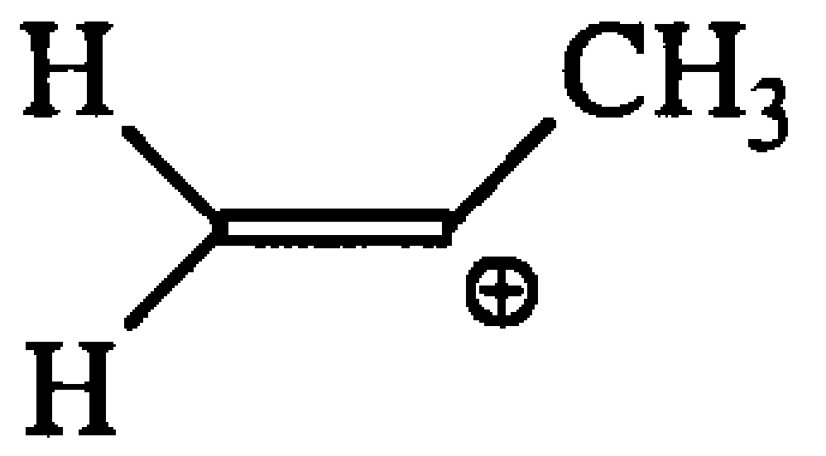
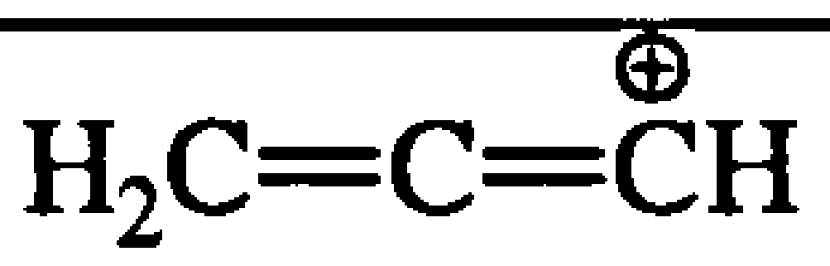
^{13}C NMR - See appendix 2.9



δ /ppm = 141.2 (2), 117.2 (1), 114.5 (8 or 9), 114.4 (8 or 9), 41.7 (5), 30.4 (6), 20.6 (4), 20.0 (3), 10.6 (4)

Mass Spectrometry - See appendix 2.10

M/Z	Assignment
146	$M^{+\cdot}$
131	$[M - CH_3]^+$
104	
91	

41	
39	 $H_2C{=}C{=}\overset{\oplus}{C}H$
27	$[HC{\equiv}N]^{+\bullet}$

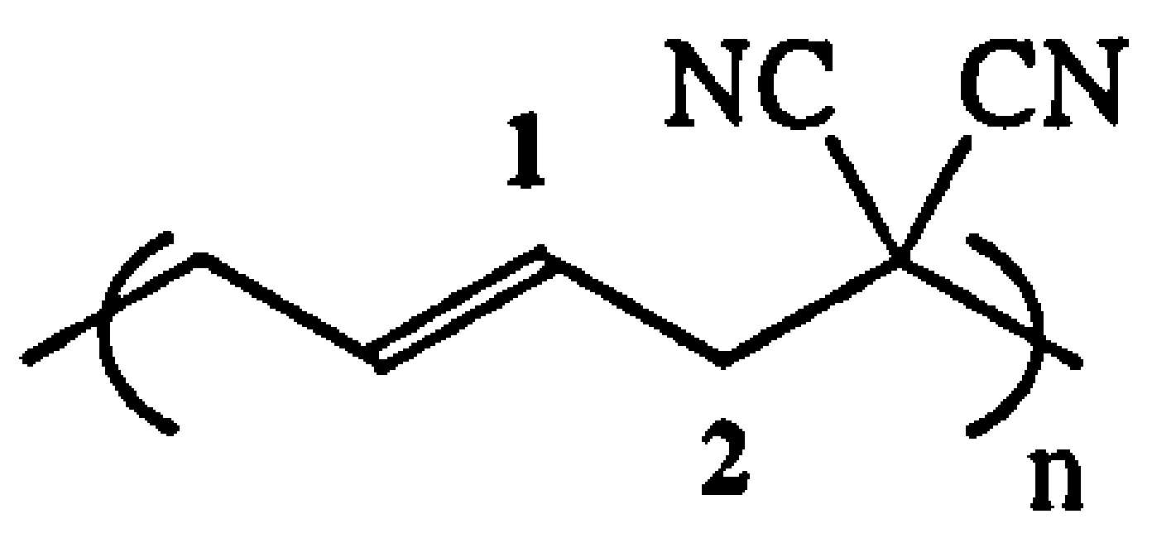
3.6.4 Polymerisation of 1,1-dicyano-2-vinylcyclopropane monomers

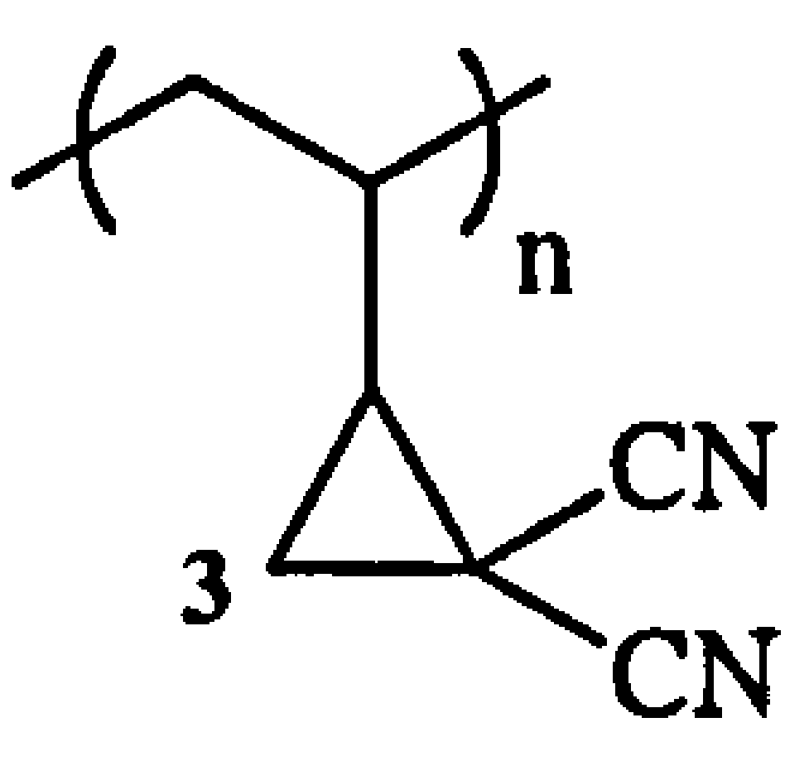
The monomer (0.354 g 3 mmol) was weighed into an ampoule. The required amount of initiator and dry solvent if required, were added. The content of the ampoule were frozen and degassed by the freeze/thaw method. The ampoule was left under vacuum and placed in an oil bath at the required temperature for the desired length of time. The bulk polymerisation yielded a hard white/yellow solid which was chipped out of the ampoule, ground to a fine dust and washed in methanol. The solution polymerisation yielded a white precipitate which was washed in methanol. The solid was filtered from the methanol, washed in more methanol and dried in a vacuum oven at 40°C overnight.

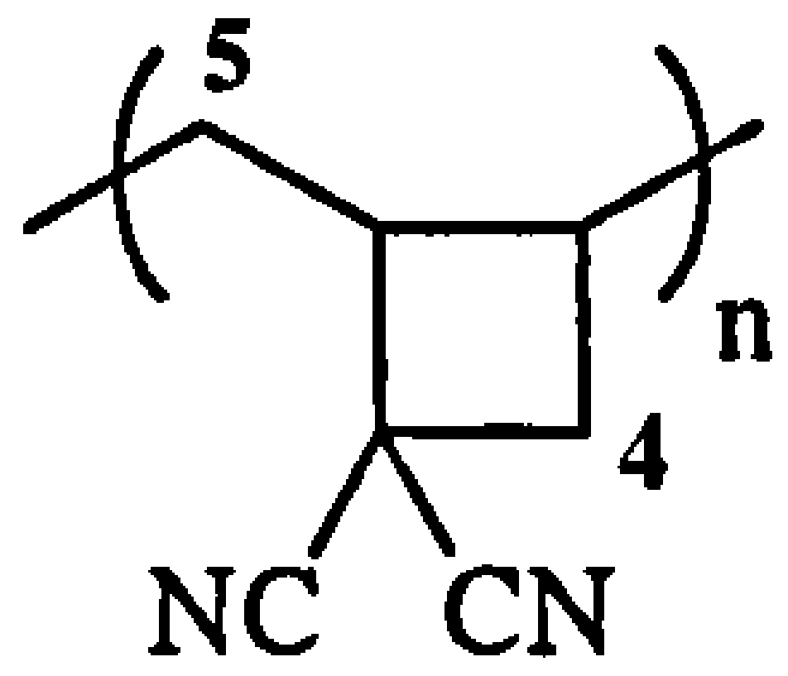
3.6.4.1 Characterisation

Infra-red Spectroscopy - All spectra were indistinguishable. The spectrum of sample E is shown as a typical spectrum. See appendix 2.11
2253 cm^{-1} (CN stretch), 1447 cm^{-1} (methylene rocking absorption), 968 cm^{-1} (*trans* double bond absorption).

^{1}H NMR - The spectrum of sample D is shown as a typical spectrum in appendix 2.12



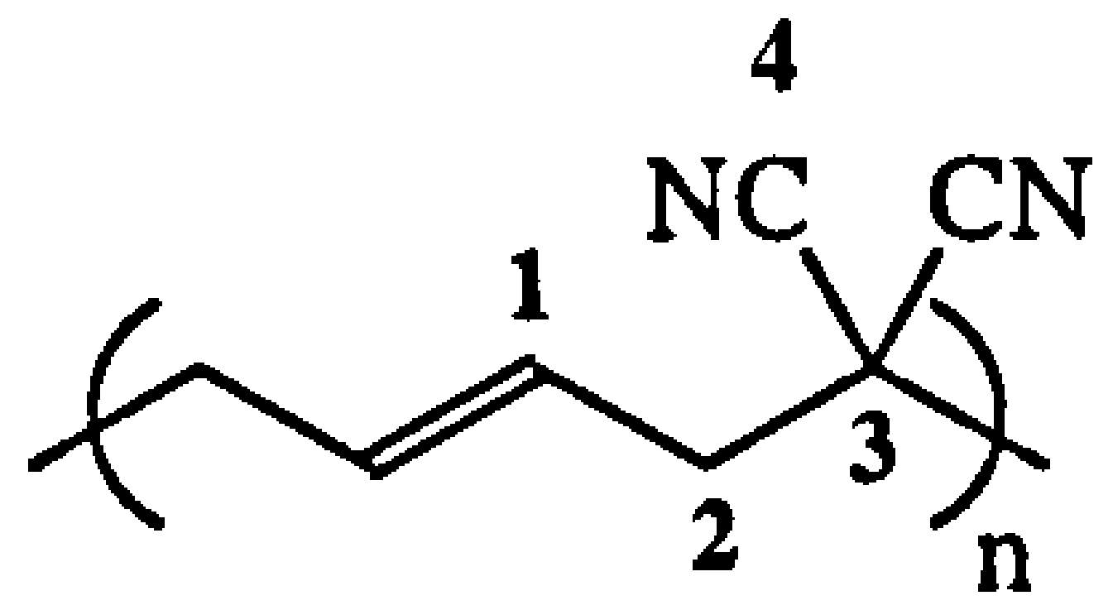




δ / ppm = 5.90 (1), 3.01 (d,5), 2.92 (2), 1.30 (4), -0.13 (3)

Peaks **1**, **2** ,**3** and **4** are unresolved multiplets

^{13}C NMR - All spectra were indistinguishable. The spectrum of sample F is shown as a typical spectrum. See appendix 2.13



δ / ppm = 129.84 (1), 115.87 (4), 38.86 (2), 38.20 (3)

Gel Permeation Chromatography - Gel permeation chromatography (GPC) results are shown below. See appendix 2.14 for the GPC traces.

Sample	Mw	Mn	Polydispersity
A	213 000	77 000	2.8
C	180 000	44 000	4.1
D	189 000	54 000	3.5
E	58 000	23 000	2.5
F	35 000	15 000	2.4
H	284 000	93 000	3.1
I	179 000	69 000	2.6

Differential Scanning Calorimetry - See appendix 2.15 for the GPC trace of sample A which was typical of the GPC traces produced.

Sample	Glass Transition Temperature / °C
A	78.0
C	74.6
D	68.0
E	88.4
F	77.1
G	69.7
H	82.3

Elemental Analysis

	Found								
	Calculated	A	C	D	E	F	G	H	I
C%	71.2	69.9	70.6	70.4	70.6	70.5	70.6	70.9	70.5
H%	5.3	5.2	5.1	5.1	5.3	5.1	4.9	5.2	5.1
N%	23.8	22.6	23.1	23.1	23.1	23.2	22.6	22.9	23.2

3.7 References

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Chapter 4

Copolymerisation of butyl acrylate and 1,1-dicyano-vinylcyclopropane

4. Attempted emulsion copolymerisation of 1,1-dicyano-2-vinylcyclopropane and butyl acrylate

4.1 Introduction

In chapter 3, the synthesis of a polymer from the free-radical polymerisation of 1,1-dicyano-2-vinylcyclopropane was reported. This polymer was found to be an insoluble solid with a Tg well above room temperature and therefore too high for our purposes.

The aim of the work reported in this chapter was to form copolymers between butyl acrylate and 1,1-dicyano-2-vinylcyclopropane using emulsion free-radical polymerisation. Butyl acrylate homopolymer is an easily processable rubbery polymer with a Tg of -54°C.[1] It was hoped that the incorporation of butyl acrylate into the vinylcyclopropane polymer would lower the Tg and make the polymer more soluble.

4.2 Emulsion polymerisation

An emulsion is a two phase system containing two liquids (in this case water and monomer) that are mutually insoluble or sparingly soluble under normal conditions and to which an emulsifier is added.

Emulsifiers are a special class of surfactants which have limited solubility in water but are capable of forming hydrated aggregates called micelles when the critical micelle concentration is exceeded. These micelles are formed due to the nature of the surfactant molecule. The molecule has a hydrophilic polar or ionic portion and a hydrophobic non-polar, non-ionic portion. The molecules arrange themselves so that the hydrophilic portions are oriented outwards towards the external aqueous phase whilst the hydrophobic portions are pointing inwards. Smaller micelles are usually spherical but larger micelles tend towards cylindrical shapes. These aggregates usually comprise 50 to 100 molecules of surfactant.

The physical picture of emulsion polymerisation is based on the qualitative picture of Harkins[2] and the quantitative treatment of Smith and Ewart.[3]

The main components in emulsion polymerisation are the monomer(s), water, emulsifier and initiator.

As monomer is added to the water, a very small fraction dissolves, for example, butyl acrylate is soluble to the extent of 0.2 g/L at 25°C. A larger, but still small amount of the monomer is absorbed by the micelles causing them to swell in size.[4] If the amount of monomer added exceeds that which can be absorbed by the micelles, then, after thorough mixing, the monomer forms droplets, the size of which depends on the extent of agitation. The emulsion consists of monomer-swelled micelles, monomer droplets stabilised by adsorbed surfactant molecules, solubilised monomer molecules and solublised emulsifier dispersed in water. In a typical emulsion polymerisation, the number of monomer droplets of ≥1μm (10 000Å) is 10^{10}-10^{11} per millilitre together with 10^{18} micelles of 10-100Å diameter.

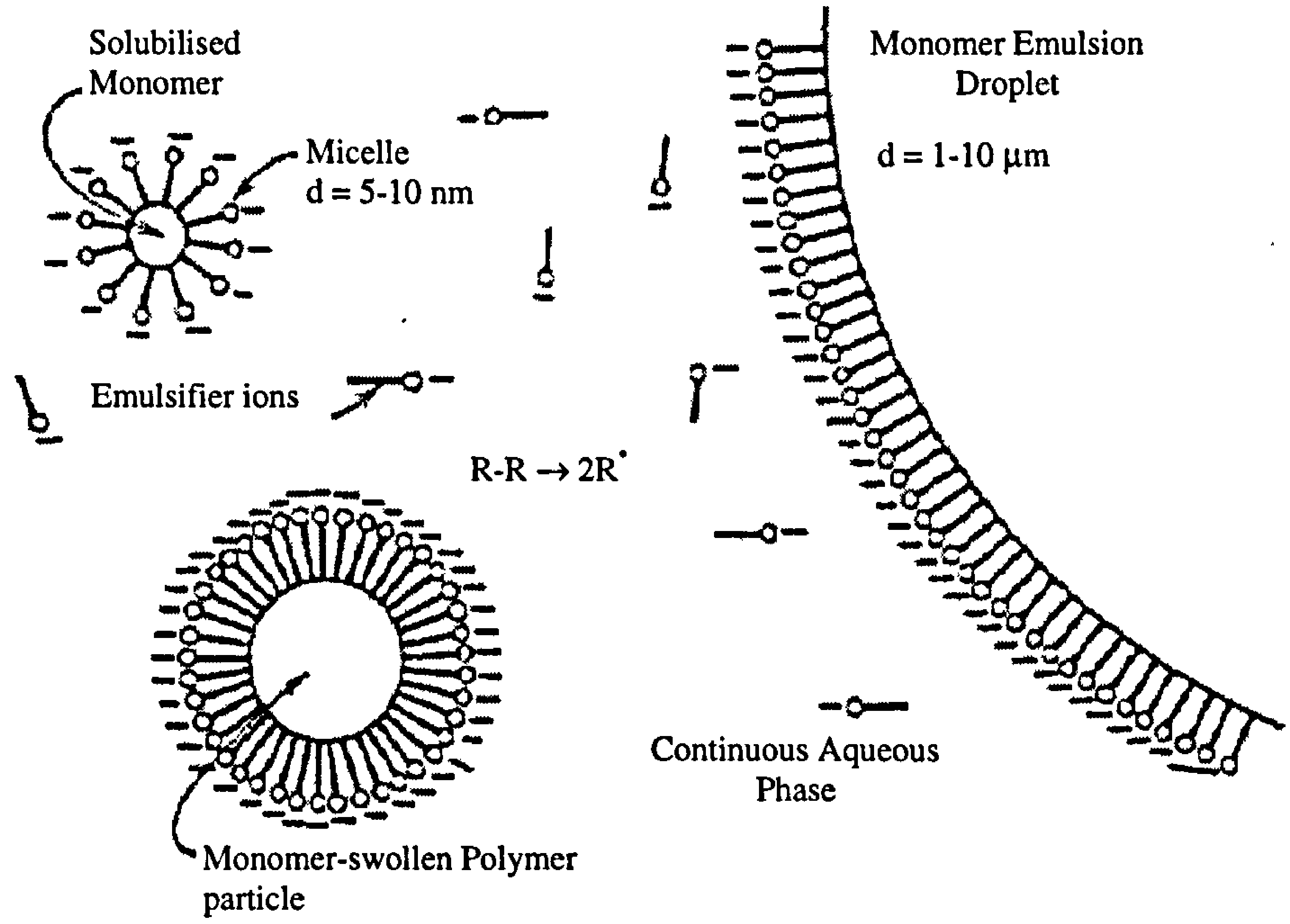


Figure 4-1 Composition of an emulsion

Initiating species are formed in the aqueous phase and it is therefore vital that de-ionised and de-gassed water are used since the presence of foreign ions or oxygen would interfere with the initiation process. The initiating radicals either attack solubilised monomer molecules forming polymer chain radicals which diffuse into the micelles, or the initiating radicals themselves move directly into the micelles. In is in these micelles that polymerisation occurs. This is the main difference between emulsion and suspension polymerisation. In suspension polymerisation, the initiating radicals are soluble in the monomer and the radicals enter monomer droplets which become the sites of reaction.

The emulsion system owes its high rates of polymerisation and the high molecular weights obtained to the separation of the sites where primary radicals form from those where chain growth occurs.

In emulsion polymerisation, growth of the polymer chain within the micelle is extremely rapid and monomer is supplied to the micelles by diffusion from the shrinking monomer droplets, allowing the polymer chain to continue to grow. This movement of monomer from the monomer droplets to the micelles is driven thermodynamically since the formation of polymer within the micelle decreases the monomer concentration inside the micelle. As the polymer grows, the micelles expand and molecules of dissolved surfactant are adsorbed onto the surface of the growing polymer particles. The point is rapidly reached where the surfactant concentration falls below the critical micellar concentration. At this point, inactive micelles, that is, those not containing a reaction site, become unstable and disappear with the dissolution of the micellar surfactant and the movement of the monomer into the reactive micelles. Very soon, all of the surfactant in the system has been absorbed by the polymer particles and the monomer droplets are relatively unstable and would coalesce if agitation was halted.

Polymerisation continues at a steadily decreasing rate as the monomer concentration in the polymer particles decreases. Final conversions of 100% are usually achieved, the final polymer particles having diameters of the order of 500 to 2000 Å.

Termination of the polymer chains occurs in the same manner as normal free-radical polymerisation, that is, by combination or disproportionation. There are two consequences of the emulsion that must be taken into account when considering termination. The size of the polymer particle is small and therefore, unless radical mobility is reduced by a highly entangled environment, two free-radicals do not coexist within a particle for a significant period without termination. Secondly, the polymer particles provide isolation for the growing polymer chain. In bulk, solution or suspension processes free radicals in close proximity may collide whereas in the emulsion process radicals in different particles cannot combine. It is this factor that leads to the high molecular weights that are achieved in emulsion polymerisation.

4.2.1 Initiators

Two types of initiator system are used; usually known as reflux- and redox-systems. Reflux initiators are often water-soluble peroxidic initiators such as potassium persulphate which is the most commonly used initiator for acrylate polymerisations.

$$^{\ominus}O_3S{-}O{-}O{-}SO_3^{\ominus} \longrightarrow 2\,SO_4^{\bullet\ominus}$$

The initiating particles result from the thermal dissociation of the persulphate anion into sulphate radical anions. The rate of dissociation increases with rising temperature.

Redox initiators are water-soluble peroxide initiators combined with reducing agents which increase the rate of dissociation of the initiator at a given temperature. The most commonly used redox-system is persulphate with ferrous iron.

$$S_2O_8^{2-} + Fe^{2+} \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet -}$$

Often a second reducing agent such as glucose or fructose is added to recycle the ferric back to ferrous iron.

Redox systems are ideal when moderate to low temperatures are required (+50 to -50°C).

4.2.2 Emulsifiers

The role of the emulsifier is complex and changes during the different stages of the polymerisation. Firstly the emulsifier is responsible for the acceleration of the polymerisation. Micelles formed from the emulsifier provide sites where rapid polymerisation can occur. Without the emulsifier, the monomer would be unsolubilised and would form a separate layer, considerably reducing the probability of reaction with a radical generated in the water. Secondly, the emulsifier stabilises the monomer-polymer particles and ultimately the final polymer emulsion preventing the formation of less stable, larger aggregates. Most surfactants are charged and consequently the particles carry a charged surface layer and it is this which inhibits agglomeration.

There are several different types of emulsifiers and no satisfactory method of predicting which is the most desirable for a polymerisation. It is necessary to carry out laboratory studies to select the appropriate surfactant for a particular process.

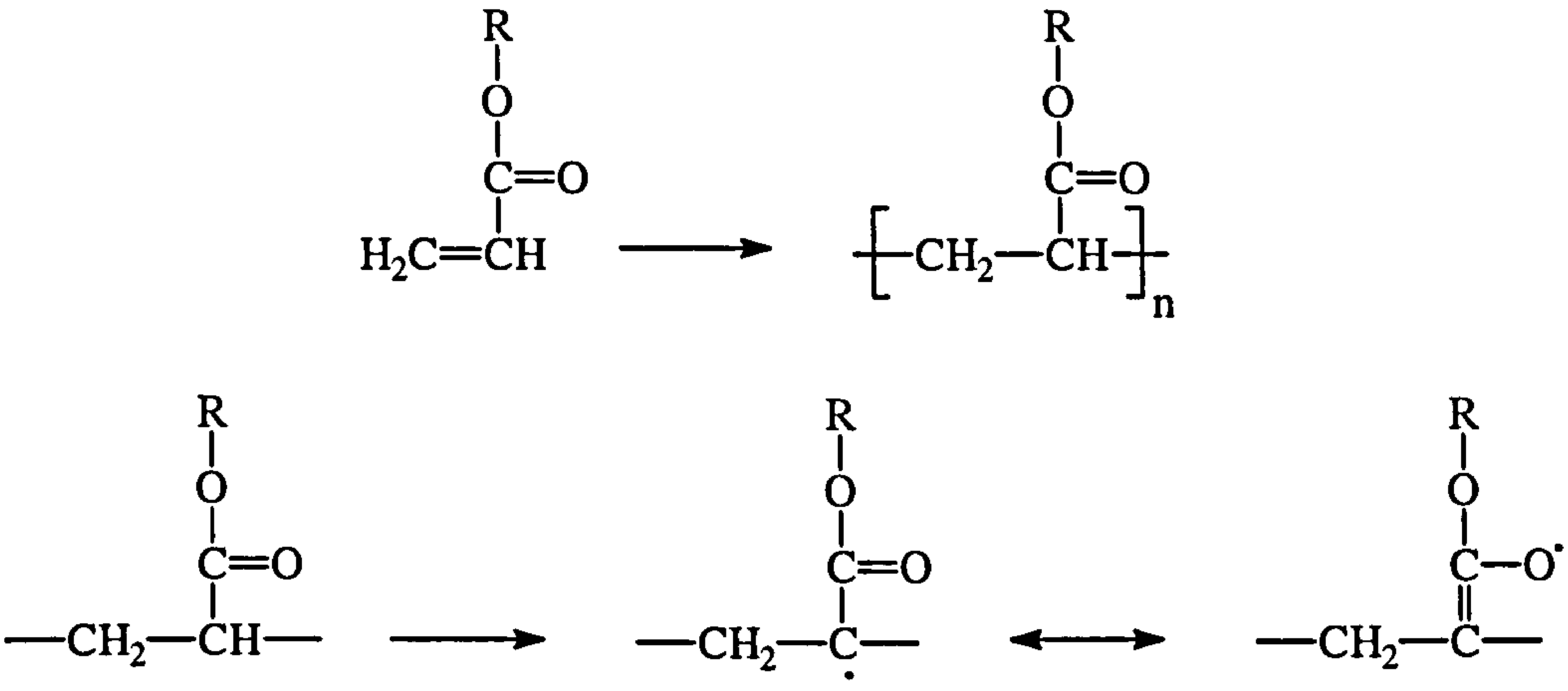
Anionic surfactants are the most commonly used surfactants in emulsion polymerisation. These include fatty acid soaps (sodium or potassium stearate, laurate, palmitate) sulphates and sulphonates (sodium lauryl sulphate and sodium dodecylbenzene sulphonate). Many of them have low critical micellar concentrations and therefore relatively low amounts can be used to form emulsions.

Non-ionic surfactants, for example those containing poly(ethylene oxide) and poly(vinyl alcohol), prevent coagulation of monomer droplets and polymer particles in the emulsion polymerisation process by the steric repulsion that occurs when two micelles come into close contact. They are rarely used on their own but more often in combination with ionic surfactants.

Although emulsion polymerisation would not be effective without the surfactants, the main disadvantage of emulsion polymerisation is the fact that these surfactant residues are extremely difficult to remove from the polymer, even by washing and re-precipitation.

4.2.3 Emulsion polymerisation of acrylates[5]

Emulsion polymerisation is presently the predominant process for the commercial polymerisation of various acrylates. It is used to polymerise acrylate monomers because the high rate and heat of polymerisation of acrylates make the control of bulk polymerisation difficult whilst in suspension polymerisation there is a tendency for the soft polymer beads to coalesce. Solution polymerisation leads to solutions of high viscosity which are difficult to handle. The high viscosity which arises in solution polymerisation occurs due to the ease with which it is possible to abstract a tertiary hydrogen which then leads to branching and cross-linking. This ease of abstraction is due to the stabilisation of the resulting radical.



Emulsion polymerisation is used to overcome these problems. The physical state of the emulsion system makes it easy to control the process. The aqueous media allows for good heat dissipation allowing a rapid but readily controlled polymerisation giving high yields of high molecular weight polymer.

4.3 Emulsion homopolymerisation of butyl acrylate

The homopolymerisation of butyl acrylate was carried out using sodium persulphate as initiator and Triton X-100 (t-octylphenoxypolyethoxyethanol) and sodium dodecyl sulphate as emulsifiers under the various conditions shown below to establish the reaction time and initiator/monomer ratio required.

	Time/min	Initiator/monomer molar ratio	Volume of stock initiator solution / cm^3	% yield
A	120	1 : 371.5	1.3	77.1
B	60	1 : 371.5	1.3	82.8
C	30	1 : 371.5	1.3	87.9
D	30	1 : 371.5	1.3	77.6
E	30	1 : 371.5	1.3	81.1
F	30	1 : 241.5	2.0	74.8
G	30	1 : 241.5	2.0	86.4
H	30	1 : 241.5	2.0	91.1

Table 4-1 Summary of conditions used for the emulsion homopolymerisation of butyl acrylate. (Details in experimental section)

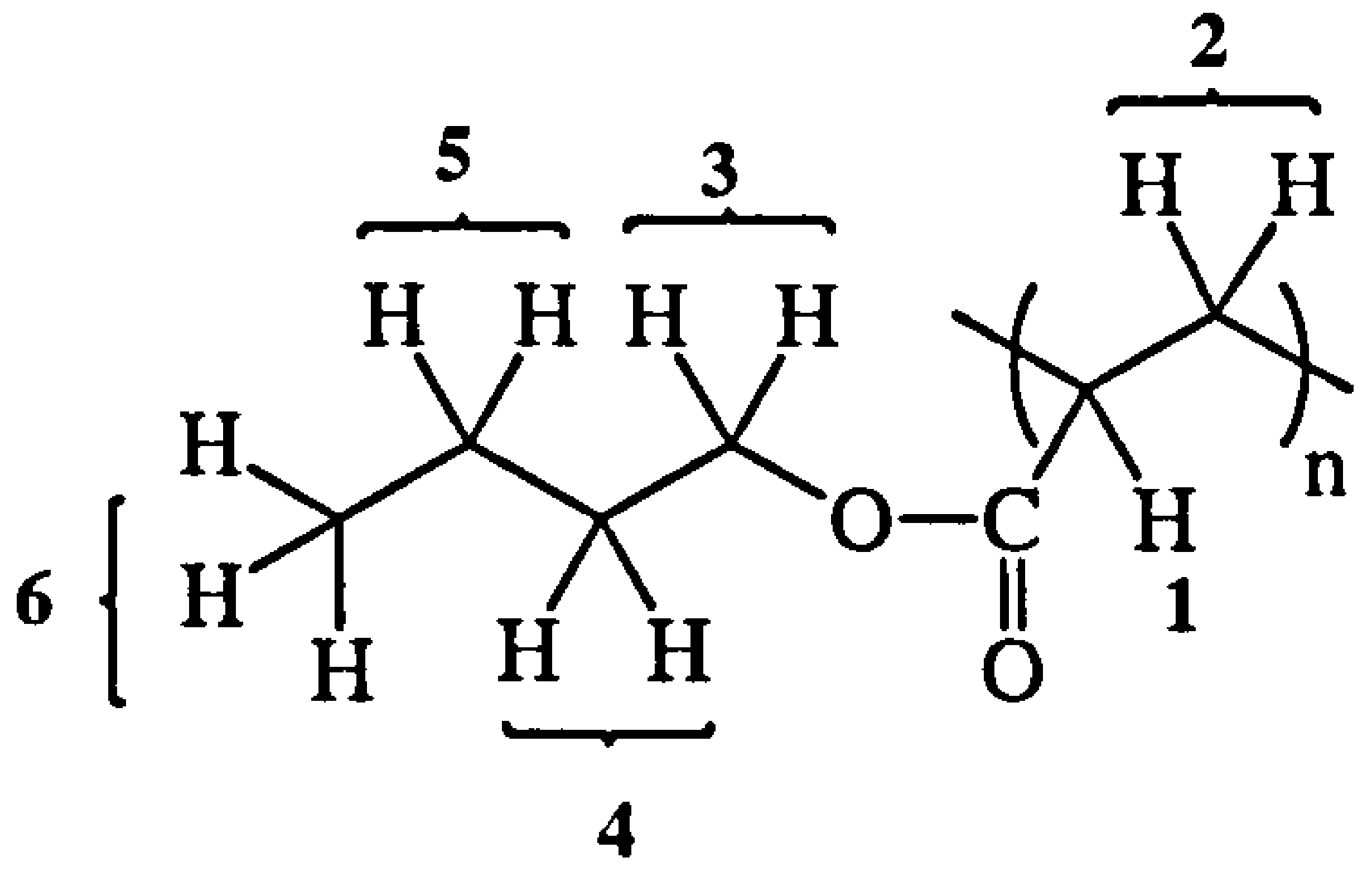
It can be seen that polymerisation is complete after 30 minutes and a longer reaction time does not increase the yield obtained.

The polymers produced were all rubbery white solids. These polymers were analysed using ^1H and ^{13}C NMR, infra-red spectroscopy, thermogravimetry (TG), differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and elemental analysis.

4.3.1 Analysis

Infra-red spectroscopic analysis of the polymers lead to identical spectra and showed absorbtions for the ester C=O stretch at 1733 cm^{-1}.

^1H and ^{13}C spectra were assigned by comparison with the literature.[6,7] The spectra are complicated by the tacticity of the polymer. In the ^1H NMR, the peaks corresponding to the methylene hydrogens (**2**) in the backbone of the polymer chain are split and partially hidden under the $-CH_2-$ peaks of the pendant chain (**4**, **5** and **6**) due to the various environments of these backbone methylene hydrogens. See Figure 4-2.



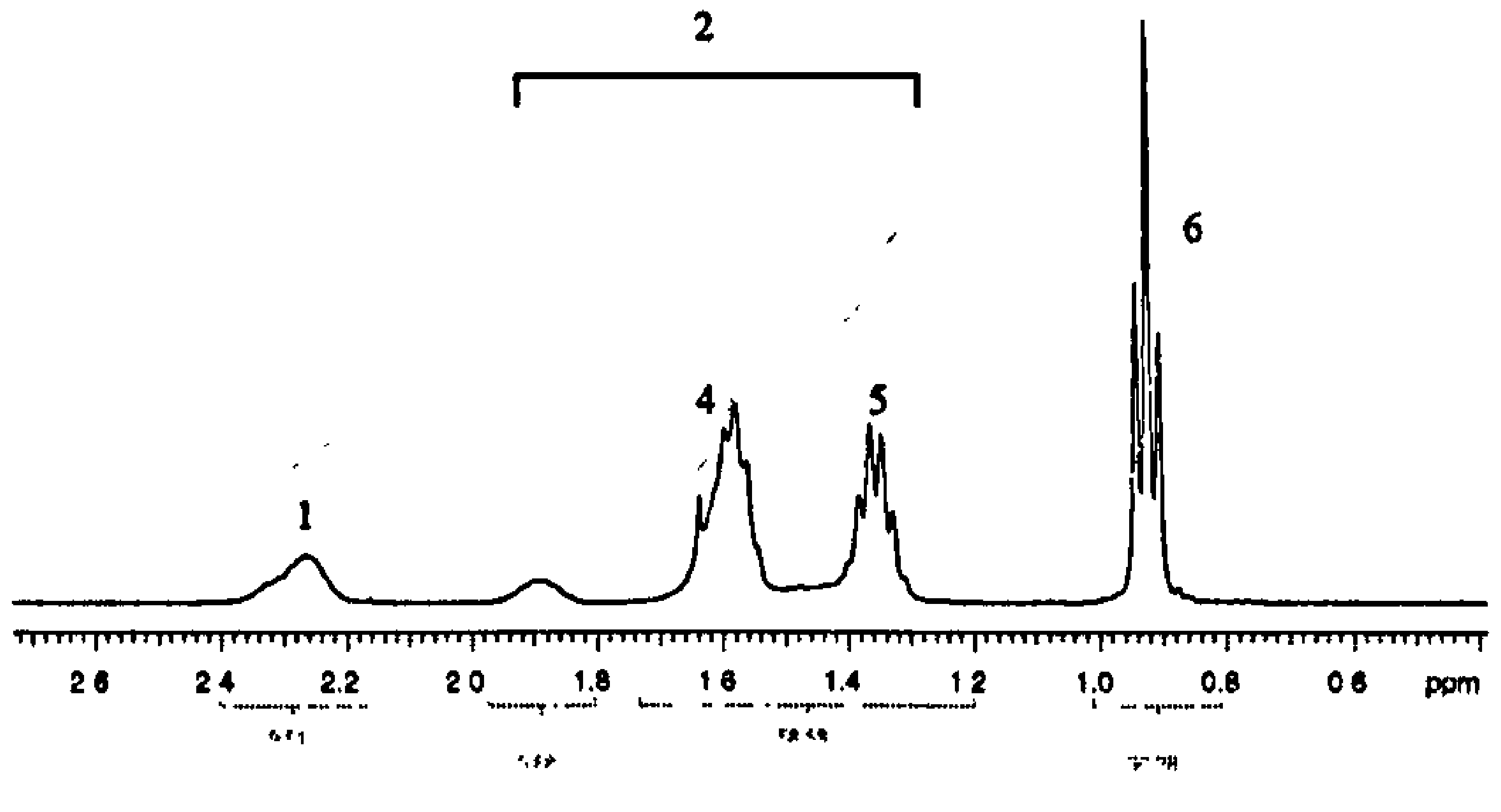
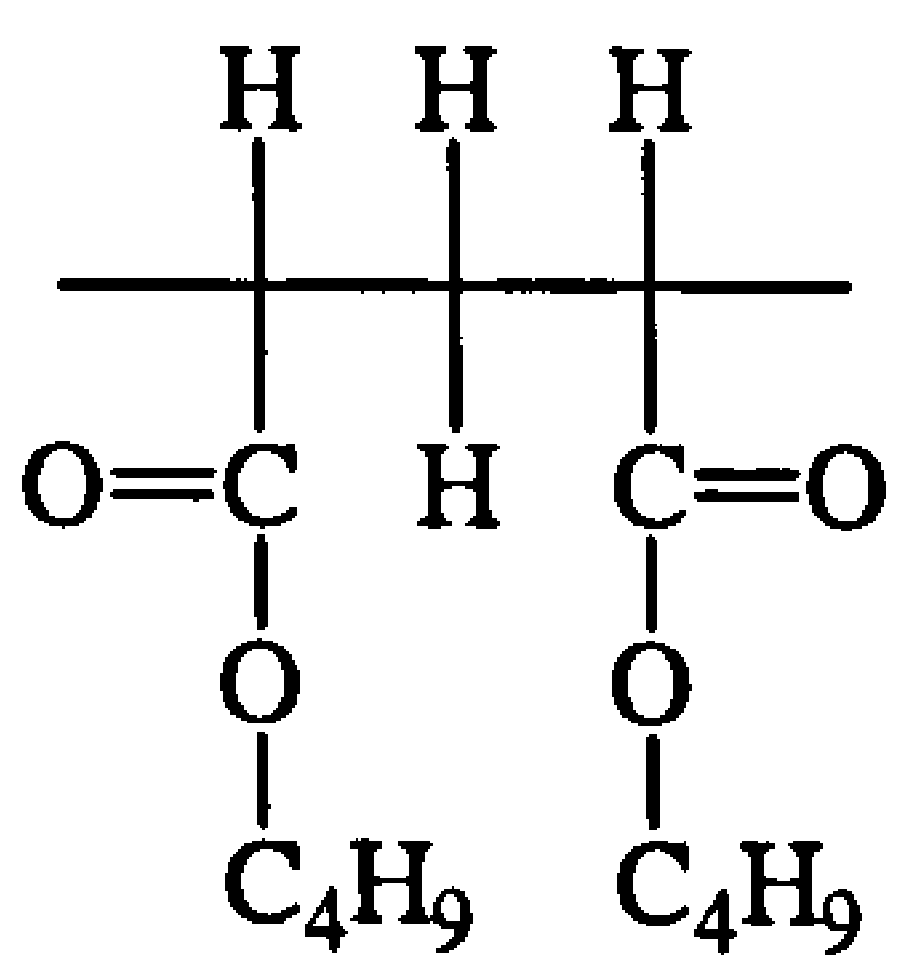
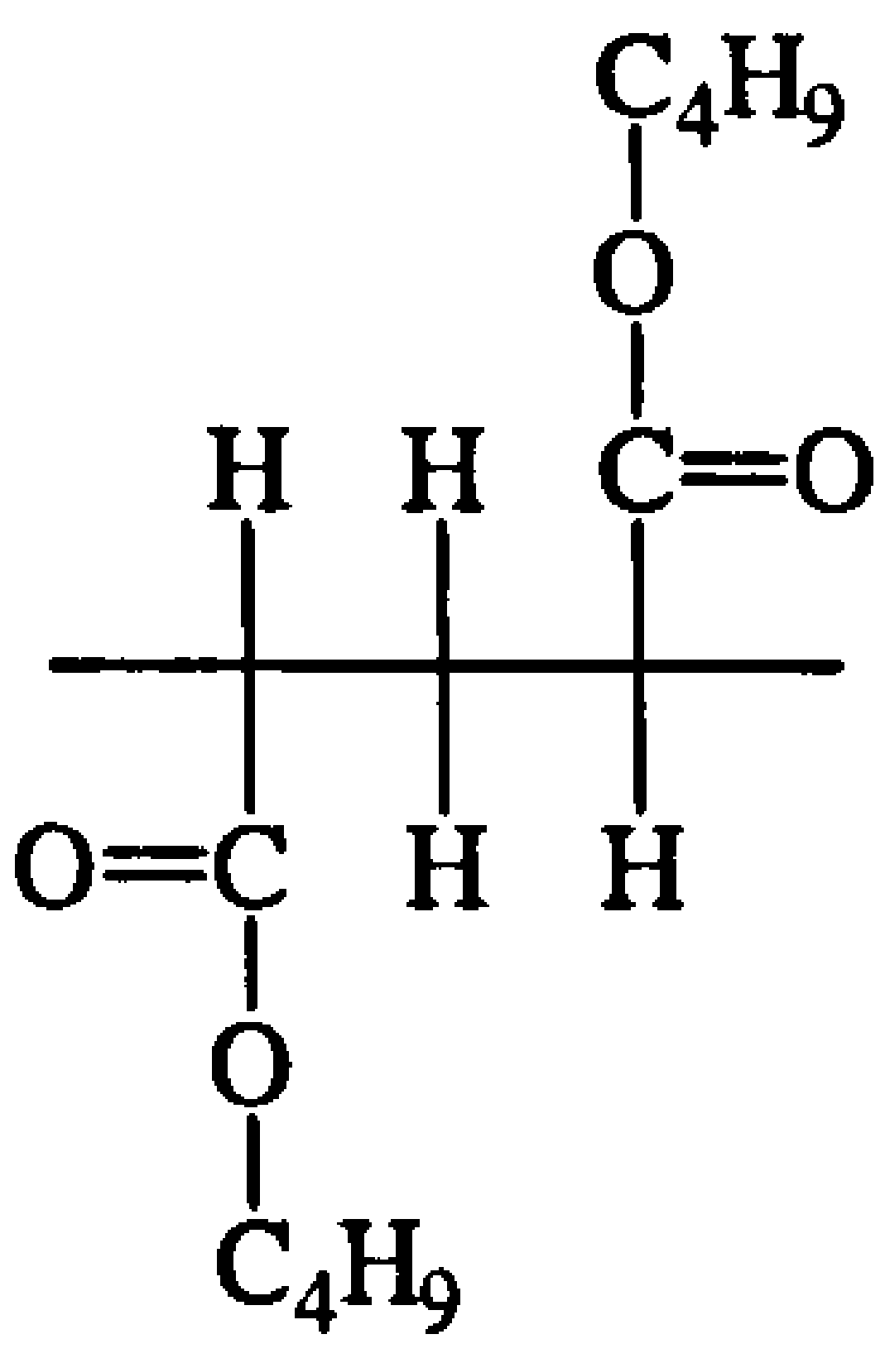


Figure 4-2 ^1H NMR spectrum of butyl acrylate homopolymer

The diagram below shows meso and racemic diads illustrating the two possibilities for the configuration of the two closest chiral centres. In practice the configuration of more remote centres has a large contribution to the splitting of the two methylene hydrogens.



meso (m)



racemic (r)

The methylene carbon peak in the ^{13}C NMR spectra also show splitting due to tacticity effects and this is shown below.

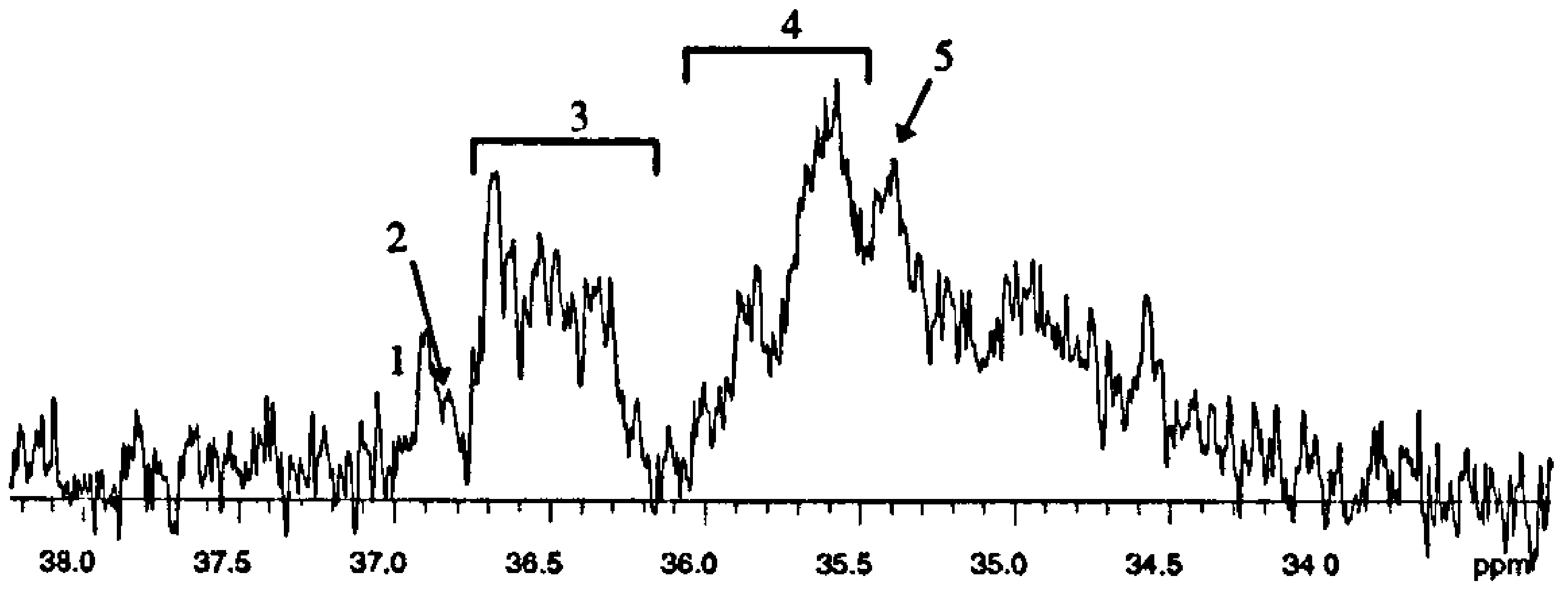


Figure 4-3 ^{13}C NMR in the backbone methylene carbon region

In a paper by Suchoparek this splitting is analysed in detail using one and two dimensional NMR.[6] Shift values given for the various sequences of diads were compared to those obtained in this work and it was possible to make some assignments of the peaks due to the methylene backbone carbon as shown in Table 4-2.

Peak Number	Assignment
1	mrmrm, mrrrm, rmr, rrr
2	mrrrr, mrmrr
3	mrr, mmr
4	mrm
5	mmm

Table 4-2 Peak assignments for the splitting pattern of the backbone methylene carbon peak in the ^{13}C NMR spectrum of poly(butyl acrylate)

The conclusion of the NMR spectroscopic analysis is that the poly(butyl acrylate) produced is atactic *i.e.* there is a statistical distribution of meso and racemic diads.

Thermogravimetry (TG) showed all samples to be stable up to 200°C and differential scanning calorimetry showed the glass transition temperatures to be in the region of -46°C which is fairly close to the literature value of -54°C.[1]

Gel permeation chromatographs were recorded for samples F, G and H only. In these cases, the relative amount of monomer to initiator lead to lower molecular weight polymers. The other samples were not analysed successfully owing to experimental problems. The solutions formed by dissolving the samples in both THF and chloroform were extremely viscous and it was difficult to filter these solutions even at very low concentrations (3mg/mL). Analysis of these solutions was attempted but two effects were noted. Firstly a large polydispersity (~8) was observed and secondly the flow rate through the column was significantly decreased, presumably because blocking was occurring. In view of this it was not possible to gain any useful information and therefore GPC analysis of samples A to E was discontinued.

It can be concluded that the molecular weights of the polymer sample A to E are higher than those for samples F to H as would be expected for the higher ratio of monomer to initiator. These high molecular weights lead to a high solution viscosity even at low concentrations.

Elemental analysis of all homopolymer samples were in close agreement with the calculated values.

4.3.2 Conclusion

It has been possible to establish conditions for the emulsion homopolymerisation of butyl acrylate to reproducibly obtain high yields of high molecular weight polymer in a reaction time of 30 minutes.

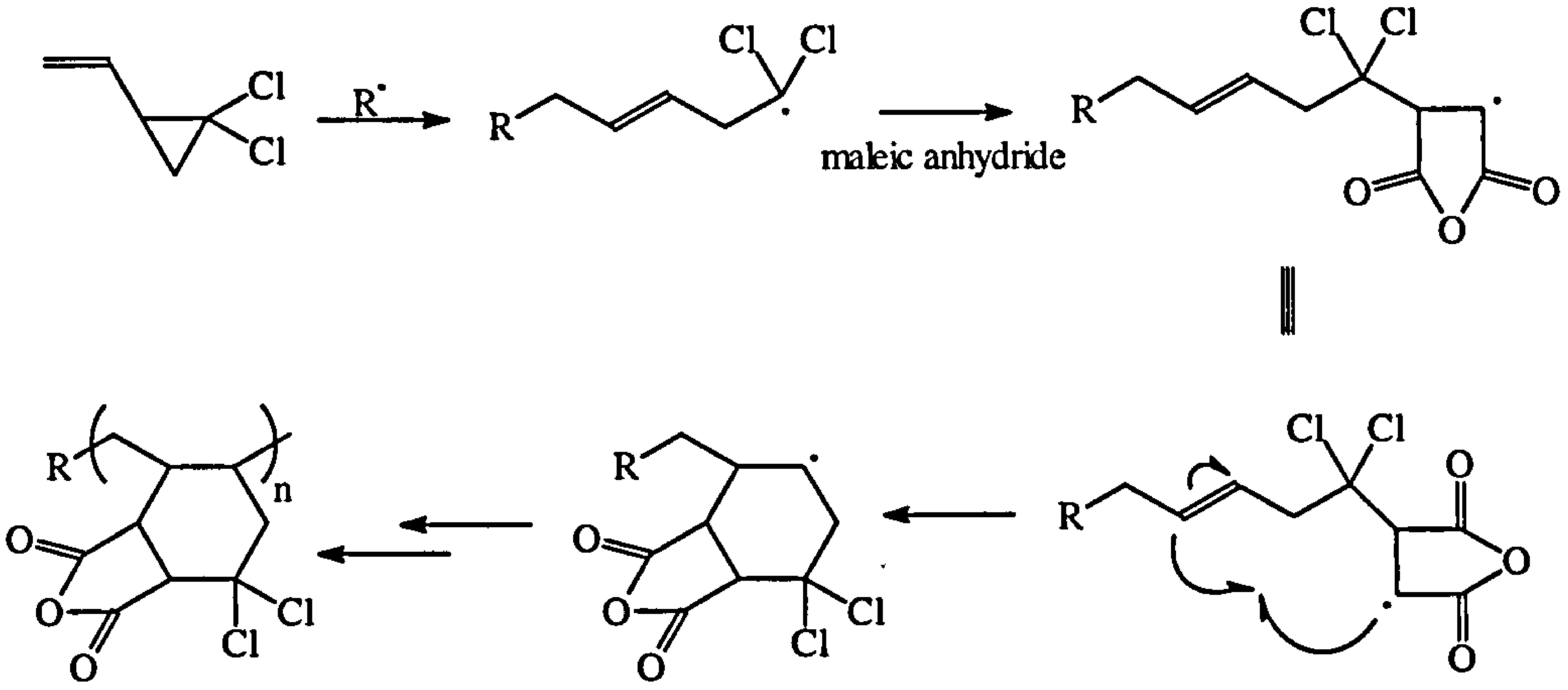
4.4 Copolymerisation of butyl acrylate and 1,1-dicyano-2-vinylcyclopropane

4.4.1 History

There are no reports in the literature of the copolymerisation of 1,1-dicyano-2-vinylcyclopropane with butyl acrylate. There are, however, several reports of the copolymerisation of vinylcyclopropane monomers with various other monomers.

In 1970, Takahashi published two papers recording the copolymerisation of 1,1-dichloro-2-vinylcyclopropane firstly with maleic anhydride[8] and secondly with methyl acrylate, methyl methacrylate and styrene.[9]

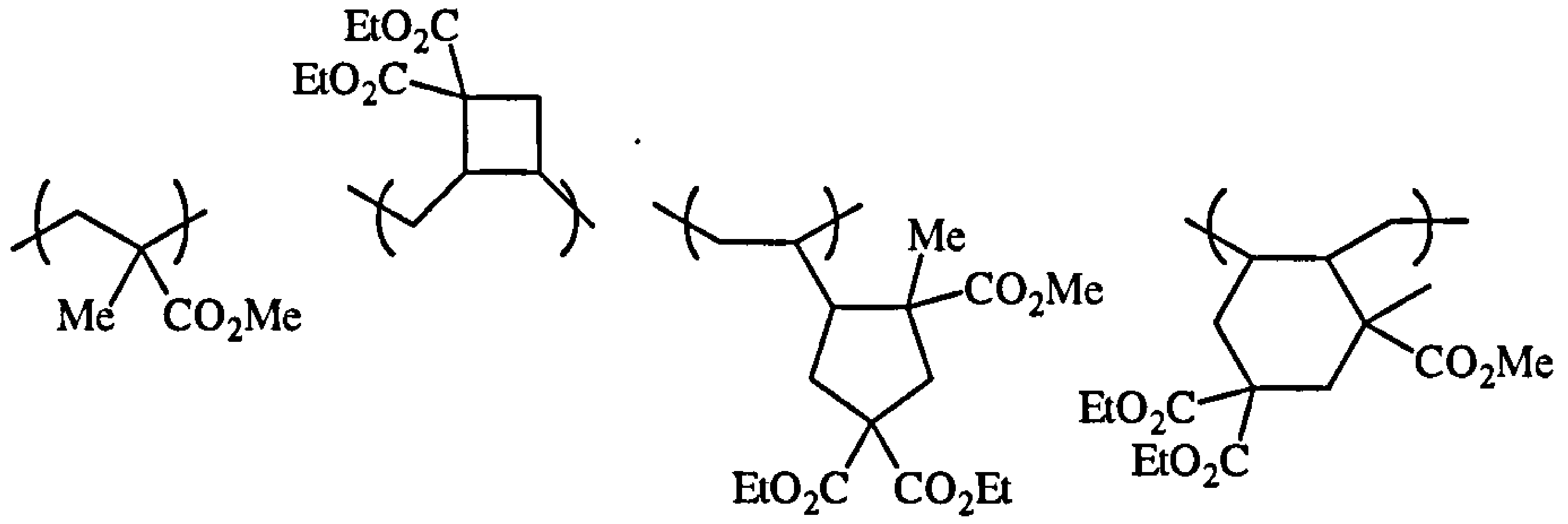
1,1-Dichloro-2-vinylcyclopropane was copolymerised with maleic anhydride using AIBN in bulk and solution free-radical processes to form a copolymers in which the unsaturation present was small and it was suggested that six-membered rings may be formed in the polymer backbone.



In the second paper, 1,1-dichloro-2-vinylcyclopropane was found to form copolymers with methyl acrylate in yields up to 15%, methyl methacrylate in yields up to 23% and with styrene, in yields up to 6%. It was again shown that the degree of unsaturation was low and dependent upon changes in the monomer feed.

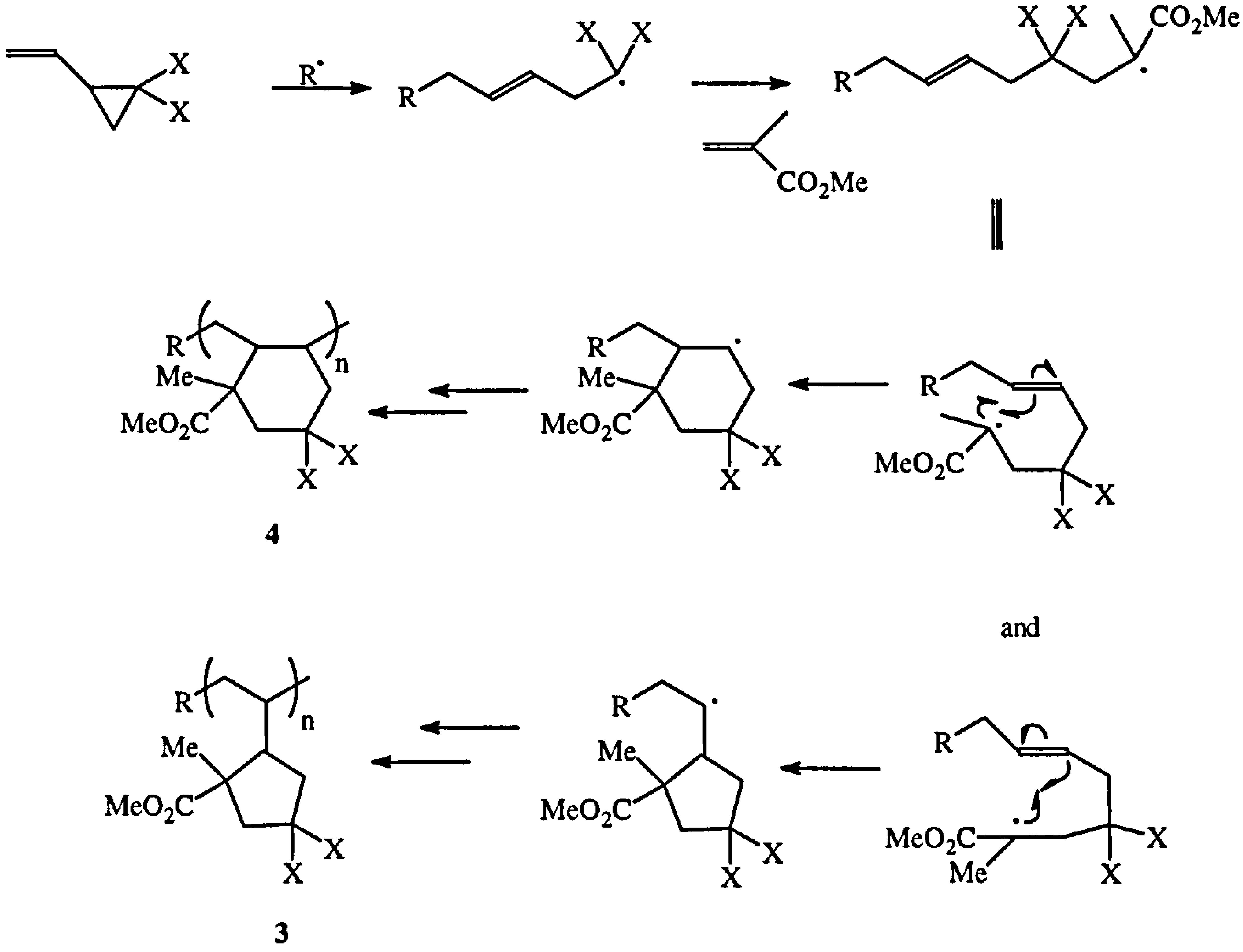
In Takahashi's work, the structures of the copolymers obtained were deduced on the basis of elemental analysis and IR spectra and the properties of the polymers were not reported.

In 1994, Sanda *et al.* published work on the copolymerisation of 1,1-diethoxycarbonyl-2-vinylcyclopropane with methyl methacrylate (MMA).[10] Yields up to 96% were obtained using AIBN as initiator, in bulk and in chlorobenzene solution polymerisations. Sanda used NMR spectroscopic analysis to ascertain the structure of the copolymers and he concluded that the polymerisation of a monomer feed of 50:50 VCP:MMA, produced a copolymer consisting of 30% VCP units. Again, the degree of unsaturation was lower than expected and Sanda proposed that the copolymer consisted of the units shown below.



1 **2** **3** **4**

Unit **1** is the methyl methacrylate unit, unit **2** is the cyclobutane rearrangement product from the VCP unit, and units **3** and **4** are rearrangement products of a VCP and methyl methacrylate unit formed as shown below.



It can be seen from both Sanda's and Takahashi's work that the copolymerisations of VCP monomers leads to many different structures and that the VCP monomer is incorporated into the copolymers only in low percentages.

The work described in this chapter was an attempt to use emulsion copolymerisation. There is only one paper on the polymerisation of VCP monomers using emulsion polymerisation published by Sanda in 1998.[11] He polymerised 1,1-diethoxycarbonyl-2-vinylcyclopropane and 1,1-dichloro-2-vinylcyclopropane using potassium persulphate in the presence of a soap, (sodium lauryl sulphate) and in the absence of a soap (dispersion polymerisation). He found that 1,1-diethoxycarbonyl-2-

vinylcyclopropane polymerised well both with and without the soap producing high yield of polymer with an $\overline{Mn}$ of 30-60,000. The emulsion polymerisation in the presence of soap produced the highest yield and the highest molecular weight polymer although the olefin content was decreased from the dispersion and bulk polymerisation products. Dispersion copolymerisations of 1,1-diethoxycarbonyl-2-vinylcyclopropane with vinyl acetate and acrylonitrile were carried out. The copolymerisation with vinyl acetate proceeded satisfactorily to afford copolymer in a 64% yield. Copolymerisation with acrylonitrile was unsuccessful although Sanda showed that copolymerisation proceeded as expected in bulk polymerisation. This lack of success with copolymerisation was thought to be due to difference in solubilities of the two monomers.

Sanda found that 1,1-dichloro-2-vinylcyclopropane did not polymerise successfully by emulsion polymerisation.

4.4.2 Attempted emulsion copolymerisation of butyl acrylate and 1,1-dicyano-2-vinylcyclopropane

4.4.2.1 Butyl acrylate (4.5 g) and VCP (0.5 g) monomer mixture

Firstly a monomer mixture of butyl acrylate (4.5 g, 35.1 mmol) and 1,1-dicyano-2-vinylcyclopropane (0.5 g, 4.2 mmol) was formed and emulsion polymerisation of the mixture was attempted using the conditions established in the studies on the homopolymerisation of butyl acrylate although a longer reaction time was used.

Time/min	Initiator/monomer molar ratio	Volume initiator stock solution / cm^3
120	1 : 241.5	0.98

Table 4-3 Conditions for the attempted copolymerisation of 1,1-dicyano-2-vinylcyclopropane with butyl acrylate

After 30 minutes, the polymer produced was precipitated in an acetone/methanol mixture to give a yellowish elastomeric polymer in 54% yield.

4.4.2.1.1 Analysis

Infra-red spectroscopic analysis gave a spectrum identical to that of poly(butyl acrylate) with no evidence of a peak due to a cyano group which would be found in a spectral window at about 2248 cm^{-1}.

The ^{1}H and ^{13}C NMR spectra were identical with those of butyl acrylate homopolymer. In the ^{1}H NMR there is no trace of a peak at ≈6ppm corresponding to the vinylic protons of the vinylcyclopropane ring-opened unit.

Differential scanning calorimetry gave a Tg of -38 °C. This shows no significant change from the value obtained for the homopolymer of butyl acrylate (-46°C).

Gel permeation chromatography showed a single peak with $\overline{Mn}$ = 126 000, $\overline{Mw}$ = 216 000 and a pdi of 1.72 consistent with simple homopolymerisation of butyl acrylate.

Elemental analysis detected no nitrogen in the polymer and gave C, 65.37% and H, 9.52% in good agreement with the calculated values for the butyl acrylate homopolymer of C, 65.60% and H, 9.44% confirming that the vinylcyclopropane monomer has not been incorporated into the polymer.

4.4.2.1.2 Conclusion

These results suggested that the copolymerisation had been unsuccessful and that no VCP monomer had been incorporated. It was clear that the only polymer produced was poly(butyl acrylate).

4.4.2.2 Butyl acrylate (0.5 g) and VCP (4.5 g) monomer mixture

It was decided to repeat the copolymerisation attempt using a greater amount of vinylcyclopropane monomer in order to increase the probability of it being incorporated into the copolymer.

Attempts were made to polymerise a monomer mixture of butyl acrylate (0.5 g, 3.9 mmol) and dicyano vinylcyclopropane (4.5 g, 38.1 mmol) using the same conditions as in the previous reaction.

Time/min	Initiator/monomer molar ratio	Volume initiator stock solution / cm^3
120	1 : 241.5	1.21

Table 4-4 Conditions for the attempted copolymerisation of 1,1-dicyano-2-vinylcyclopropane with butyl acrylate

Using these conditions a very low yield of fine white powder was obtained. This powder was analysed by infra-red analysis, ^1H NMR, DSC and elemental analysis.

4.4.2.2.1 Analysis

Infra-red spectroscopic analysis produced a spectrum very different to that of the butyl acrylate homopolymer with a band at 2250 cm^{-1} indicating the presence of a cyano functionality and a strong band at 970 cm^{-1} indicating the presence of *trans* double bonds. The C-O stretching band at 1163 cm^{-1} was not present although a weak band at 1727 cm^{-1} suggested the presence of some C=O functionality. Comparison of the infra-red spectrum with that obtained and reported in chapter 3 for the 1,1-dicyano-vinylcyclopropane homopolymer revealed a marked similarity, the only difference being the presence of the band at 1727 cm^{-1}. This seemed to suggest that the polymer formed contained a small amount of butyl acrylate. It is possible that the band 1727cm^{-1} may be due to residual butyl acrylate monomer since it was possible to detect the odour of butyl acrylate monomer in the polymer sample, although the spectra was not changed by washing and prolonged drying under vacuum of the product.

The polymer was found to have limited solubility and ^1H NMR was carried out in DMSO at 80°C.

The ^1H NMR spectrum was complicated and it was not possible to assign all peaks. A clear peak was observed at 5.9 ppm suggesting the presence of olefinic protons and a peak at 2.9 ppm which corresponded to the methylene protons in the homopolymer of 1,1-dicyano-2-vinylcyclopropane. The peaks appearing around 0 ppm could correspond to the ring protons of a vinylcyclopropane defect unit. This suggests that the VCP monomer has not undergone exclusively 1,5-ring-opening polymerisation but also 1,2-type polymerisation where the ring structure is retained.

There were several broad ill-defined peaks which could have indicated the presence of small amount of butyl acrylate polymer but NMR seems to support the hypothesis that the attempted copolymerisation has produced predominantly VCP homopolymer.

Differential scanning calorimetry gave a glass transition temperature of 83°C. This is in close agreement with the values obtained for the VCP homopolymers again confirming the formation of the VCP homopolymer rather than a copolymer.

It was not possible to perform GPC owing to the limited solubility of the polymer produced.

Elemental analysis showed values in the same region as calculated for the VCP homopolymer although agreement was not exact. This was to be expected as NMR and IR suggest the presence of a trace of butyl acrylate either as polymer or residual monomer.

4.4.2.2.2 Conclusion

The conclusions drawn from this second attempt at copolymerisation of 1,1-dicyano-2-vinylcyclopropane with butyl acrylate are that when the VCP is in considerable excess, the polymer formed is predominantly the VCP homopolymer with both 1,5-ring-opened and 1,2-type polymerisation units present. There may be minor incorporation of butyl acrylate as suggested by IR and NMR but this incorporation, if real, is negligible.

Several other emulsion copolymerisations were attempted at different monomer ratios but, in all cases, no copolymer was formed.

4.4.3 Attempted solution copolymerisation of butyl acrylate and 1,1-dicyano-2-vinylcyclopropane

In order to ascertain whether the inability of the monomers to form copolymers was a function of the emulsion polymerisation process, it was decided to attempt the copolymerisation as a solution free-radical process. A monomer mixture of butyl acrylate (1 g, 7.8 mmol) and 1,1-dicyano-2-vinylcyclopropane (1 g, 8.5 mmol) was prepared and an attempt was made to polymerise it using AIBN in benzene at 60°C with a reaction time of 20 hours.

After the required reaction time the ampoule contained a clear, pale yellow solution with no insoluble precipitate. Under these conditions, VCP homopolymer would precipitate since it is insoluble in benzene. The solution was added to methanol and a yellow powdery solid was obtained. After drying, this solid was analysed by ^{1}H and ^{13}C NMR, infra-red spectroscopy, DSC, GPC and elemental analysis.

4.4.3.1 Analysis

Close inspection of the solid obtained after drying revealed that the solid was heterogeneous in nature consisting of a yellow solid and a white powder. This lead us to suspect that the reaction had lead to the formation of the two homopolymers.

Infra-red spectroscopic analysis revealed the peaks characteristic of both homopolymers with a cyano peak at 2248 cm^{-1} and a strong ester peak at 1734 cm^{-1}.

^{1}H and ^{13}C NMR were recorded for a chloroform solution although a powdery residue remained (possibly VCP homopolymer). In both NMR spectra peaks attributed to both homopolymers were visible.

DSC analysis gave evidence which contradicted the hypothesis of the formation of two homopolymers and supported the theory that a copolymer had been formed. A single Tg was observed at 42°C. This is considerably different to either of the homopolymer glass transition temperatures and suggests that a copolymer has been formed.

It was not possible to perform GPC owing to the insolubility of the powdery portion of the solid in chloroform and THF.

4.4.3.2 Conclusion

The results of this study are inconclusive. It is not clear whether a copolymer or two homopolymers have been formed. Visual inspection suggests inhomogeneity and the solubility of a portion of the solid in chloroform whilst the powdery portion remains undissolved suggests that the two homopolymers have formed. However, the appearance of a single glass transition temperature in a region distinct from that of either of the homopolymers is reasonably good evidence for the formation of a copolymer.

4.5 Summary

The copolymerisation of 1,1-dicyano-2-vinylcyclopropane with butyl acrylate does not proceed successfully under emulsion copolymerisation conditions. The formation of the homopolymer of the monomer in excess is formed. It is possible that in the case of excess VCP that there is minor incorporation of butyl acrylate into the polymer. This inability to copolymerise may be due to the differences in solubilities or reactivity.

In solution copolymerisation, it is not clear whether two homopolymers have formed or whether a copolymer has been produced.

Owing to the ambiguity in the results of this work, it was decided to abandon this approach of forming copolymers and it was decided to investigate new VCP monomers which it was hoped would produce a polar polymer with elastomeric prpoerties. This work is reported in the following chapters.

4.6 Experimental

4.6.1 General Methods

Benzene was dried by prior to use by refluxing with sodium/benzophenone. AIBN was recrystallised from acetone. Butyl acrylate was washed three times with 10% sodium hydroxide, three times with de-ionised water, dried over calcium chloride and vacuum transferred prior to use. A stock solution of the initiator was prepared by dissolving 1.92 g (8.1 mmol) of sodium persulphate in 50 cm^3 of distilled water in a volumetric flask. All other reagents were used as supplied.

Infra-red spectra were recorded on a Perkin Elmer 1600 series FTIR. The spectra were recorded between NaCl discs or as a KBr disc. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 400 MHz spectrometer. The solvent used was deuterated chloroform with TMS as internal reference or deuterated DMSO. Gel permeation chromatography was carried out in chloroform using a Knauer HPLC pump (model 64), Waters model R401 differential refractometer detector and 3 PLgel columns with pore sizes of 10^2, 10^3 and 10^5 Å (column packing PLgel 5μm mixed styrene-divinyl benzene beads). The sample solutions were filtered through a Whatman WTP type 0.2μm filter to remove any particulate before injection. The columns were calibrated using Polymer Laboratories polystyrene standards (162-770 000amu). Thermogravimetry (TG) was carried out using a Stanton Redcroft TG 760 series and differential scanning calorimetry (DSC) was performed using either a Perkin Elmer DSC 7 or a Pyris 1.

4.6.2 Emulsion polymerisation of butyl acrylate

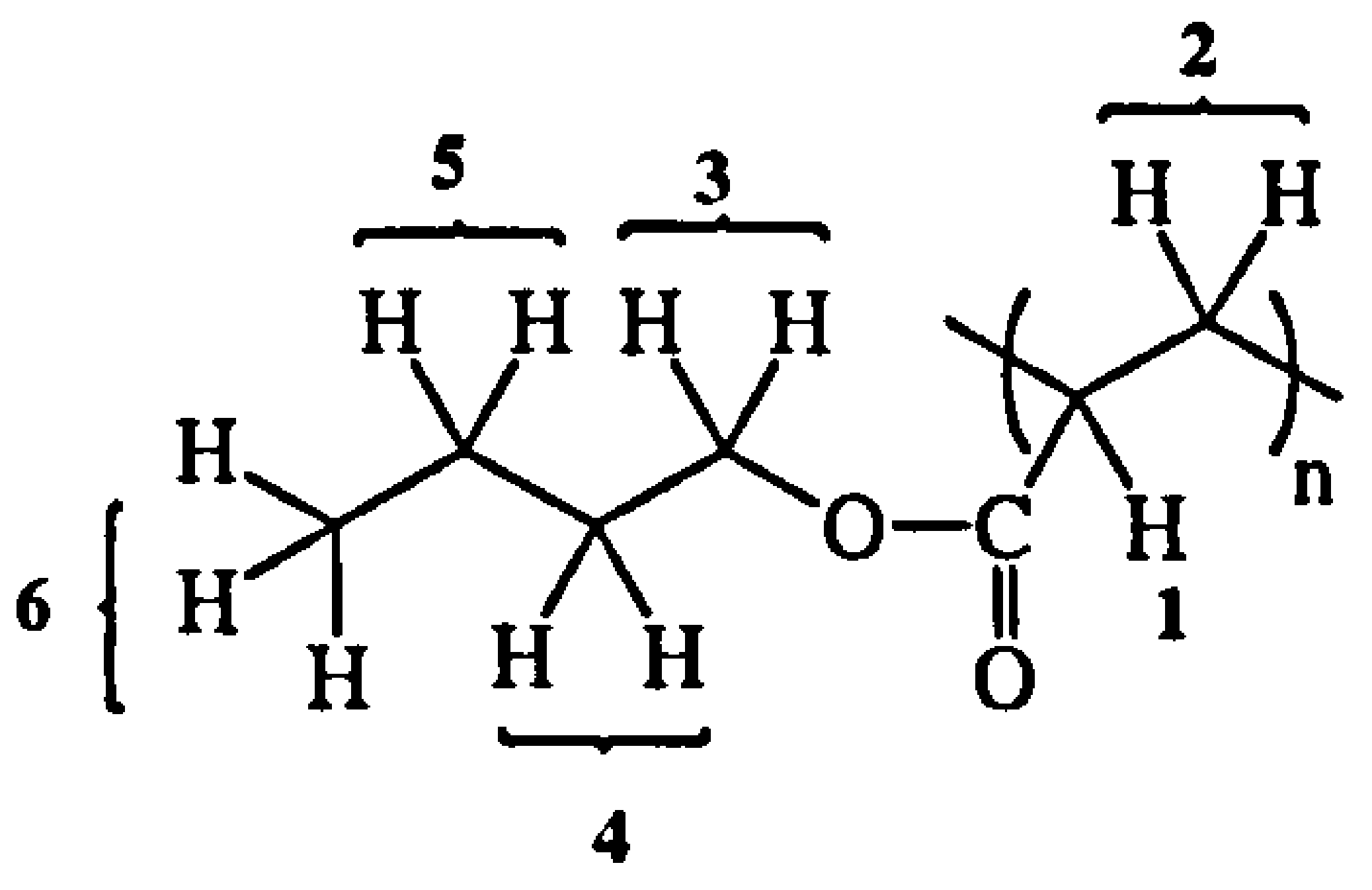
De-ionised water (50 cm^3) was placed in a flat bottomed flange. Dry, oxygen-free nitrogen was bubbled through the water for 30 minutes to expel all oxygen from the water.

Butyl acrylate (10 g, 78 mmol), Triton X-100 (0.5 g) and sodium dodecylsulphate (0.04 g) were added to the water under nitrogen. The flange was sealed under nitrogen and the mixture was stirred vigorously using a mechanical stirrer. The mixture was heated to 90°C in an oil bath, the sodium persulphate stock solution was injected through the suba seal and the mixture was stirred for the required reaction time. The mixture was allowed to cool and was transferred to a large beaker. The polymer was coagulated using a 9:1 mixture of acetone and methanol. The resulting gel was washed for 2 hours with de-ionised water in an attempt to remove all surfactant. The resulting white, rubbery polymer was dried over night in a vacuum oven at 40°C.

4.6.2.1 Characterisation of the butyl acrylate homopolymer

Infra-red Spectroscopy:- All spectra were identical. The spectrum of sample F is shown as a typical spectrum. See appendix 3.1
2959 cm^{-1} (C-H stretch), 1733 cm^{-1} (C=O stretch), 1451 cm^{-1} (C-H bend), 1163 cm^{-1} (C-O stretch)

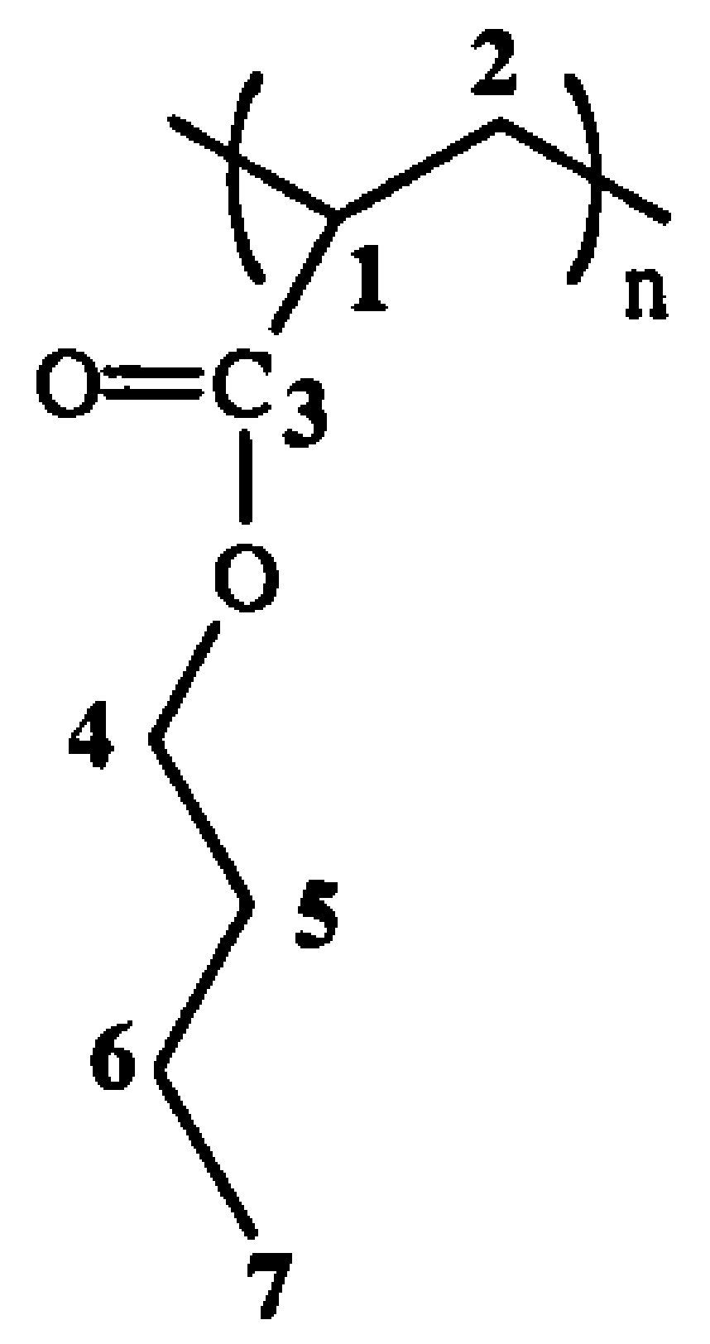
^{1}H NMR - See appendix 3.2



δ / ppm = 4.02 (m,**3**), 2.27 (broad s,**1**), 1.90-1.33 (m, **2**), 1.58 (m,**4**), 1.37 (m,**5**), 0.93 (m,**6**)

Intensity ratio 2:1:2:2:2:2

^{13}C NMR - See appendix 3.3



δ / ppm = 174.4 (3), 64.3 (4), 41.3 (2), 35.3 (1), 30.5 (5), 19.0 (6), 13.6 (7)

Assignments were made using a DEPT spectrum.

Differential Scanning Calorimetry - see appendix 3.4 for the DSC trace of sample H which was typical of the DSC traces produced

Sample	Tg /°C
A	-46.32
B	-46.38
C	-46.33
D	-46.51
E	-46.90
F	-46.47
G	-46.47
H	-46.68

Gel Permeation Chromatography - see appendix 3.5 for GPC trace of sample F which was typical of the GPC traces produced

Sample	$\overline{Mn}$	$\overline{Mw}$	Polydispersity
F	760 000	1091 000	1.44
G	688 000	784 000	1.14
H	537 000	1150 000	2.14

Elemental Analysis

		Found							
	Calculated	A	B	C	D	E	F	G	H
C%	65.6	65.3	65.0	65.4	65.2	65.4	65.3	65.4	65.5
H%	9.4	9.7	9.5	9.7	9.6	9.7	9.3	9.5	9.4

4.6.3 Typical emulsion copolymerisation

De-ionised water (50 cm^3) was placed in a flat bottomed flange. Dry, oxygen-free nitrogen was bubbled through the water for 30 minutes.

Butyl acrylate, 1,1dicycano-2-vinylcyclopropane, Triton X-100 (0.25 g) and sodium dodecylsulphate (0.02 g) were added to the water under nitrogen. The flange was sealed under nitrogen using a suba seal and the mixture was stirred vigorously with a mechanical stirrer. The mixture was heated to 90°C in an oil bath, the sodium persulphate stock solution was injected through the suba seal and the mixture was stirred at 90°C for 30 min. The mixture was allowed to cool and then transferred to a large beaker. The polymer was coagulated using a 9:1 mixture of acetone and methanol. The resulting gel was washed for 2 hours with de-ionised water. The resulting polymer was dried over night in a vacuum oven at 40°C.

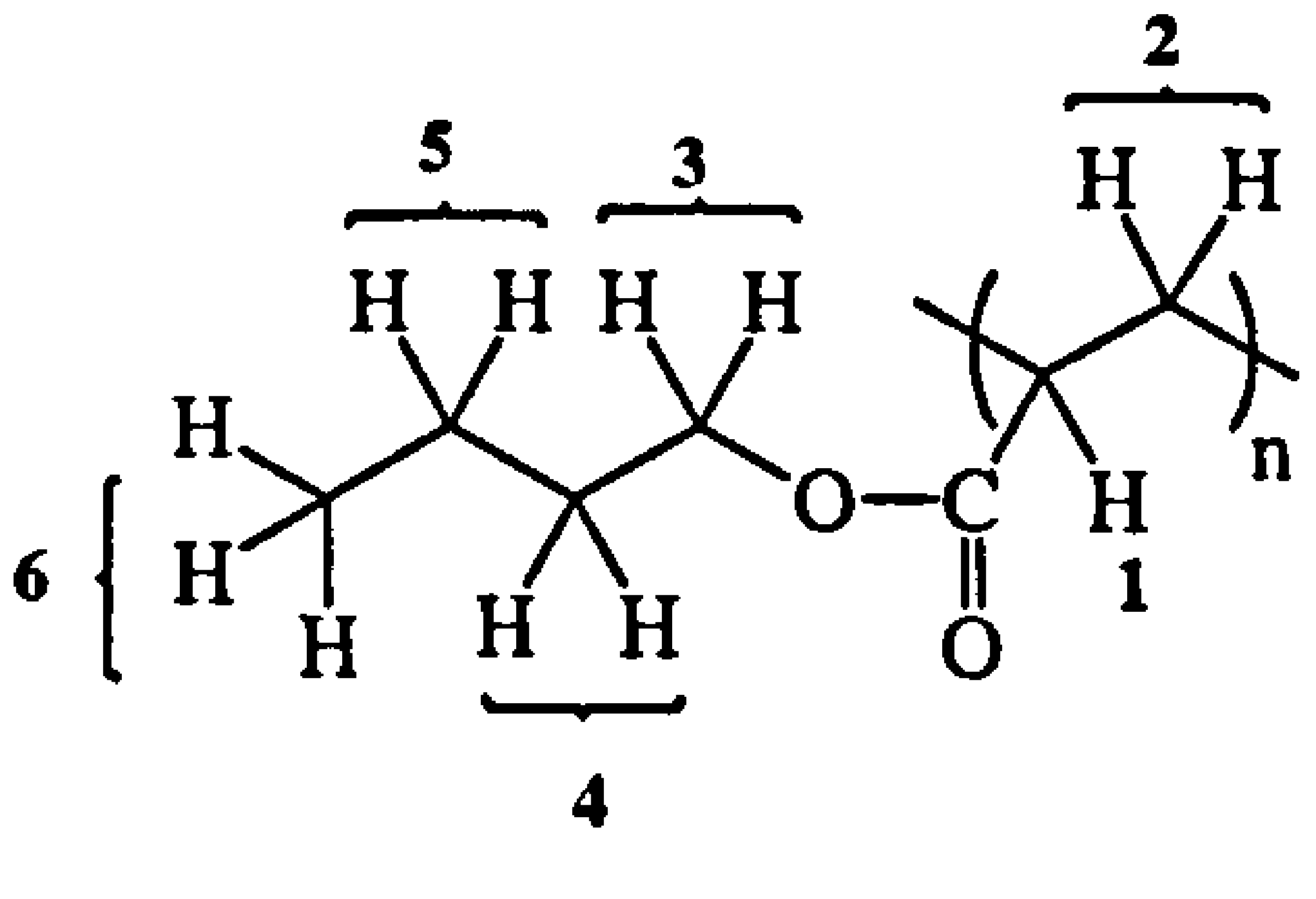
4.6.3.1 Characterisation of the polymers produced from the attempted emulsion copolymerisation

4.6.3.1.1 Butyl acrylate (4.5 g) and VCP (0.5 g) monomer mixture

Infra-red Spectroscopy - See appendix 3.6

2959 cm^{-1} (C-H stretch), 1734 cm^{-1} (C=O stretch), 1451 cm^{-1} (C-H bend), 1164 cm^{-1} (C-O stretch)

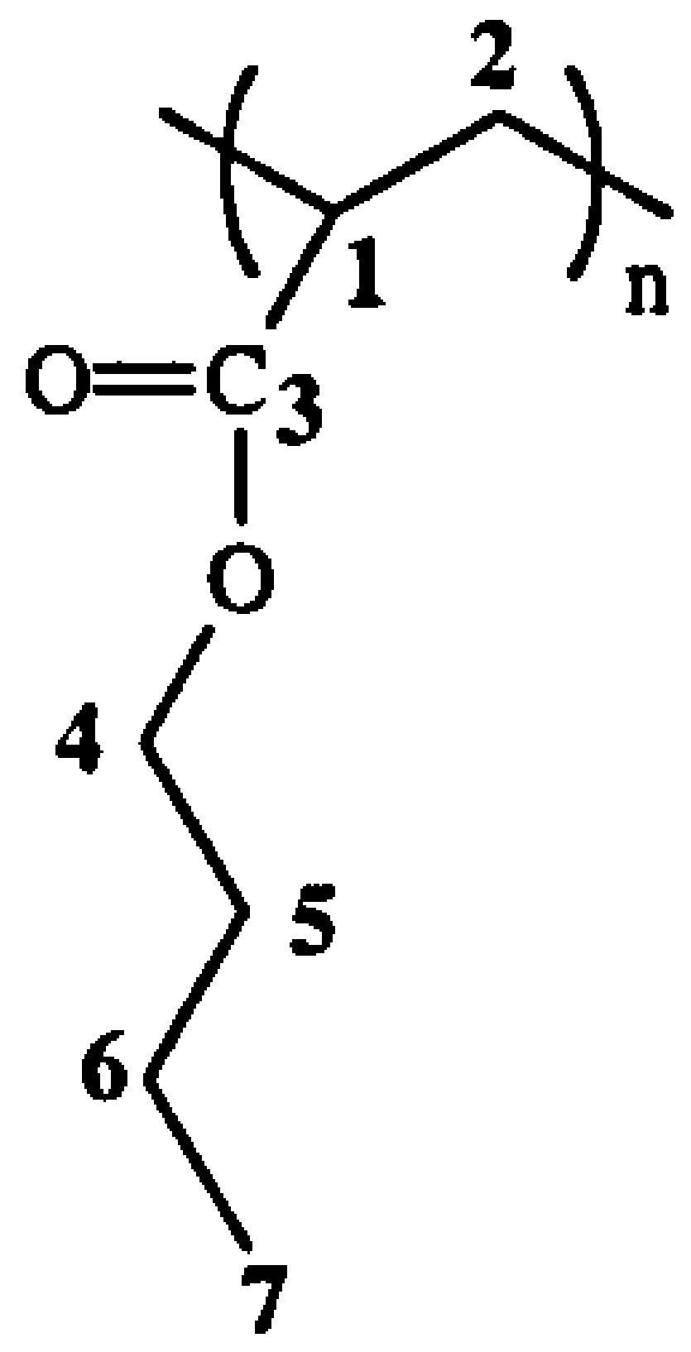
^{1}H NMR - See appendix 3.7



δ / ppm = 4.02 (m,3), 2.27 (broad s,1), 1.85-1.27 (m,2), 1.58 (m,4), 1.36 (m,5), 0.92 (m,6)

Intensity ratio 2:1:2:2:2:2

^{13}C NMR - See appendix 3.8



δ / ppm = 174.5 (3), 64.3 (4), 41.3 (2), 35.2 (1), 30.4 (5), 19.0 (6), 13.6 (7)

Differential Scanning Calorimetry - see appendix 3.9

Tg = -37.8°C

Gel Permeation Chromatography - see appendix 3.10

$\overline{Mn}$	$\overline{Mw}$	Polydispersity
126 000	216 000	1.7

Elemental Analysis

Calculated (for butyl acrylate homopolymer)

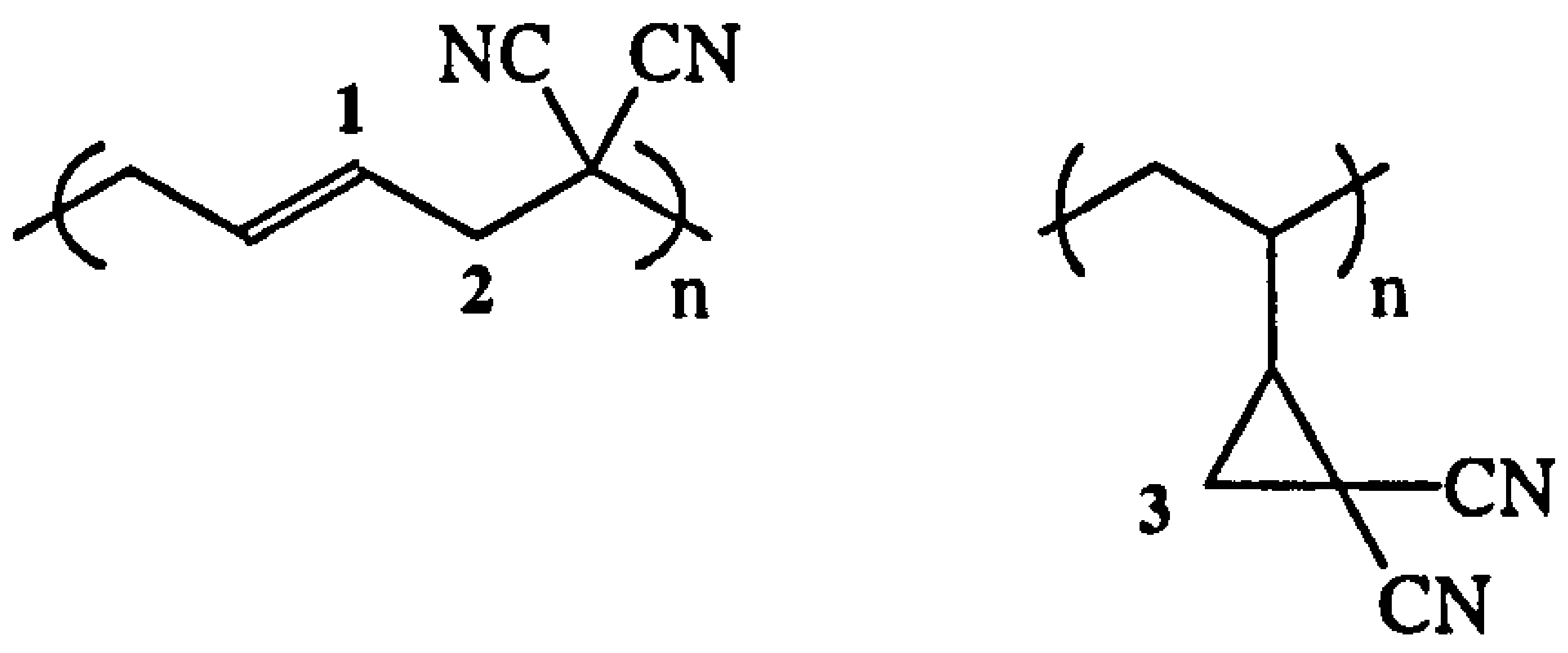
	C: 65.60%	H: 9.44%
Found	C: 65.37%	H: 9.52%

4.6.3.1.2 Butyl acrylate (0.5 g) and VCP (4.5 g) monomer mixture

Infra-red Spectroscopy - See appendix 3.11

2962 cm^{-1} (C-H stretch), 2250 cm^{-1} (CN stretch), 1727 cm^{-1} (C=O stretch), 1445 cm^{-1} (C-H bend), 970 cm^{-1} (*trans* C=C stretch)

^{1}H NMR - See appendix 3.12



δ / ppm = 5.90 (m,1), 2.92 (m,2), -0.11 (m,3)

Multiplets are unresolved

Differential Scanning Calorimetry - see appendix 3.13

Tg = 83.21°C

Elemental Analysis

Calculated (for VCP homopolymer)

	C: 71.17%	H: 5.12%	N: 23.71%
Found	C: 68.60%	H: 5.48%	N: 20.32%

4.6.4 Solution free radical copolymerisation

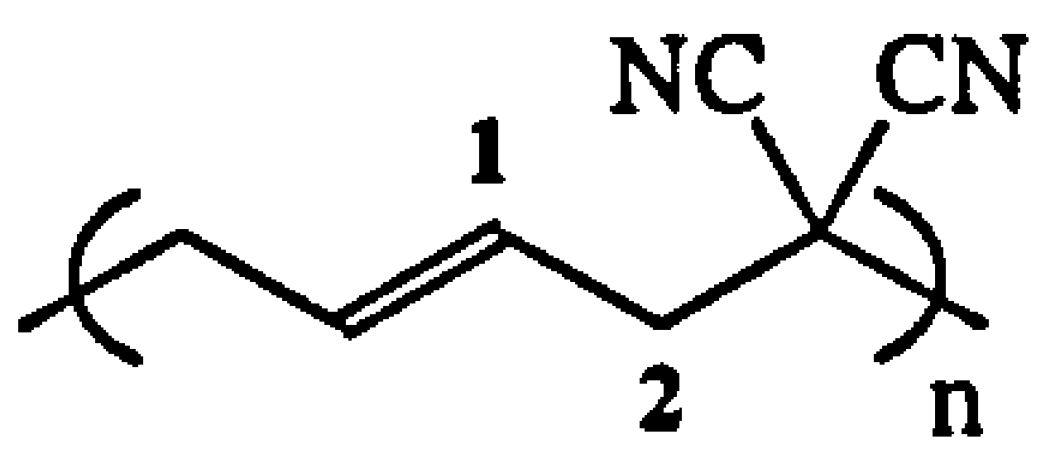
Butyl acrylate (1 g, 7.8 mmol) and 1,1-dicyano-2-vinylcyclopropane (1 g, 8.5 mmol) were weighed into an ampoule. AIBN (0.0105 g, 0.64 mmol) and dry benzene (5 cm^3) were added. The contents of the ampoule were frozen and degassed by the freeze/thaw method. The ampoule was left under vacuum and placed in an oil bath at 60°C for 20 hours. The clear, pale yellow solution formed was added to methanol and a low yield of a powdery solid was obtained.

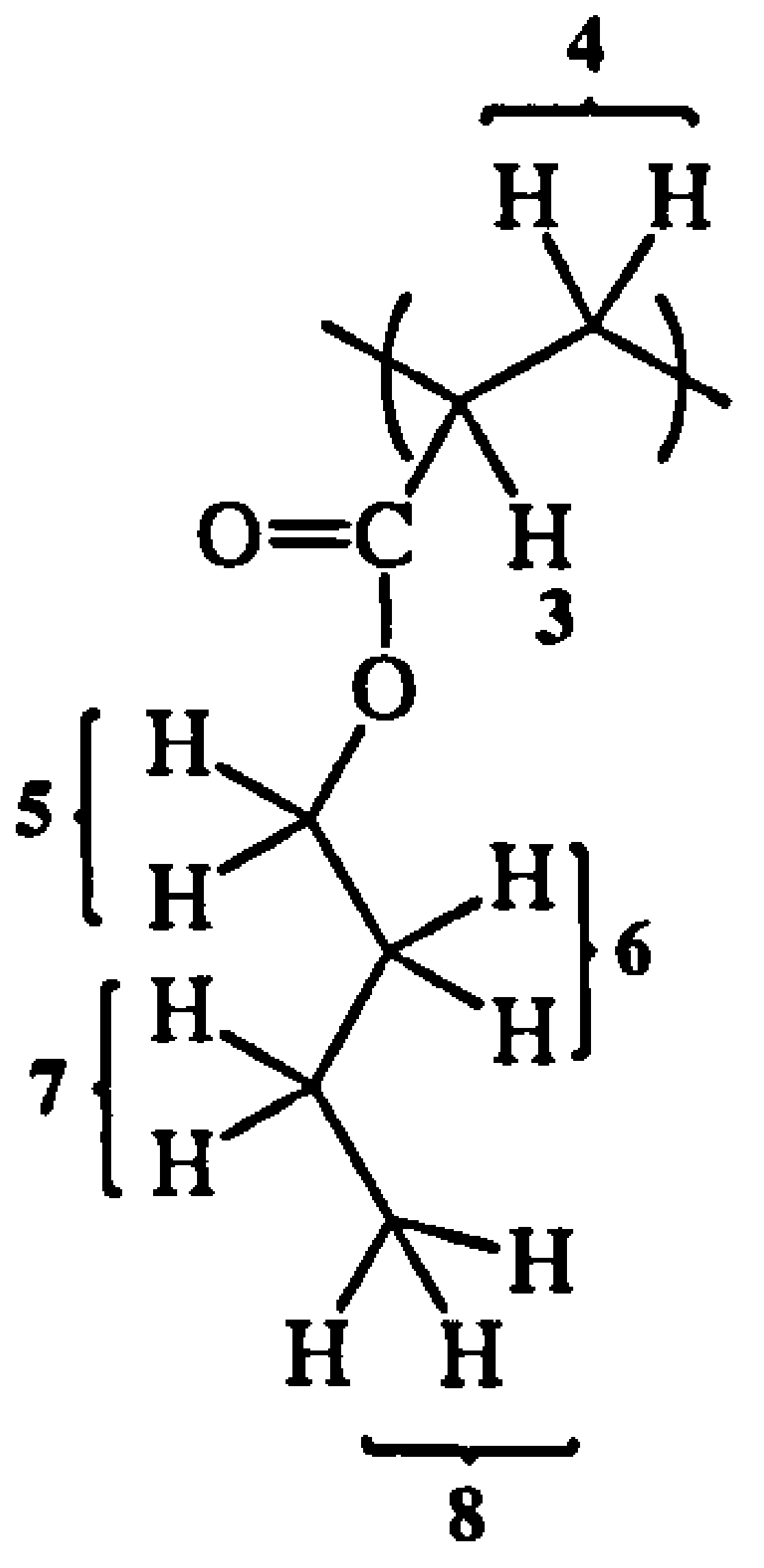
4.6.4.1 Characterisation

Infra-red Analysis - See appendix 3.14

2963 cm^{-1} (C-H stretch), 2248 cm^{-1} (CN stretch), 1734 cm^{-1} (C=O stretch), 1448 cm^{-1} (C-H bend), 1175 cm^{-1} (C-O stretch), 975 cm^{-1} (*trans* C=C stretch)

^{1}H NMR - See appendix 3.15

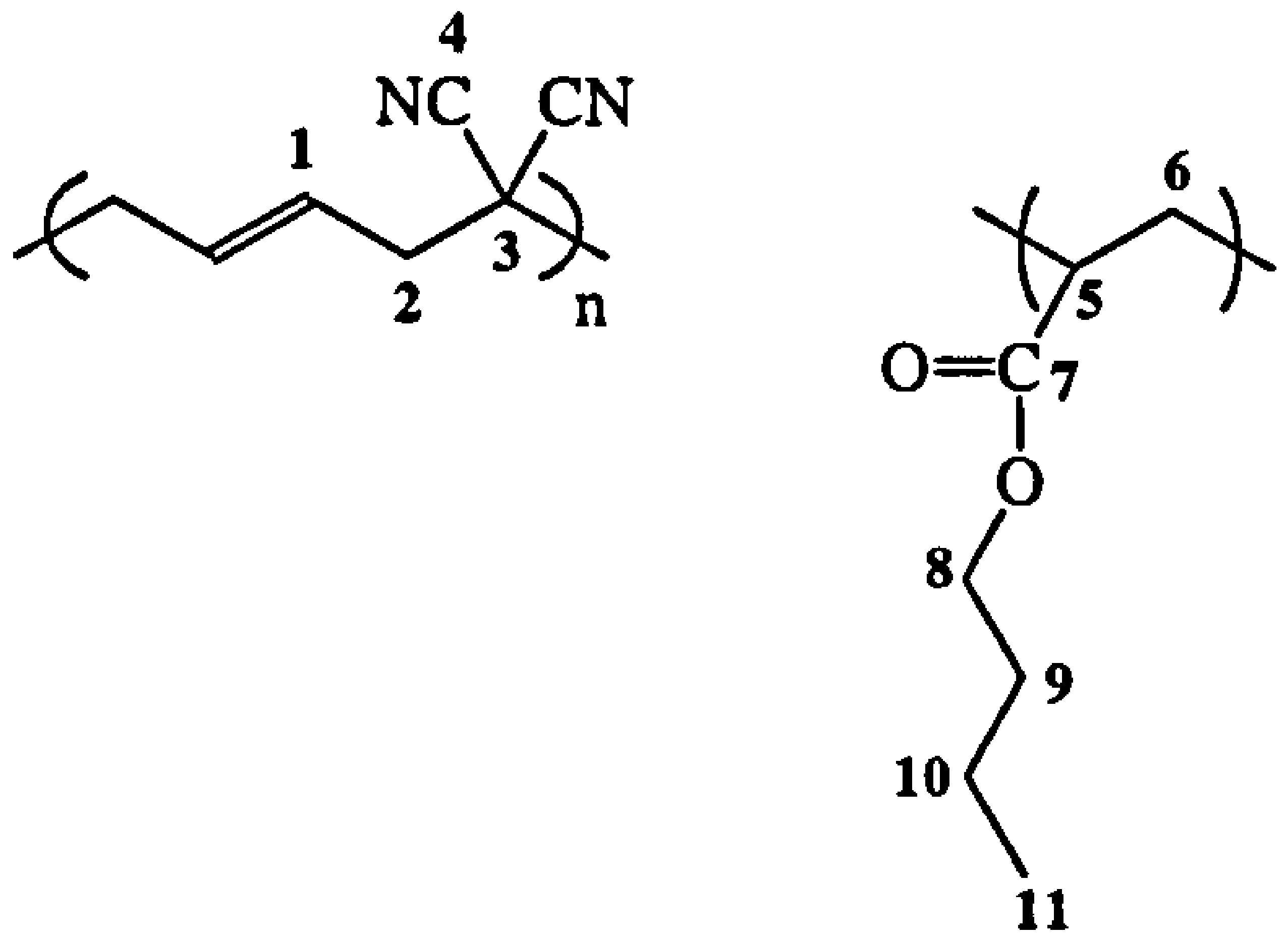




δ / ppm = 5.94 (m,1), 4.06 (m,5), 2.81 (m,2 and 4), 2.21 (broad s,3), 1.85-1.27 (m, 4), 1.62 (m,6), 1.38 (m,7), 0.94 (m,8)

Peak at 3.48 ppm is an unidentified impurity

^{13}C NMR - See appendix 3.16



δ / ppm = 174.5 (**7**), 129.2 (**1**), 114.6 (**4**), 64.4 (**8**), 41.0 (**6**), 39.1 (**2**), 36.0 (**3**), 35.0 (**5**), 30.5 (**9**), 19.0 (**10**), 13.6 (**11**)

Differential Scanning Calorimetry - see appendix 3.17

Tg = 42.13°C

Elemental Analysis

	Calculated for BA homopolymer	Calculated for VCP homopolymer	Found
%C	65.60	71.17	67.81
%H	9.44	5.12	7.43
%N	0	23.71	11.43

4.7 References

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Chapter 5

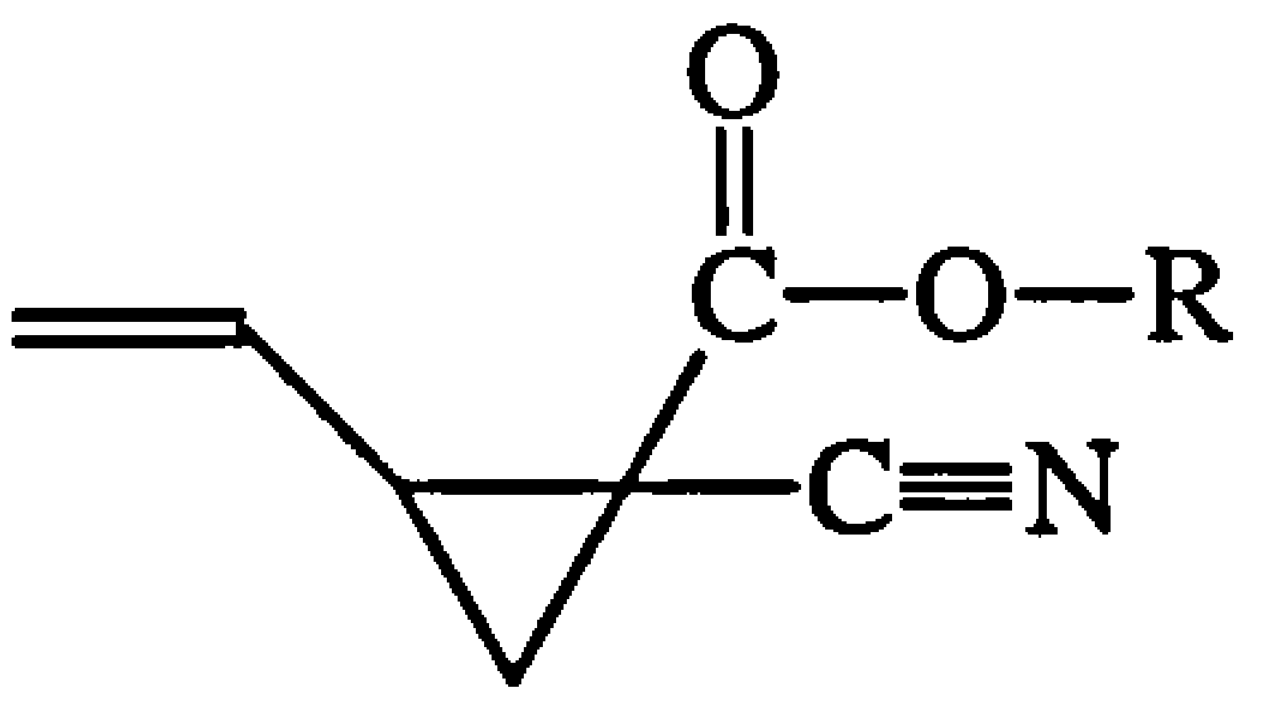
Free-radical polymerisation of vinylcyclopropane monomers containing a cyano and an ester group

5. Free-radical polymerisation of vinylcyclopropane monomers containing a cyano and an ester group

5.1 Introduction

The homopolymerisation of several 1-cyano-1-alkoxycarbonyl-2-vinylcyclopropanes by solution free-radical polymerisation is described in this chapter. The aim of this work was to produce an elastomeric polar material. In chapter 3, it was reported that the polymer formed by the free-radical polymerisation of 1,1-dicyano-2-vinylcyclopropane was an insoluble, powdery material which did not have the required elasticity or solubility. An attempt to produce a processable elastomeric material via the copolymerisation of 1,1-dicyano-2-vinylcyclopropane and butyl acrylate was reported in chapter 4. This proved unsuccessful.

The aim of the work described in this chapter was to homopolymerise several new polar vinylcyclopropane monomers in the hope that the product elastomers would retain the polar properties of the monomers. The monomers studied are shown below.



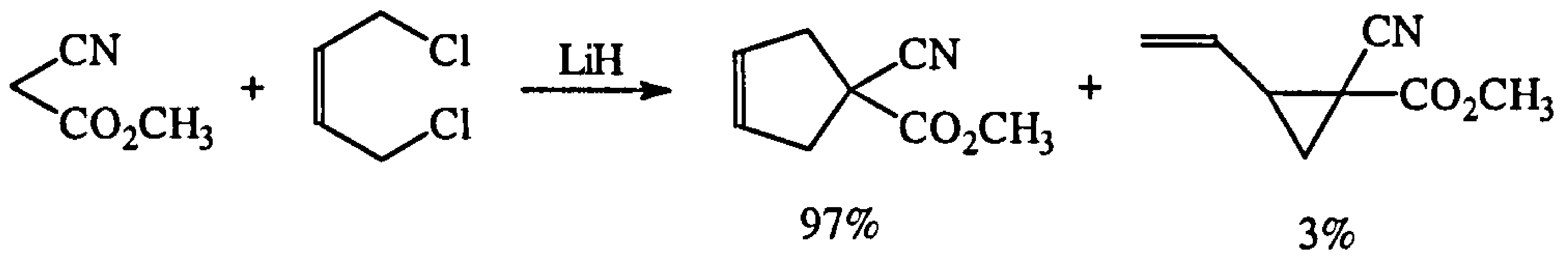
R = $C(CH_3)_3$, C_4H_9 and C_6H_{13}

It was hoped that one cyano group would be sufficient to impart the desired polarity and that the alkyl chain of the ester would cause sufficient disorder to impart solubility and would act as an internal plasticiser, lowering the Tg.

5.2 Synthesis of 1-cyano-1-alkoxycarbonyl-2-vinylcyclopropanes

The syntheses of the *tert*-butyl, n-butyl and hexyl esters have not been described previously in the literature. However, the syntheses of the methyl and ethyl esters have been reported.

The methyl ester was prepared in 1984 by Dȩpres and Greene in 3% yield as an undesired side-product in the reaction of methyl cyanoacetate with *cis*-1,4-dichlorobutene.[1]



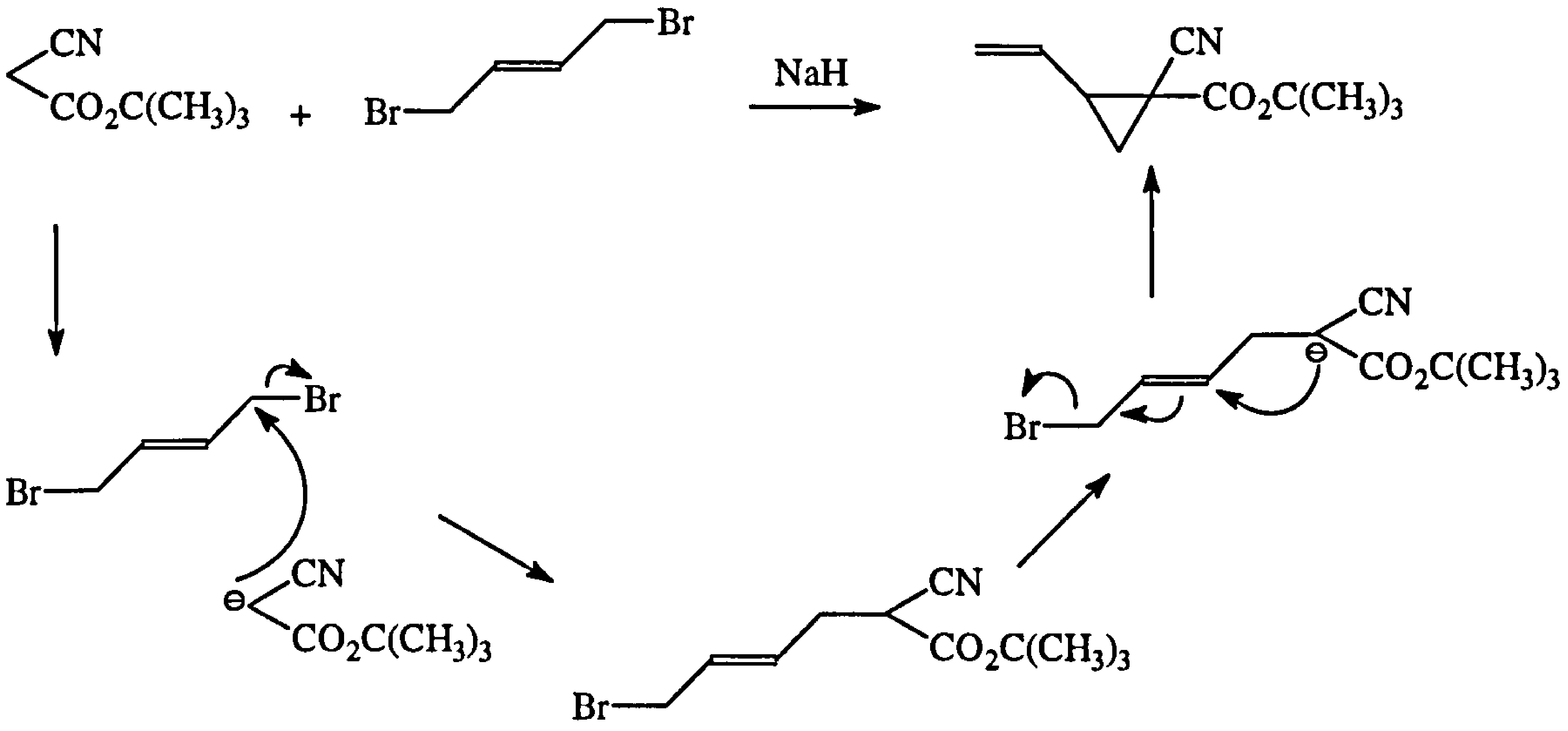
It is likely that this vinylcyclopropane derivative was produced from *trans*-1,4-dichlorobutene impurities in the *cis*-isomer.

The ethyl ester has been produced by two different groups. In 1953 Kierstead *et al.* reacted *trans*-1,4-dibromobutene with ethyl sodiocyanoacetate to produce 1-cyano-1-ethoxycarbonyl-2-vinylcyclopropane in yields up to 40%.[2] Later, in 1991, Saicic *et al.* produced the same compound by reacting *trans*-1,4-dibromobutene with ethyl cyanoacetate in the presence of sodium hydride forming 1-cyano-1-ethoxycarbonyl-2-vinylcyclopropane in yields up to 68%.[3]

It was decided to apply the method described by Saicic to the present work.

5.2.1 Synthesis of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane

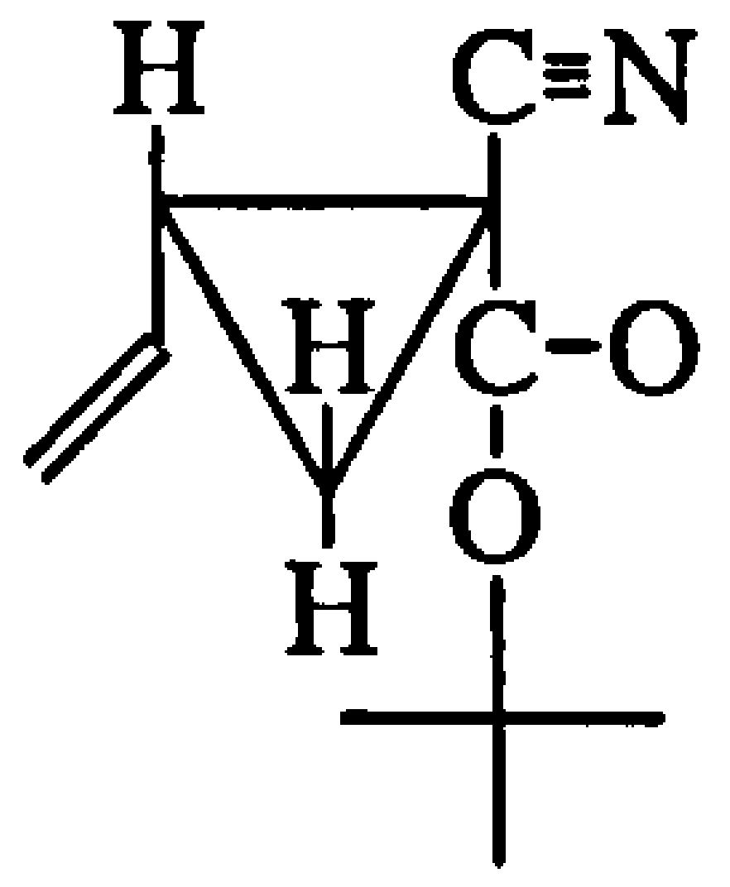
The proposed reaction scheme and mechanism for the production of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane is shown below and is analogous to the process described in chapter 3 for the preparation of 1,1-dicyano-2-vinylcyclopropane.

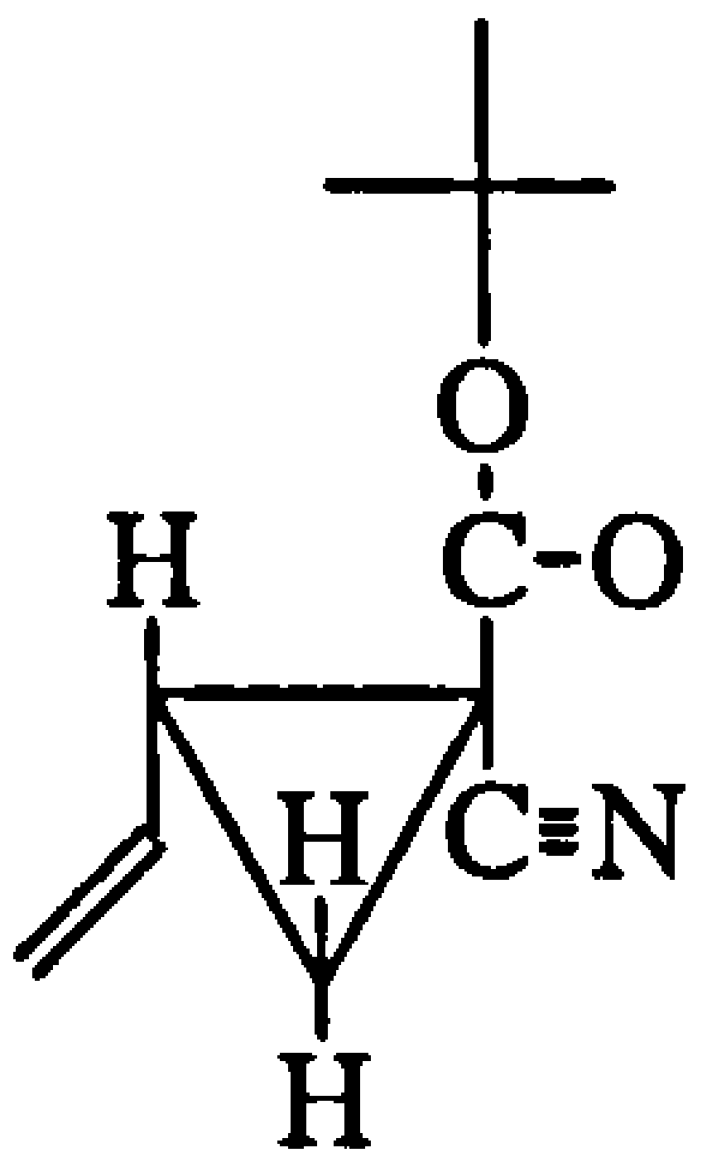


This reaction was carried out in dry THF and the desired monomer, a clear colourless oil (b.p. = 61°C/0.6mmHg), was produced in 62% yield. The monomer was characterised using ^{1}H NMR, ^{13}C NMR, infra-red spectroscopy, elemental analysis and mass spectrometry.

5.2.1.1 NMR isomer determination

This monomer can exist in the two isomeric forms shown below.





In the ^{13}C NMR spectrum, two peaks were observed for each carbon environment and in the ^{1}H NMR two peaks were observed for each hydrogen. This doubling of the number of signals corresponds to the sets of nuclear environments in the two isomers, A and B.

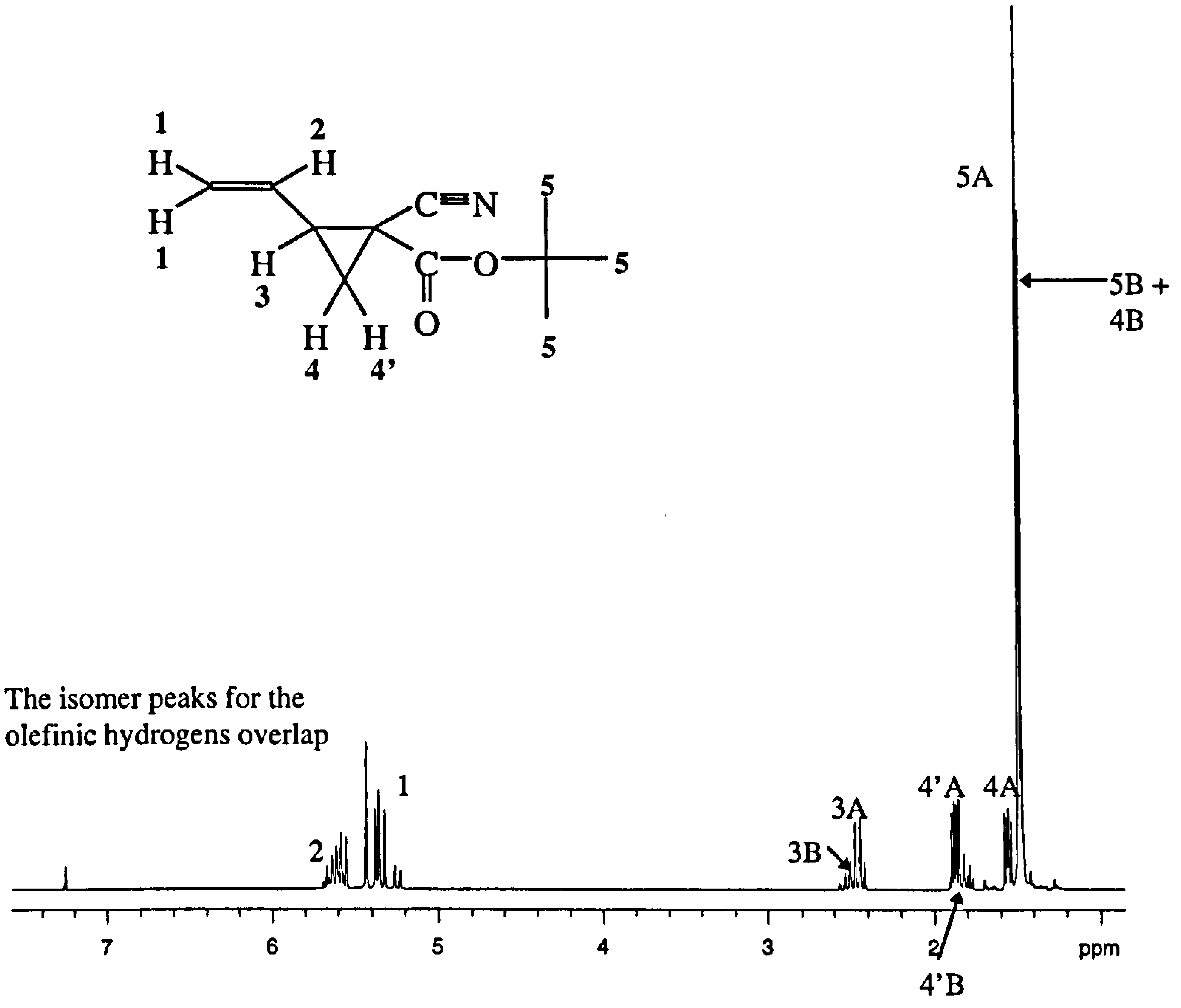
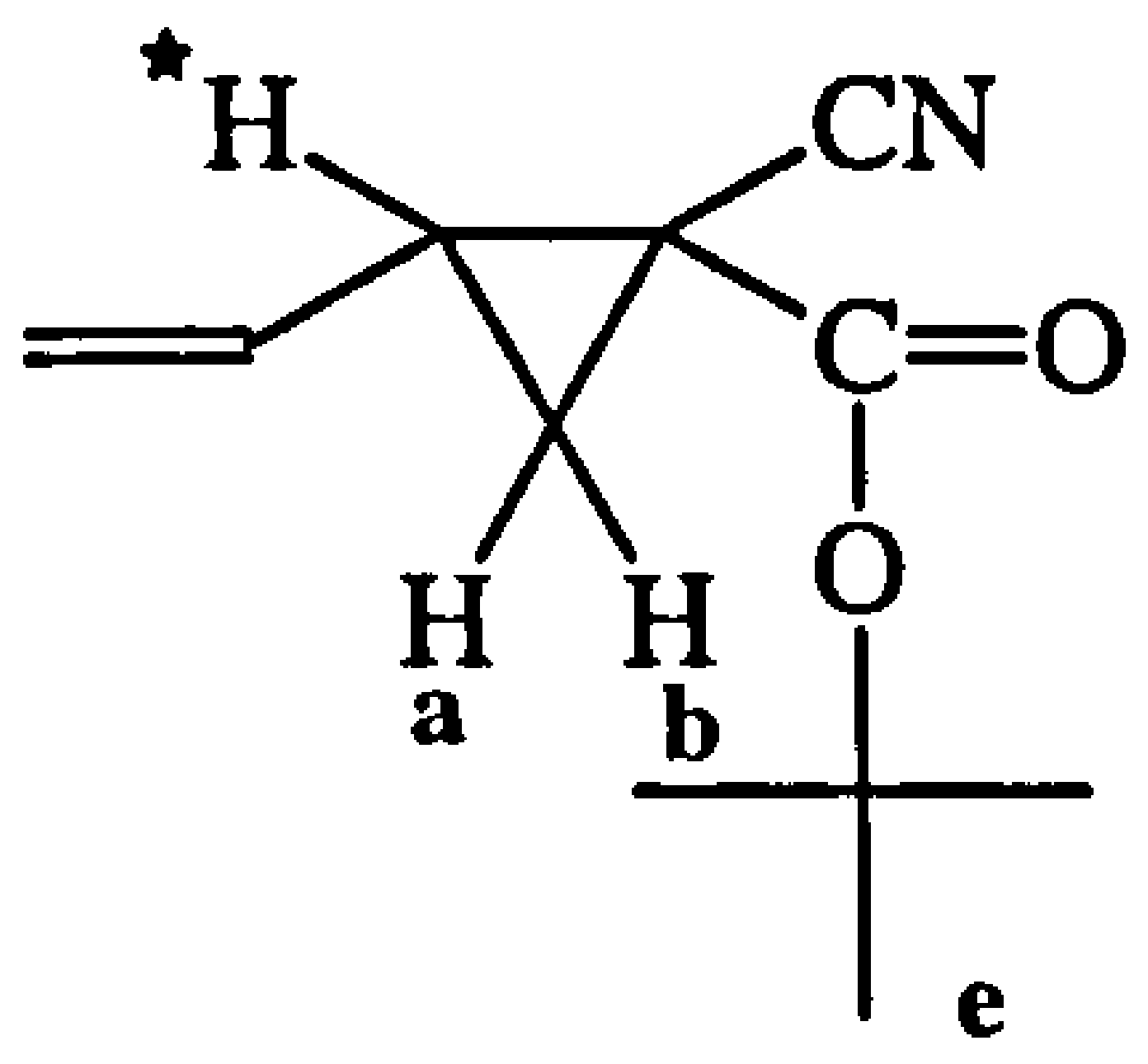


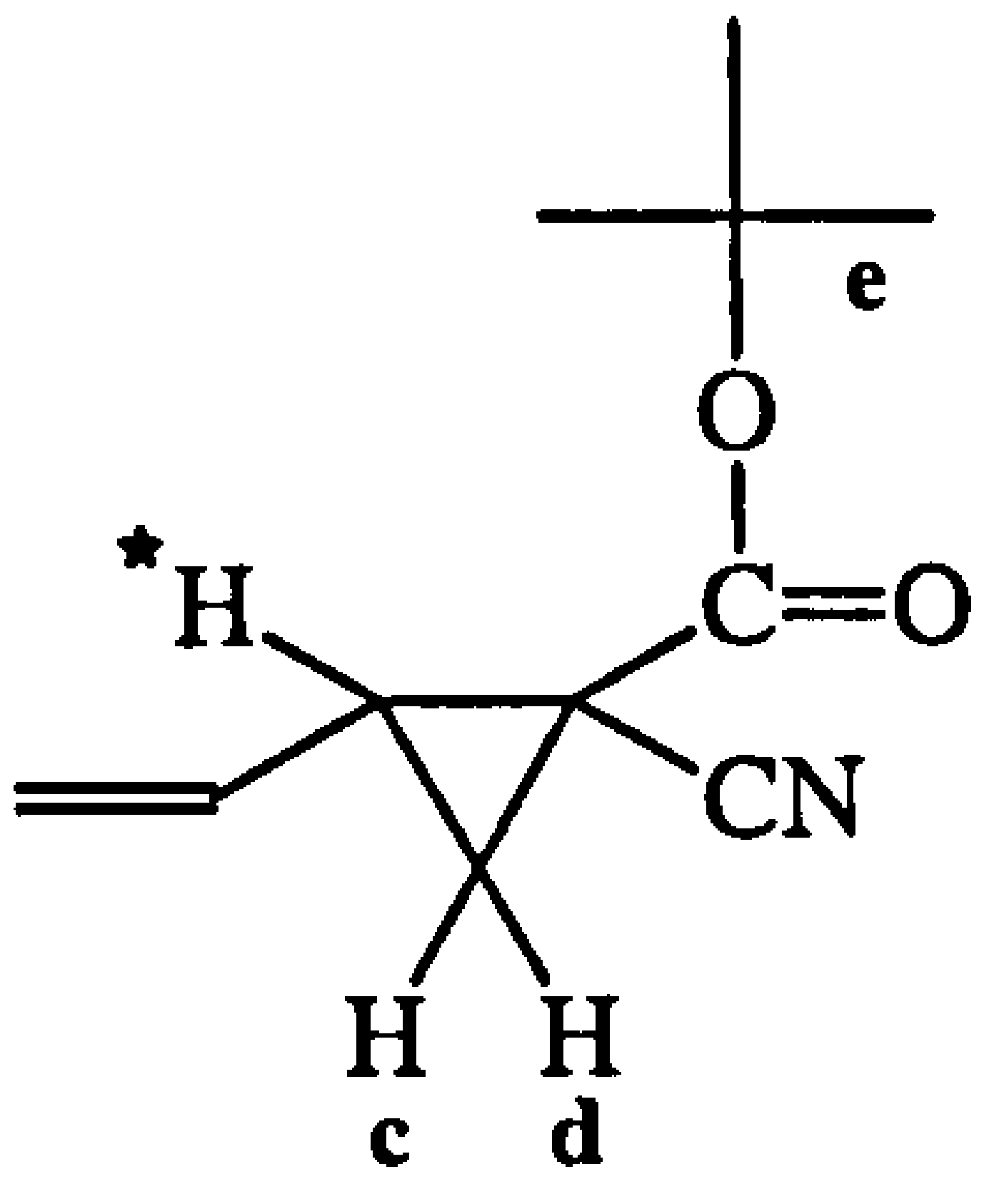
Figure 5-1 ^{1}H NMR spectrum of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane

The intensity of the two signals corresponding to the two isomeric forms are not equal. An attempt was made to determine which isomer was predominant using an NMR technique called 'double pulsed field gradient spin echo nuclear Overhauser enhancement'- DPFGSE-NOE.[4] In this technique, the two isomeric peaks for one hydrogen were irradiated alternately and inverted by applying a 180° pulse of a narrow band width. This irradiation caused two effects. Firstly, coupling was observed as an anti-phase doublet and secondly an enhancement was observed for those peaks undergoing the NOE.

The nuclear Overhauser effect causes an increase in the intensities observed for signals of nuclei close to the irradiated nuclei in space. This effect can give information on the spatial relationship of atoms which are separated by several bonds.

H_a is in the same plane as H^*





H_c is in the same plane as H^*

In the standard ^1H NMR, the hydrogen marked with a star has two peaks, one for the major isomer A at 2.45ppm and one for the minor isomer B at 2.55ppm. Both peaks were irradiated in turn and the spectra obtained are shown below. It should be noted that this procedure gives spectra in which there are sometimes small chemical shifts between the signals for a particular nucleus in the original and derived spectra according to whether coupling or enhancement is occurring.

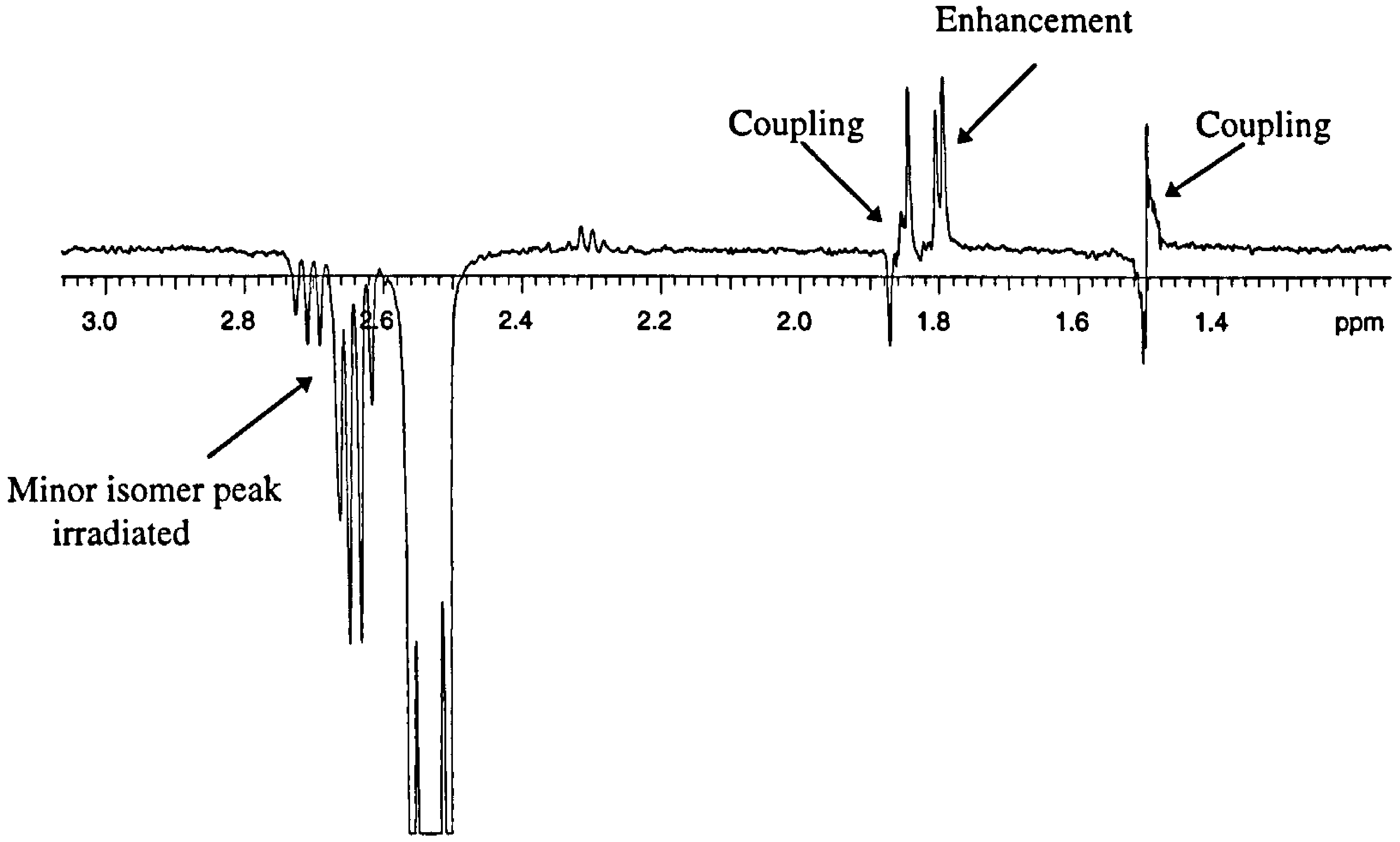


Figure 5-2 Spectrum obtained on irradiation of minor peak at 2.55 ppm in the spectrum of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane

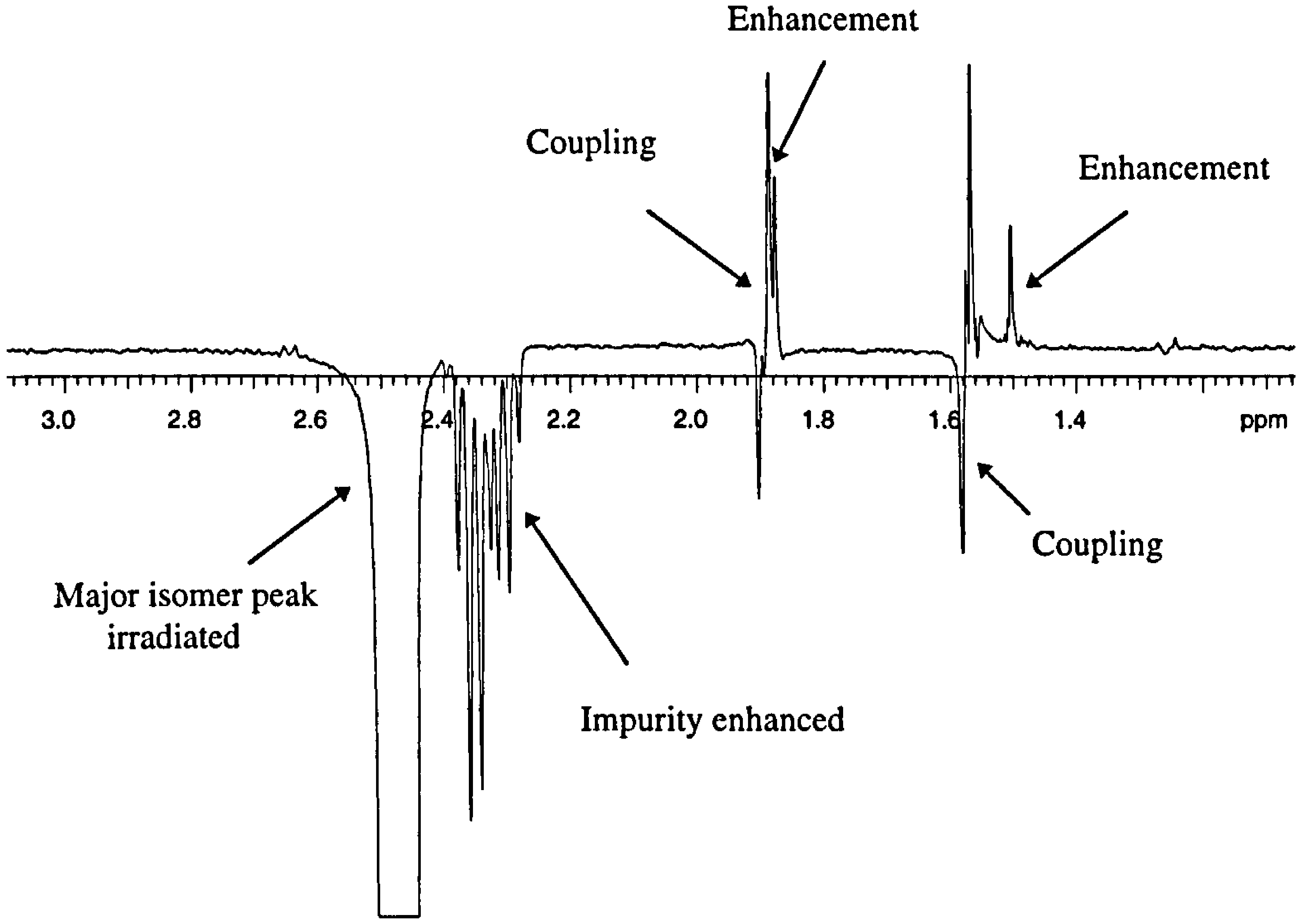


Figure 5-3 Spectrum obtained on irradiation of minor peak at 2.45 ppm in the spectrum of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane

The minor peak for isomer B at 1.50 ppm is hidden beneath the tBu peak in the standard ^{1}H NMR.

When the major isomer is irradiated, the derived spectrum shows a complex multiplet at the base of the major peak. This is an impurity that is present in such small amounts that it is not visible in the standard ^{1}H NMR. On irradiation of the major peak, the impurity peaks fall within the irradiated field width and therefore appear in the spectrum greatly enhanced.

The effects observed are tabulated below;

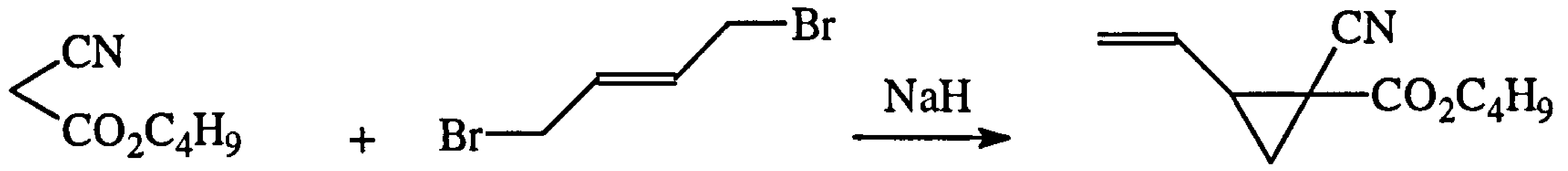
ppm	1.88	1.80	1.56	1.50	1.50
Major/Minor	Major peak	Minor peak	Major peak	Minor peak	tBu peak
Minor Irradiated	-	Coupling and Enhancement	-	Coupling	-
Major Irradiated	Coupling and Enhancement	-	Coupling		Enhancement

Table 5-1 Effects observed on the irradiation of the major and minor isomer peaks of one hydrogen in 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane

This data shows that the major isomer is that in which an NOE effect occurs between the irradiated hydrogen and the *tert*-butyl group. It can therefore be concluded that in the major isomer, which constitutes 80% of the product, the *tert*-butyl group is *trans* and the cyano group is *cis* to the vinyl group. This analysis can also be used to assign the peaks for the ring hydrogens since coupling and enhancement occur for the hydrogen on the same face of the ring as the irradiated hydrogen whereas only coupling is observed for the hydrogen on the other face of the ring. The following assignments can then be made; 1.88 ppm (**c**), 1.80 ppm (**a**), 1.56 ppm (**d**) and 1.50 ppm(**b**).

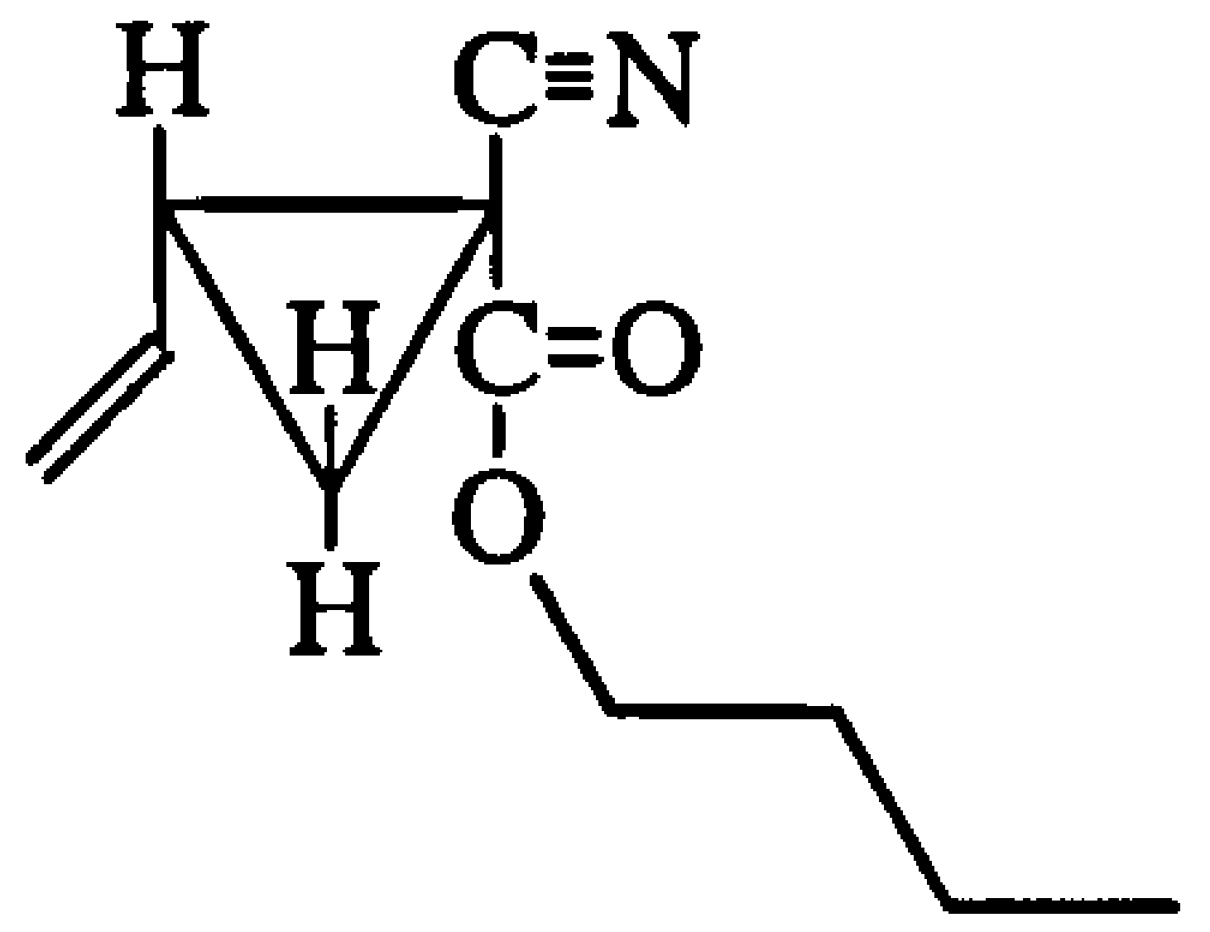
5.2.2 Synthesis of 1-cyano-1-butoxycarbonyl-2-vinylcyclopropane

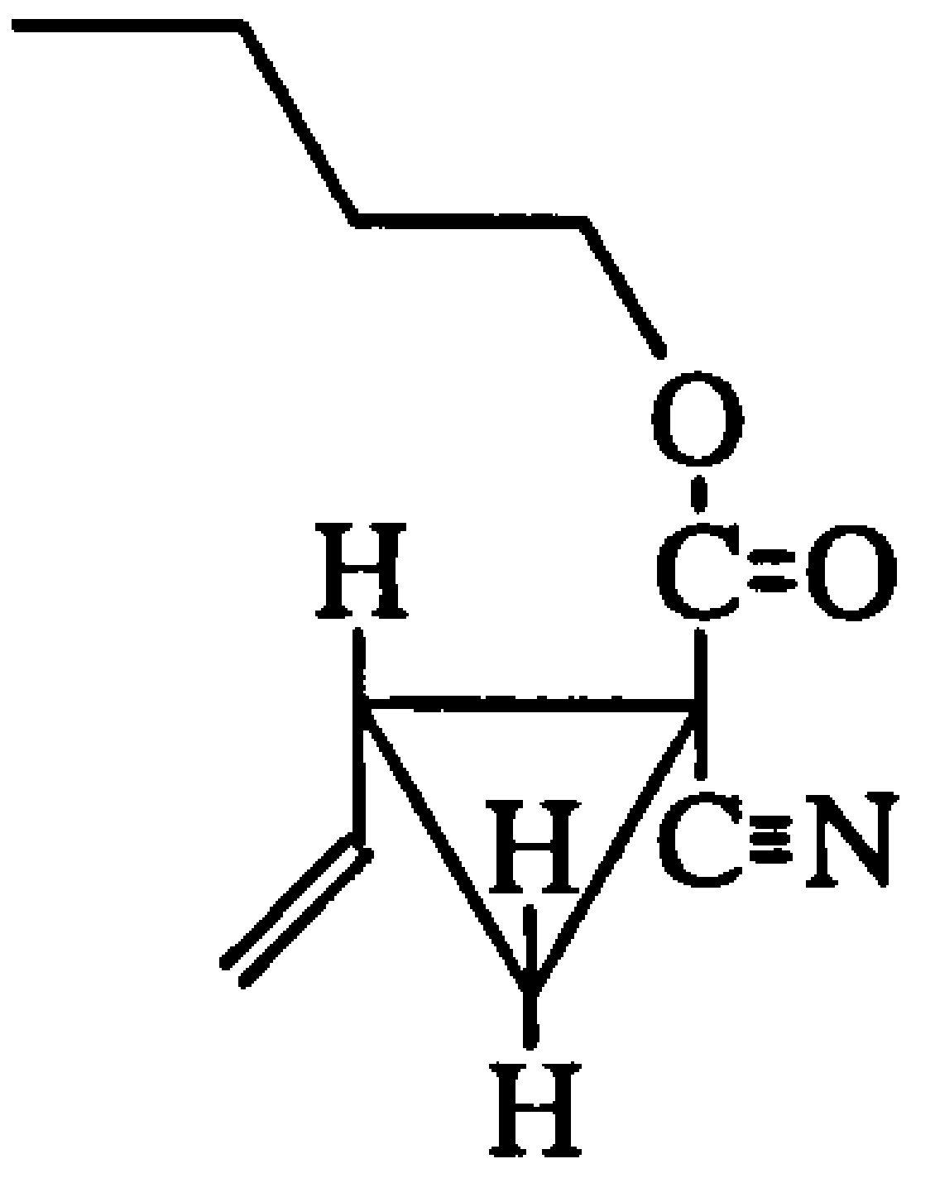
The proposed reaction scheme is shown below for the production 1-cyano-1-butoxycarbonyl-2-vinylcyclopropane.



This reaction was carried out in dry THF and the desired monomer, a clear colourless oil (b.p. = 78°C/0.2mmHg), was produced in 60% yield. The monomer was fully characterised using ^1H and ^{13}C NMR, IR spectroscopy, mass spectrometry and elemental analysis.

Again, two isomers in unequal amounts were detected.

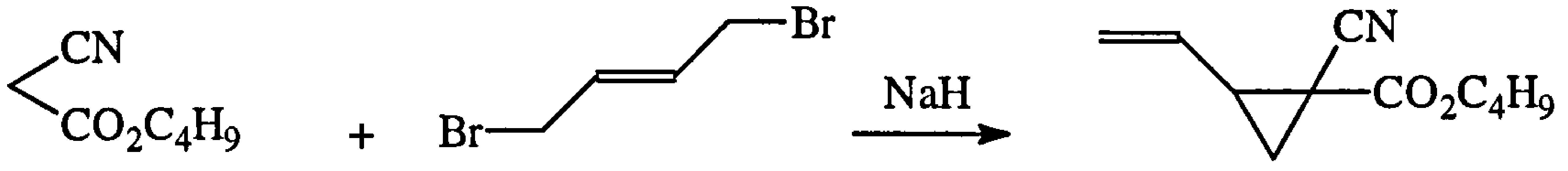




By comparing the spectra obtained with that for the *tert*-butyl ester, it was concluded that the major isomer was that in which the nitrile group is *cis* to the vinyl group.

5.2.3 Synthesis of 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane

Again, Saicic's method using sodium hydride in THF was attempted.



Unlike, the butyl cyanoacetates which are commercially available, it was necessary to synthesise hexyl cyanoacetate. One method for the production of hexyl cyanoacetate has been reported previously. In 1967, Polyakova prepared a range of cyanoacetic esters by transesterification of ethyl cyanoacetate with primary alcohols.[5] The hexyl ester was prepared in 63% yield. However, in 1985, Mori *et al.* produced octyl cyanoacetate in 86% yield by the esterification of cyanoacetic acid with 1-octanol by azeotropic removal of water using Dean-Stark apparatus.[6]

The higher yielding procedure described by Mori was used to prepare hexyl cyanoacetate. The work up of the reaction proposed by Mori involved washing the product with water, saturated sodium hydrogen carbonate and sodium chloride. It was found that on the initial washing with water, the molecule acted as a surfactant causing an emulsion to be formed. This was not surprising as the molecule consists of a polar end (the cyano and ester groups) and a long chain hydrophobic alkyl group. This emulsion proved to be extremely stable and it was therefore difficult to obtain the product. It was decided to omit this washing stage. Instead, the benzene was removed from the reaction mixture by rotary evaporation and the product, a clear colourless oil, was obtained by distillation in 94% yield (b.p. = 82°C/0.6mmHg).

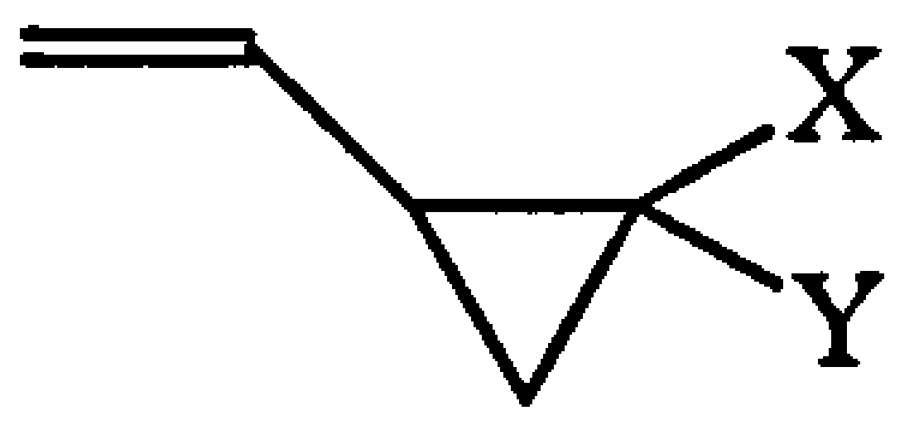
Hexyl cyanoacetate was reacted with *trans*-dibromobutene in the presence of sodium hydride in dry THF. The product, a clear colourless oil (b.p. 78°C/0.2 mmHg) was obtained by distillation in 77% yield.

Again, NMR analysis revealed the presence of two isomers, the major isomer being that in which the nitrile group is *cis* to the vinyl group.

5.3 Polymerisation of 1-cyano-1-alkoxycarbonyl-2-vinylcyclopropane monomers

5.3.1 History

There have been several examples of the polymerisation of vinylcyclopropane rings bearing ester groups. The monomers studied are shown below.



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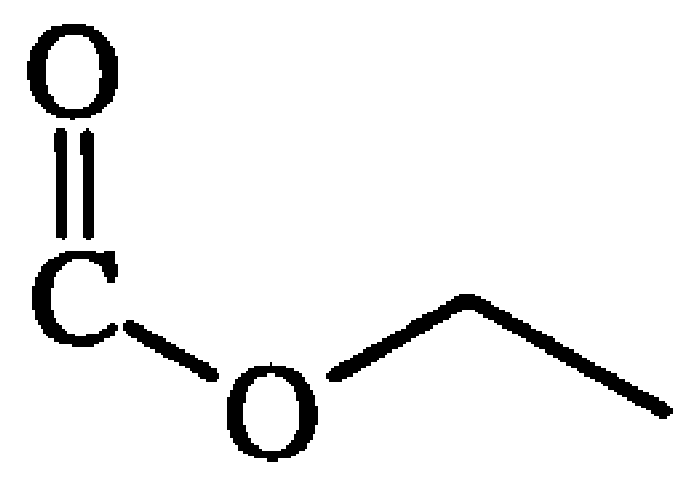
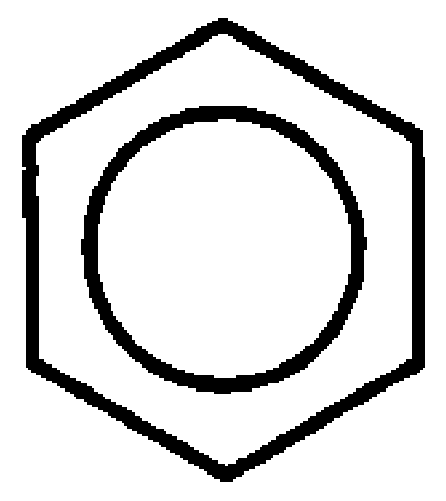
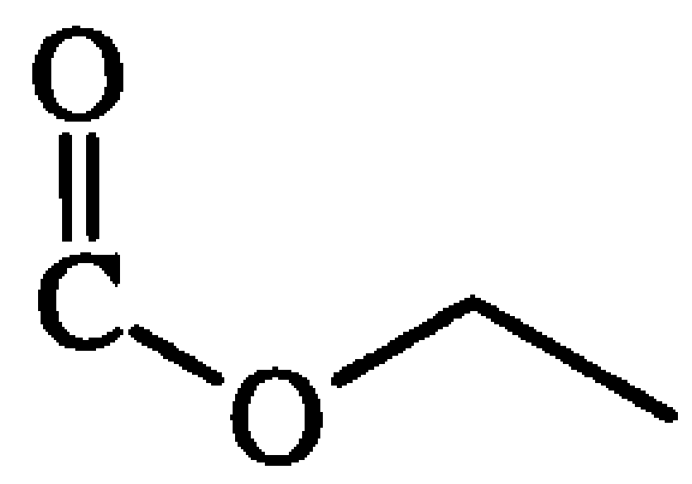
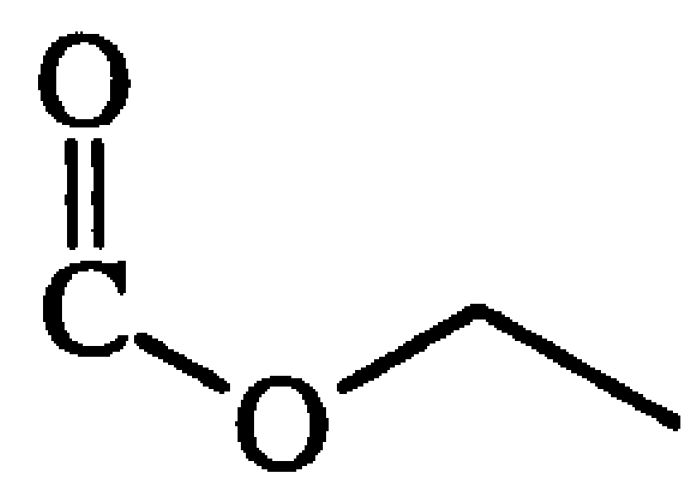
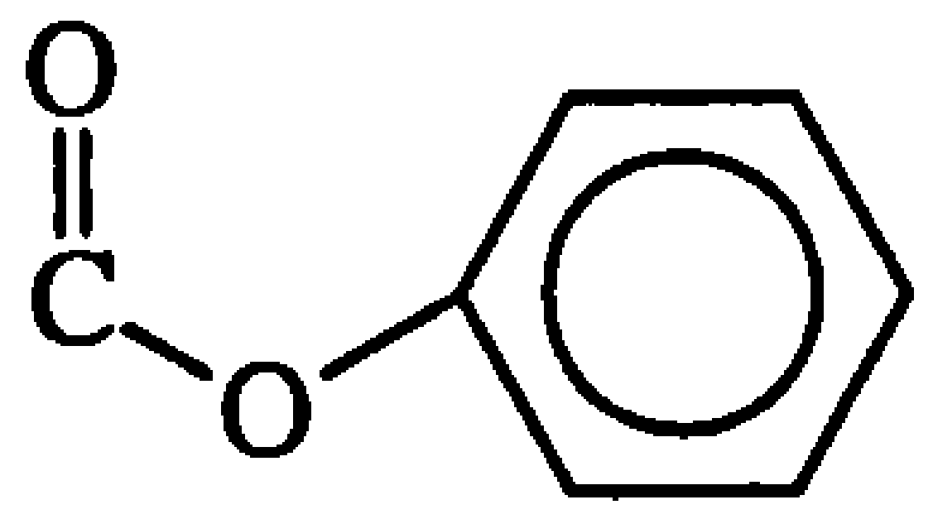
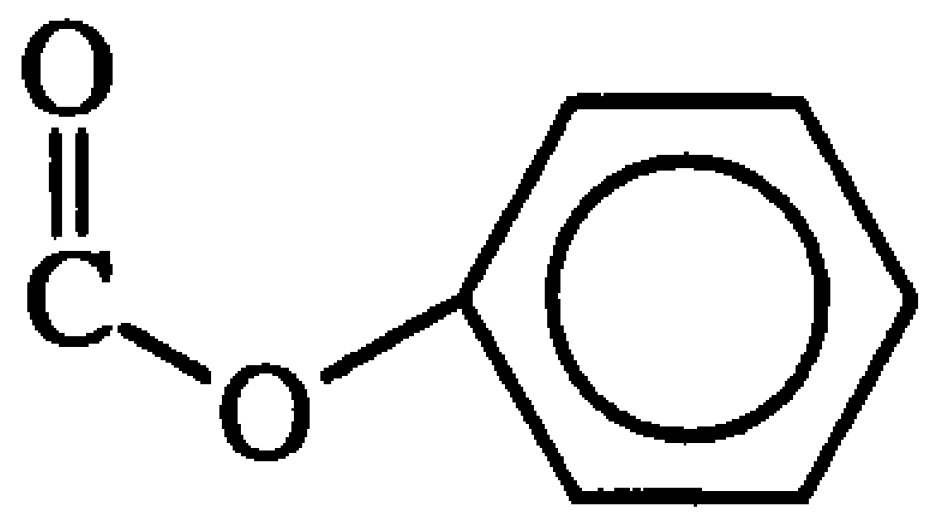
H		7,8,9
		9
CH_3		9
		10,12

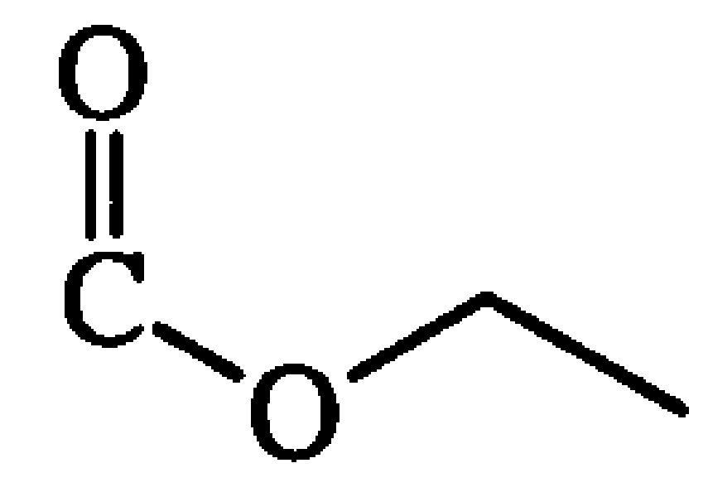
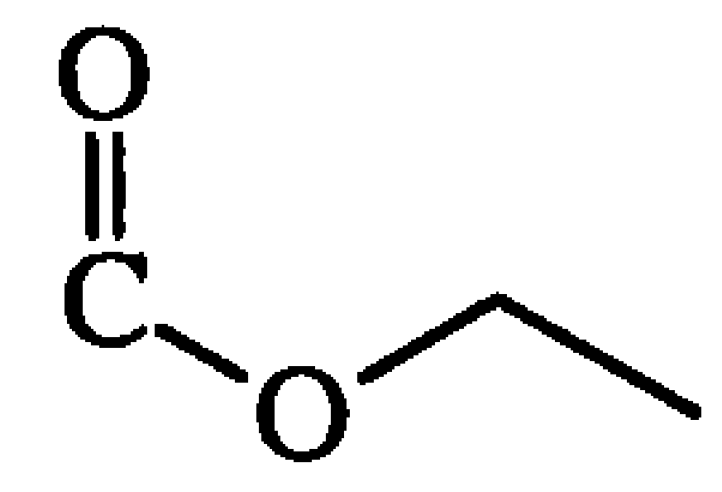
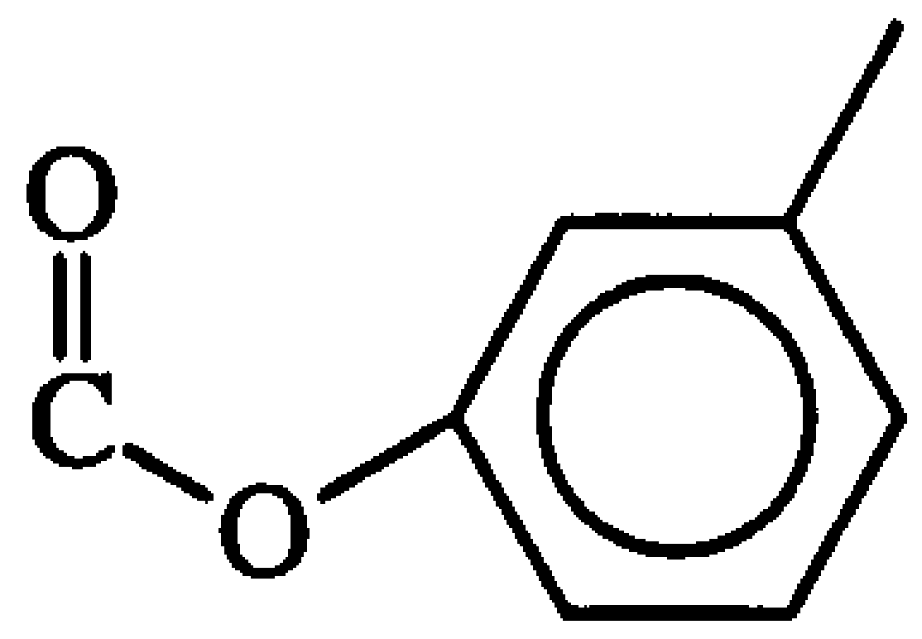
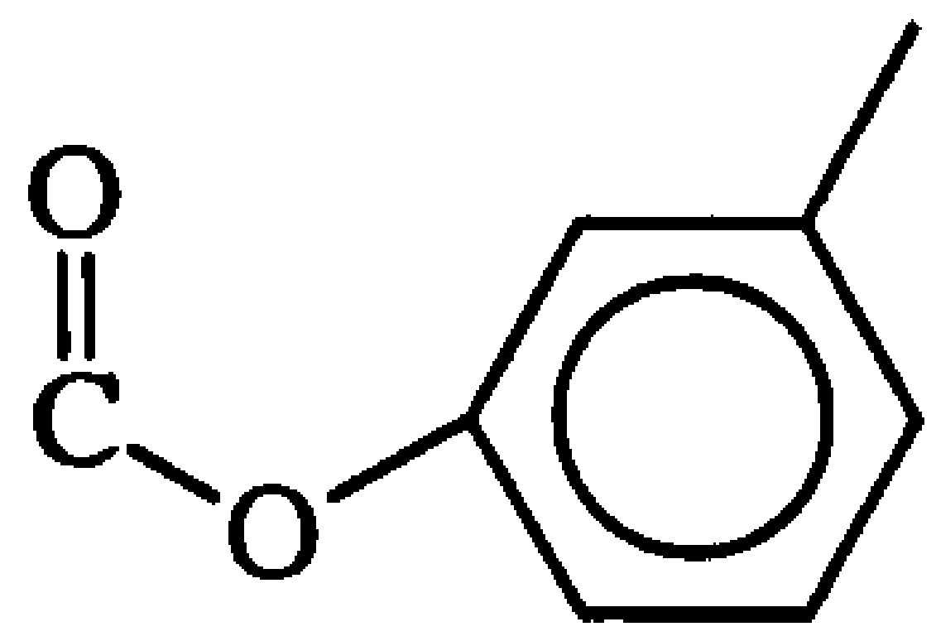
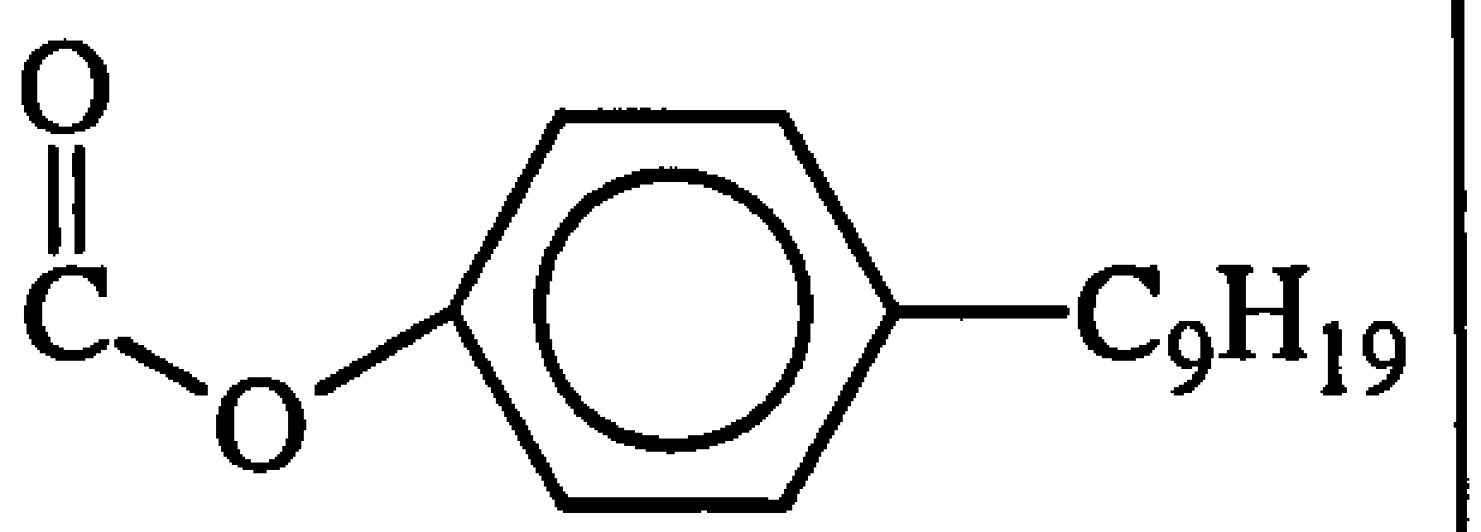
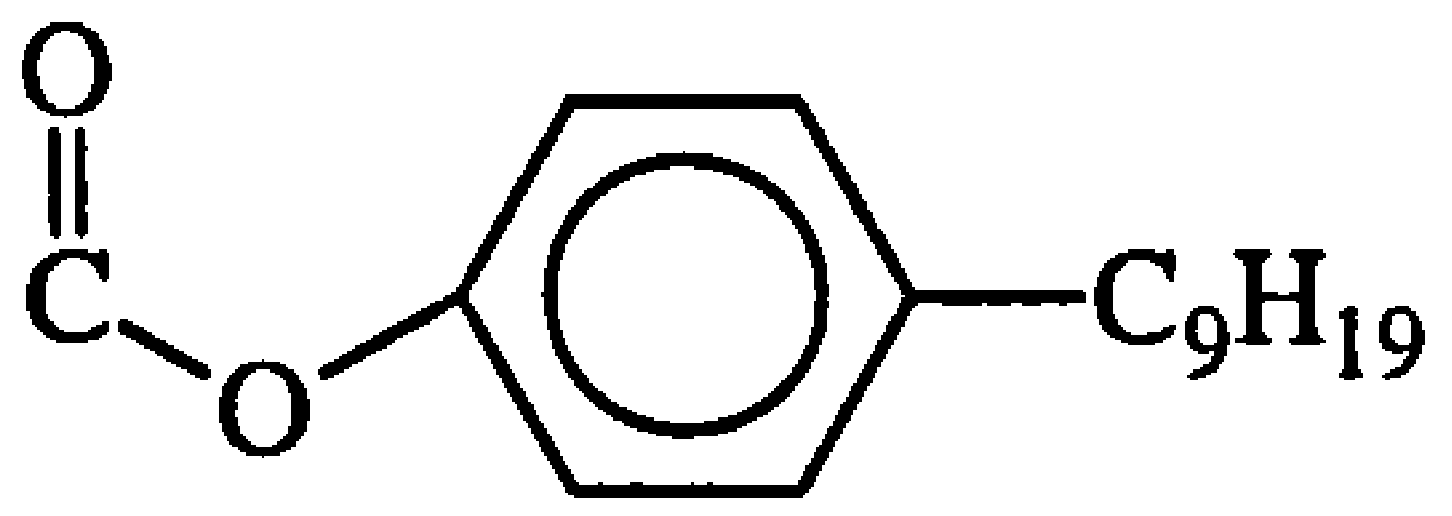
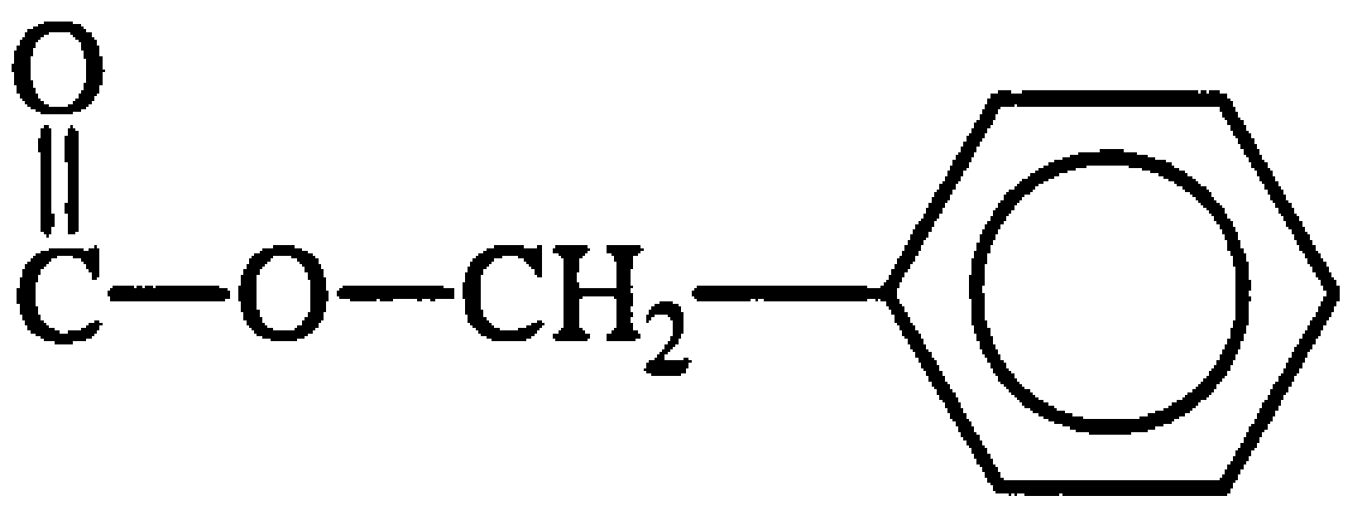
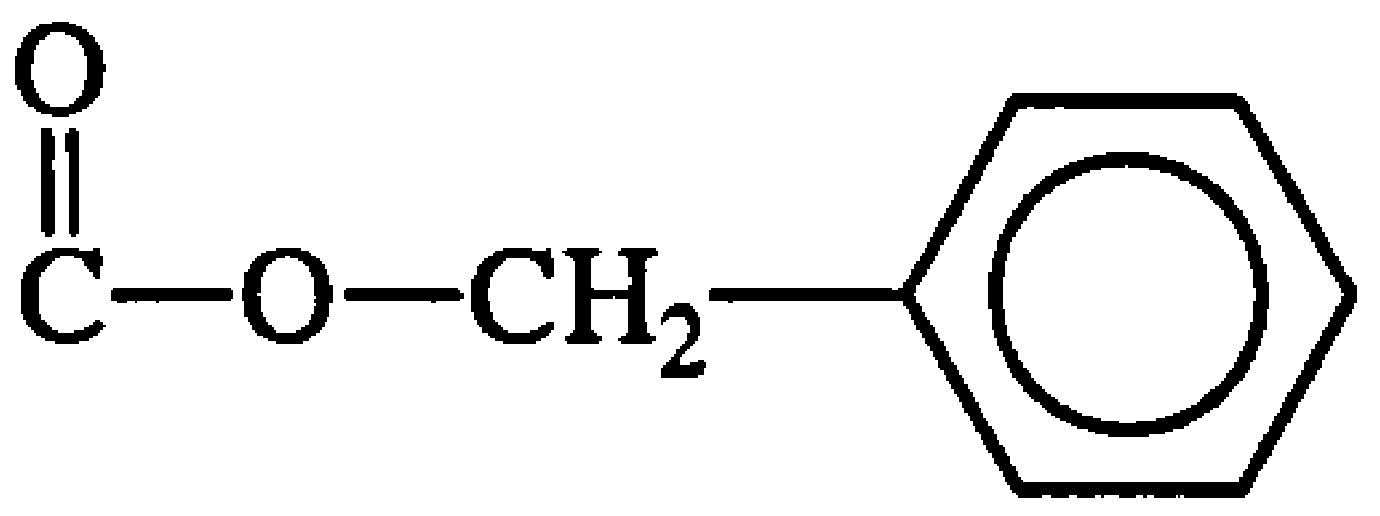
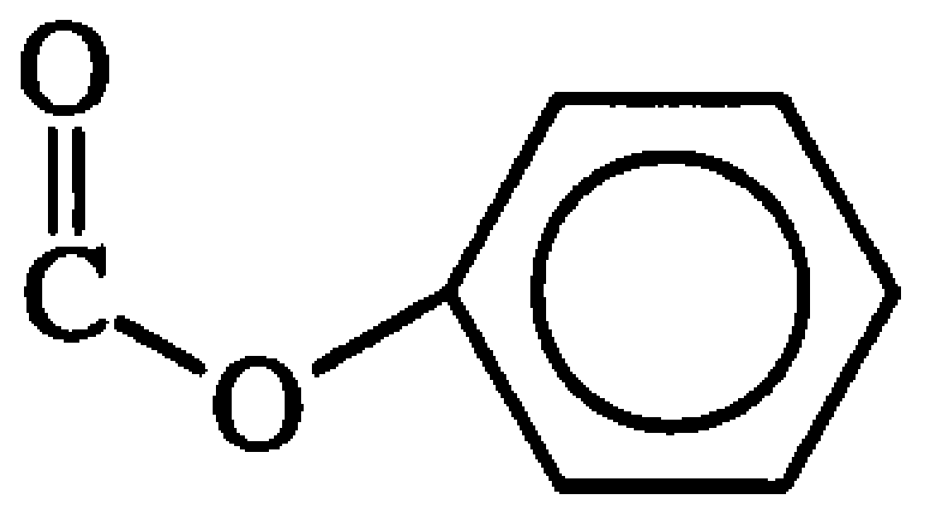
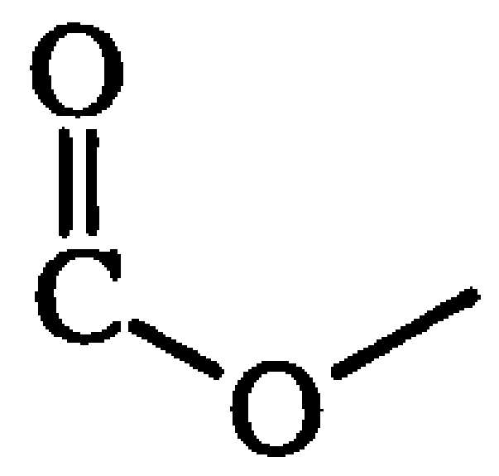
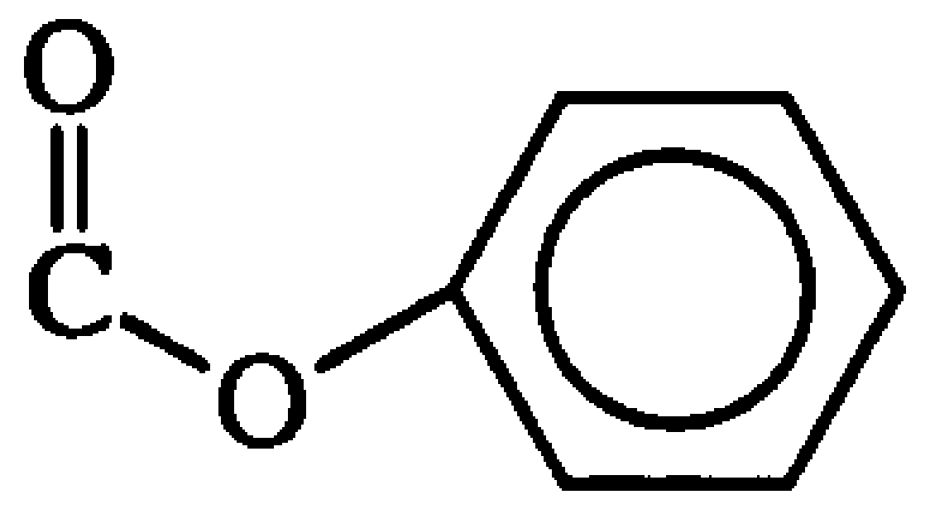
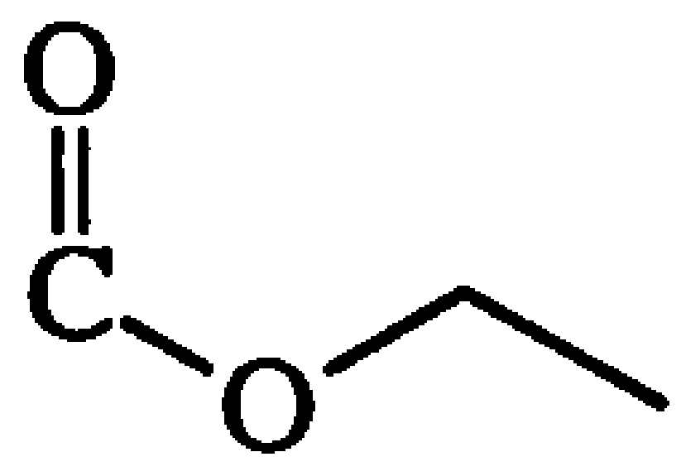
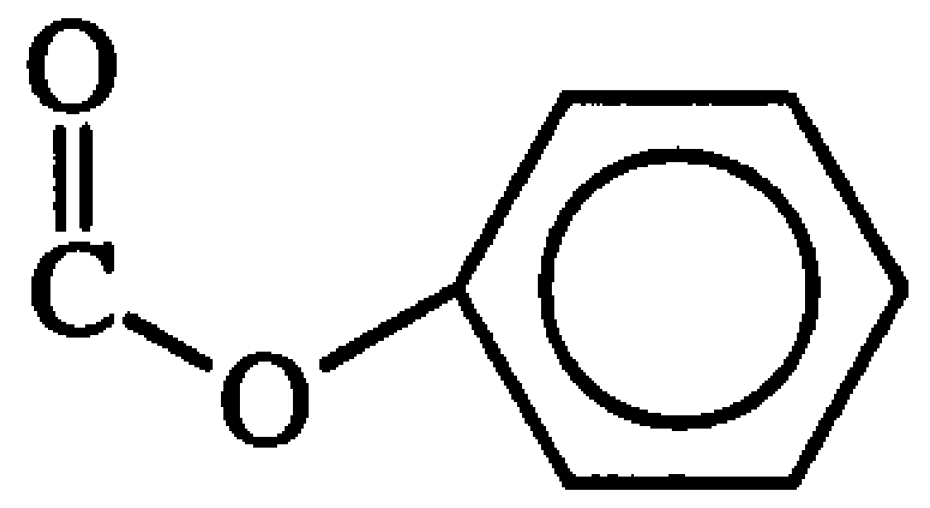
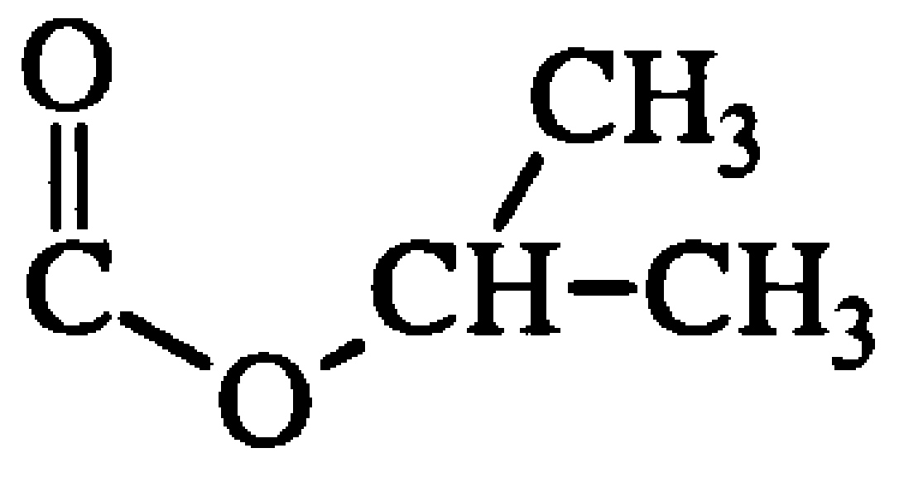
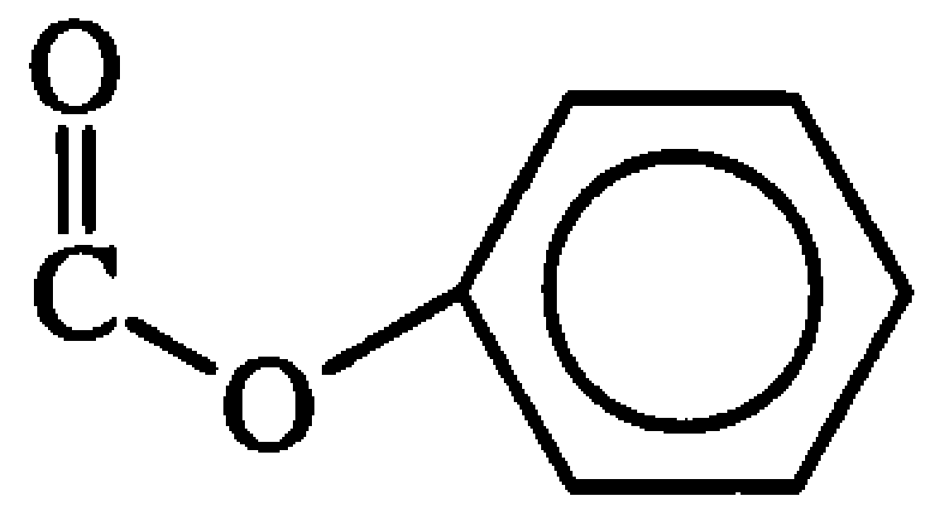
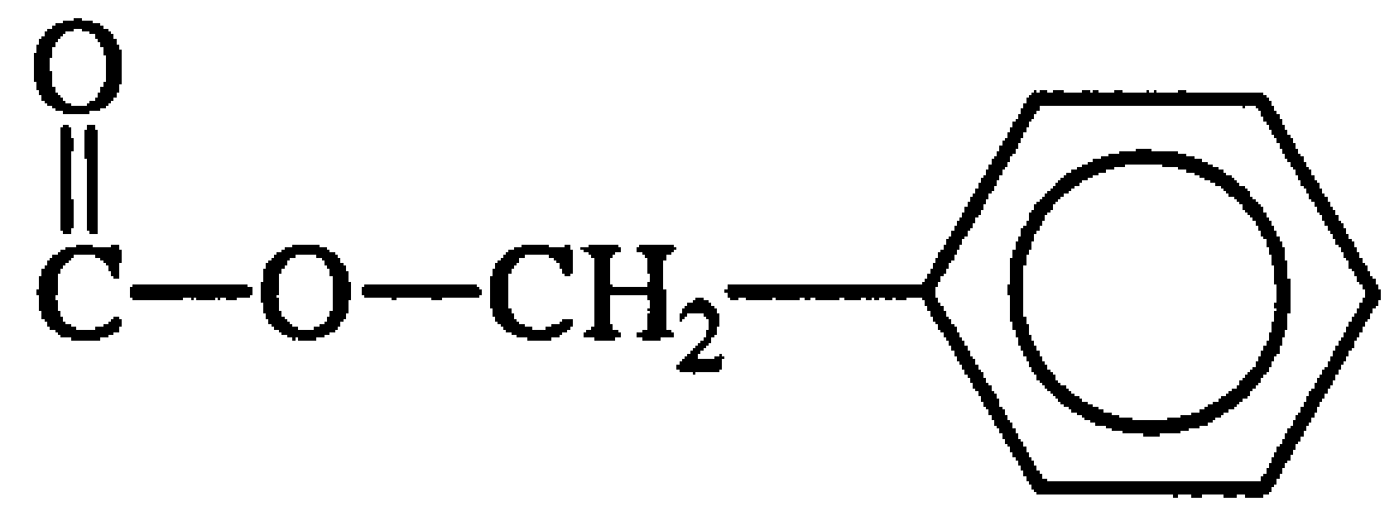
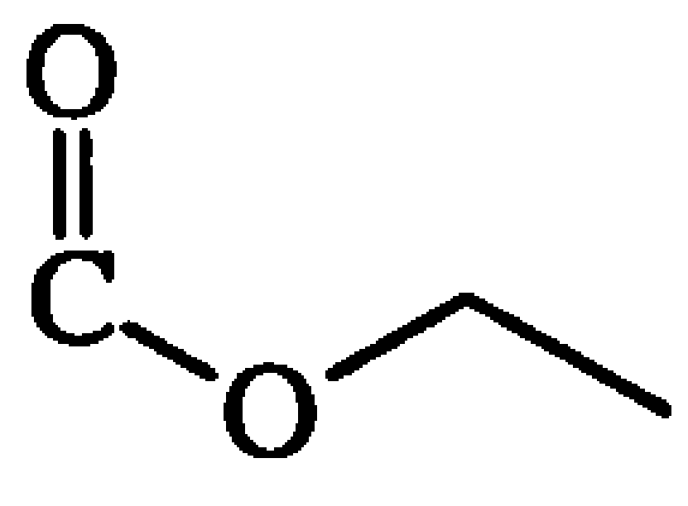
		11,12
		12
		12
		12
		13
		13
		13
		13
CN		14,15

Table 5-2 Summary of the ester-containing vinylcyclopropane monomers studied by other research groups

The esters were found to undergo predominantly radical 1,5-type ring-opening polymerisation. These monomers have been studied mainly by workers interested in materials for dental fillings because they have been shown to polymerise with low volume shrinkage. The workers have concentrated their investigations on the properties of the polymers produced rather than on the fine structure of the polymer chains. The polymer containing one cyano group and one ethyl ester group was reported to be a soluble polymer with a Tg of 29°C produced by solution polymerisation in yields up to 60%.[14,15]

5.3.2 Polymerisation of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane

The monomer was polymerised in solution (3mmol/5mL) with AIBN as initiator and benzene as solvent using the following reaction conditions. See experimental section for full details.

	Temperature / °C	Time / hours	Initiator (% mol)	Yield %	Appearance of product
A	60	20	0.1	60	white solid
B	room temp	20	0.4	no polymer produced	
C	60	20	0.4	71	white solid
D	120	20	0.4	60	yellow solid
E	60	20	1.5	64	white solid
F	60	20	3.0	60	white solid
G	60	5	0.4	26	white solid
H	60	48	0.4	72	white solid
I*	60	20	0.4	41	clear, colourless gel

* - neat monomer

Table 5-3 Summary of the conditions and results of the homopolymerisation of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane

The reaction products were viscous solutions or gels. The product polymers were precipitated by pouring the reaction mixture into excess methanol or, in the cases of the gels, by dissolving the gel in chloroform and then pouring the solution into methanol. The exception was sample I which was not soluble and was therefore dried and analysed as an unprecipitated solid.

Conditions B produced no polymer because the reaction temperature was not sufficiently high to effect the fission of the initiator into radical species. For the other conditions, it can be seen that the yields produced are very similar, the only exception being sample G where the decreased reaction time lead to a decreased yield respectively.

To determine whether there was any difference between the reactivities of the two isomers of the monomer, the methanol used in the precipitation of the polymers was removed in vacuuo and the remaining residue analysed by ^{1}H NMR. It was found that the residue was residual monomer containing both isomers in the same proportions as in the feed. This indicated that there is no marked difference in polymerisability of the two isomers.

5.3.2.1 Analysis

The ^{1}H and ^{13}C NMR spectra of the polymer samples dissolved in chloroform were all found to be identical with the exception of sample I.

An example of a typical ^{1}H NMR spectrum gained for the other samples is shown below.

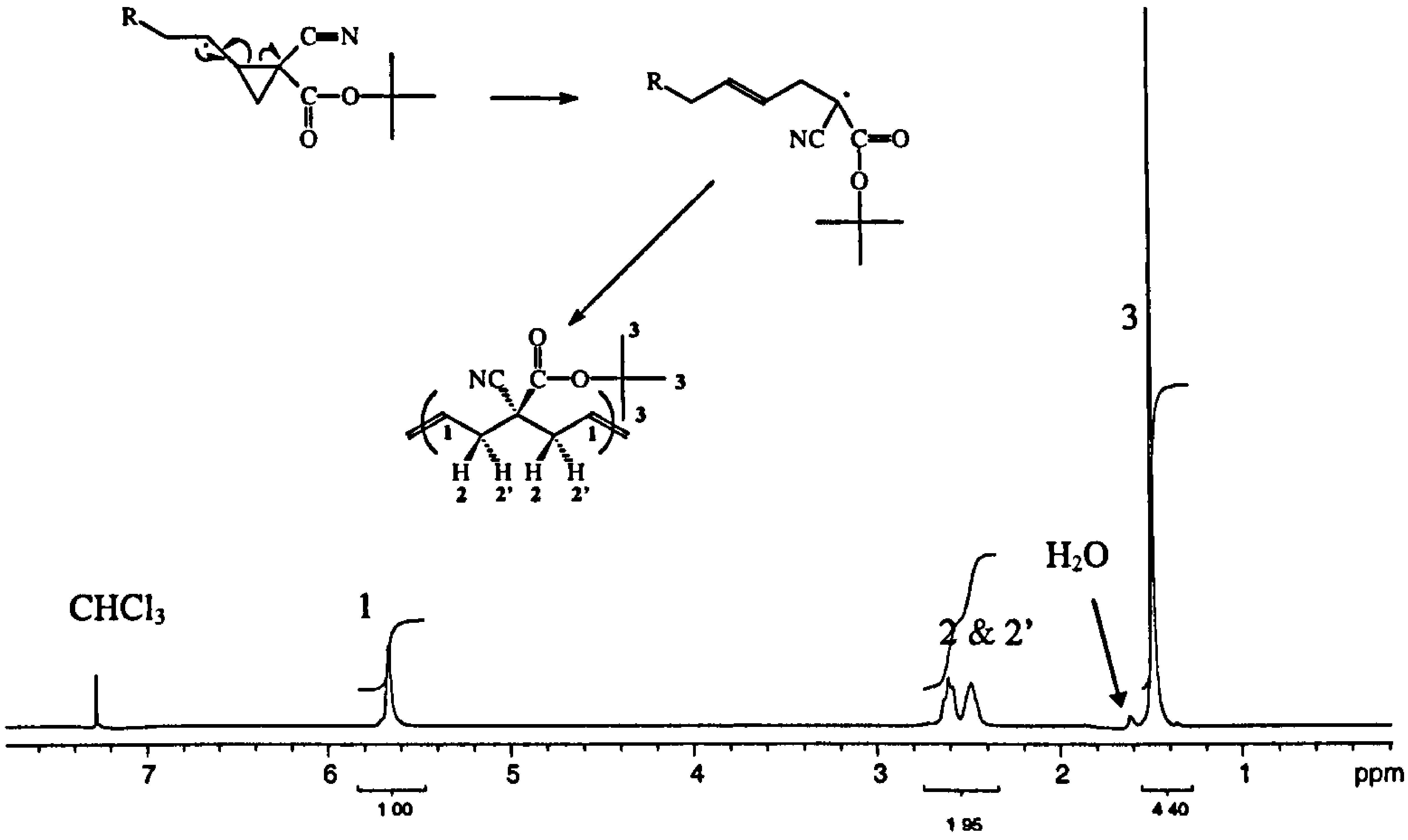


Figure 5-4 ^{1}H NMR spectrum of the homopolymer of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane

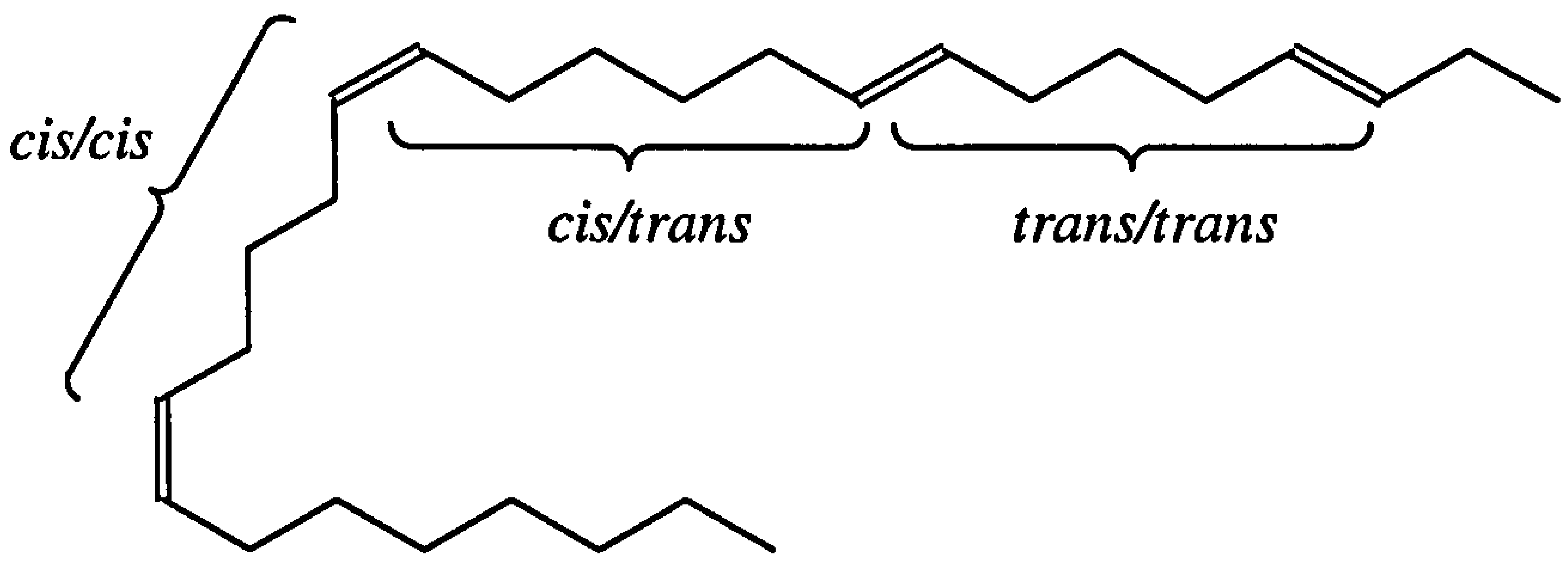
The simplicity of the spectrum suggests that the monomer has undergone exclusively 1,5-type ring-opening radical polymerisation. This is to be expected because by 1,5-ring-opening, the propagating free radical is located on the carbon with the substituents attached. These substituents stabilise the free radical making an intermediate which is considerably more stable than the 1,4-ring-opened intermediate which would have the radical site on a methylene carbon. The peak at 5.7 ppm (**1**) corresponds to the olefinic hydrogens, the broad doublet at 2.6 ppm (**2&2'**)

corresponds to the methylene hydrogens and the singlet at 1.5 ppm (3) corresponds to the *tert*-butyl hydrogens. The minor peaks marked arise from the solvent.

Sample I was analysed as a gel and therefore the ^{1}H NMR spectrum contains very broad peaks. These peaks occur at the same shifts as the peaks in the other polymer samples suggesting that it has essentially the same structure. It was not possible to dissolve and reprecipitate sample I and peaks attributed to unreacted monomer were present. It was assumed to be a crosslinked gel but direct evidence of the nature of the crosslinks was not detected.

5.3.2.1.1 *Cis/trans* isomerism

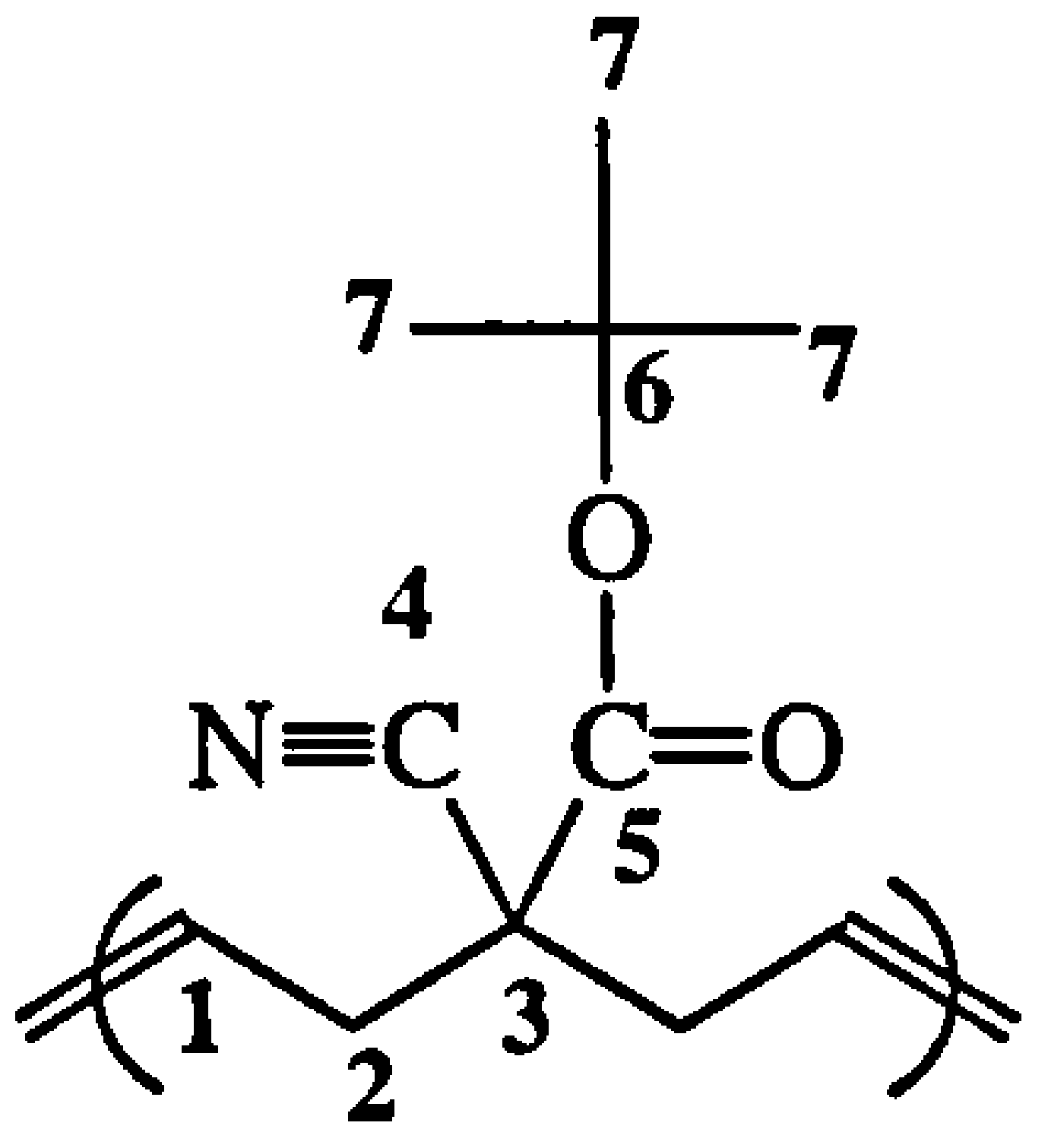
The simplicity of the spectra also indicates that there is little *cis/trans* isomerism of the double bonds. Theoretically, there are various sequences that the double bonds in the polymer could follow as shown below.



However, it seems that in this polymer a predominantly *cis/cis* or *trans/trans* chain is formed. If *cis/trans* isomerism existed, one would expect to see significant splitting in the olefinic hydrogen peak because there would be more than one environment for these hydrogens.

Infra-red spectroscopic analysis showed a band at 972cm^{-1} indicating the presence of *trans* double bonds suggesting that the double bonds in the polymer chain are predominantly *trans* in conformation. No peak was observed at 730cm^{-1} corresponding to *cis* double bonds.

The ^{13}C NMR spectra of the samples were all identical having seven peaks in the low resolution spectra corresponding to the carbon environments shown below.



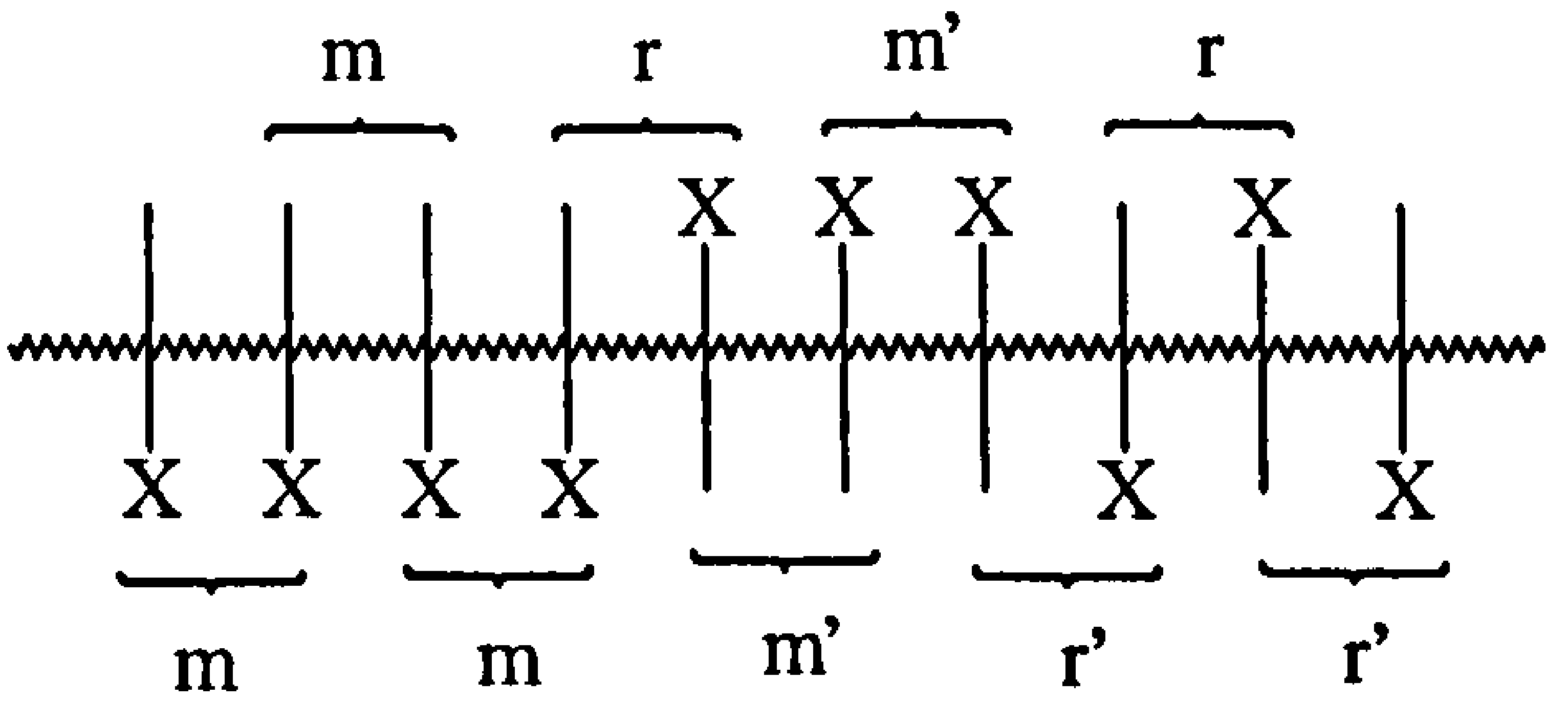
δ / ppm = 166.5 (**5**), 128.7 (**1**), 118.3 (**4**), 84.3 (**6**), 49.8 (**2**), 39.3 (**3**) and 27.8 (**7**).

No isomer peaks were observed in the carbon spectrum. The signal to noise ratio in the spectra were such that any peaks smaller than 4% of the main peak could not be distinguished from the noise. It can therefore be concluded that the polymer is greater than 96% *trans*.

Sample I again shows several extra peaks that can be attributed to residual monomer.

5.3.2.1.2 Tacticity

On close inspection of the high resolution ^{13}C NMR spectra, it became clear that the peaks corresponding to the olefinic carbons (**1**), the cyano carbons (**4**) and the carbonyl carbons (**5**) show splitting. Since we know that the polymer consists of predominantly *trans* double bonds, this splitting is not caused by the sequence of double bonds in the polymer chain. It is therefore assumed that this splitting is caused by the sequence of chiral centres in the polymer chain, that is the tacticity of the polymer. The olefinic carbons are situated between two chiral centres and these centres can be configured in either meso (m) or racemic (r) diad sequences.



where ∿∿∿∿ = —CH_2-CH=CH—CH_2—

It can be seen in the representation of a fragment of polymer backbone in the diagram above that there appears to be two kinds of meso (m, m') and racemic (r, r') diads possible. In practice only two olefinic carbon resonances are resolved which indicates that the effect of substituent stereochemistry on the olefinic carbons only extends one diad and for practical purposes the two meso configurations are magnetically equivalent as are the two racemic diads. Triad distribution is not resolved in this experiment. It can be seen that the peaks are essentially of equal integrated intensity implying that the polymer chains contain an equal number of meso and racemic diads.

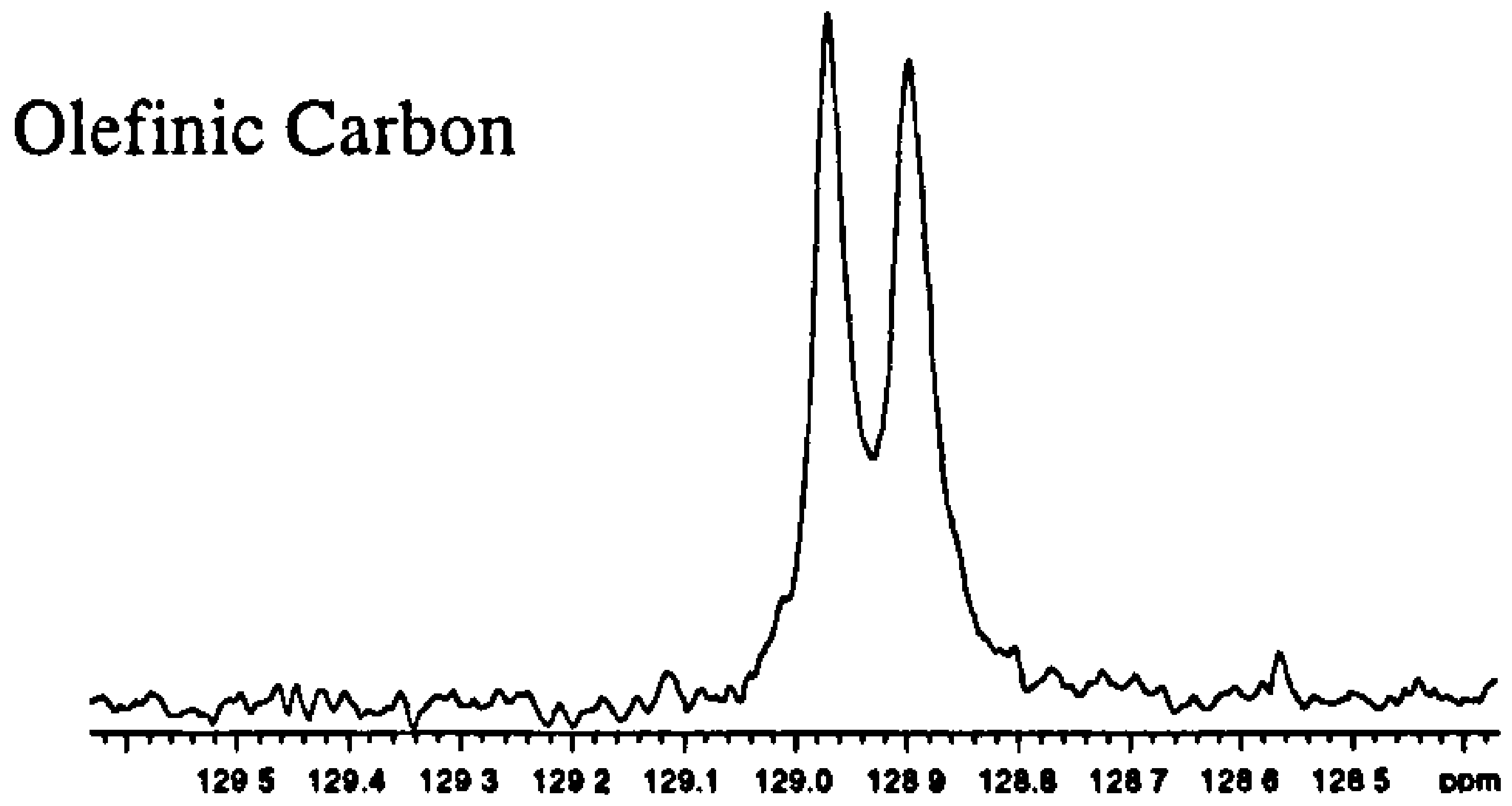
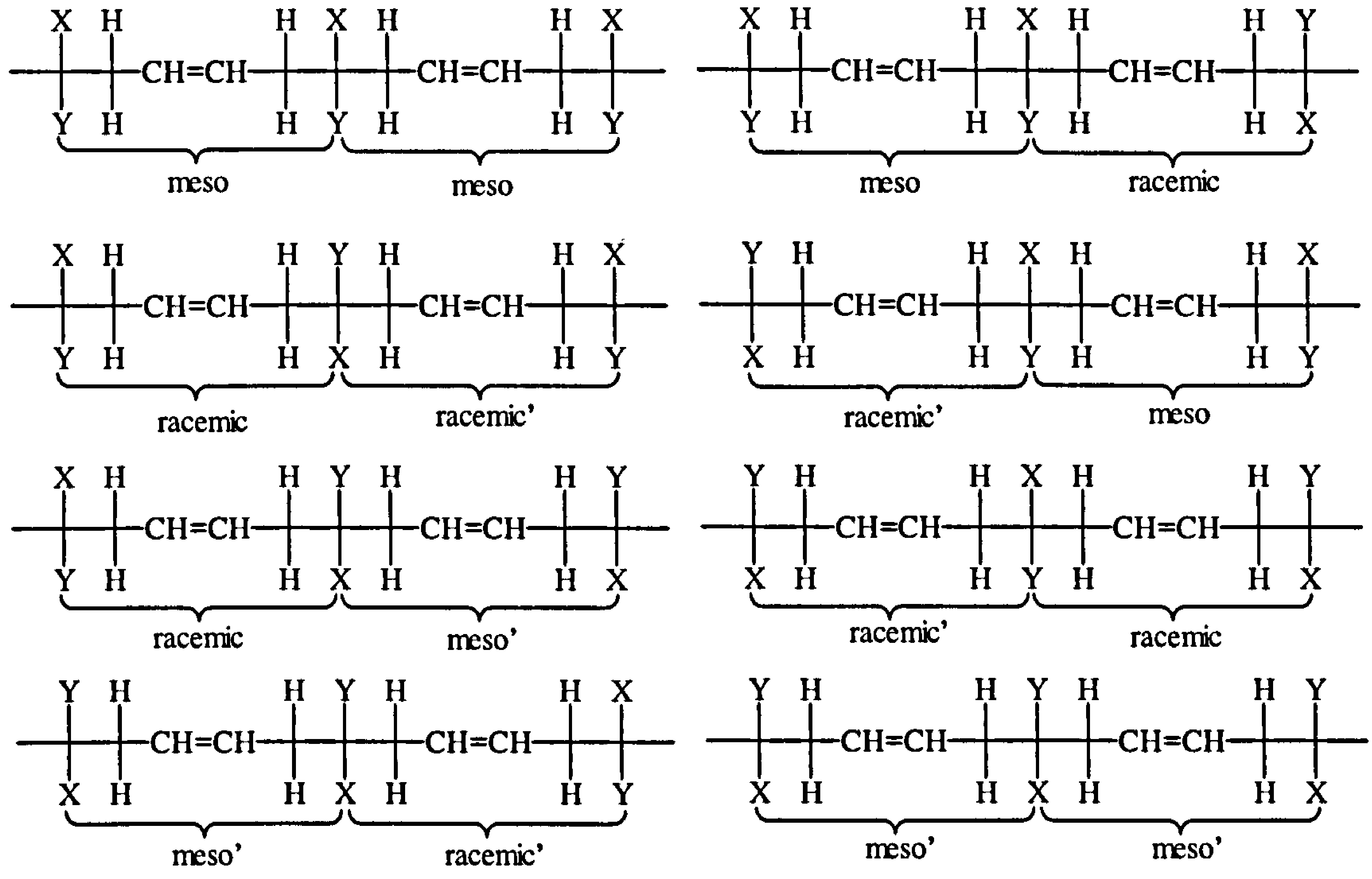


Figure 5-5 Olefinic carbon peaks in the ^{13}C NMR spectrum of the polymer of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane

This equal ratio of meso and racemic diads means that the polymer is not 100% syndio- or isotactic; in either of these cases a single olefinic carbon peak with no splitting would be observed. However, this data tells us nothing about the distribution of meso and racemic diads, that is, it does not tell us if we have a stereoblock, alternating or any intermediate distribution.

The peaks for the ester and the nitrile carbon are both split into triplets with a 1:2:1 intensity distribution and this must be due to triad effects in the polymer chain. The following combinations of meso and racemic diads are possible for an atactic polymer.



Again we assume meso and meso' are magnetically equivilent as are racemic and racemic'. It can be seen that that the ratio of meso: meso/racemic ≡ racemic/meso : racemic combinations is 1:2:1 and thus the resolved carbonyl and cyano carbon peaks indicate that the polymers produced are atactic since the observed splitting fits the theoretical splitting pattern for an atactic polymer. It can be concluded that the distribution of chirality along the polymer backbone is statistical.

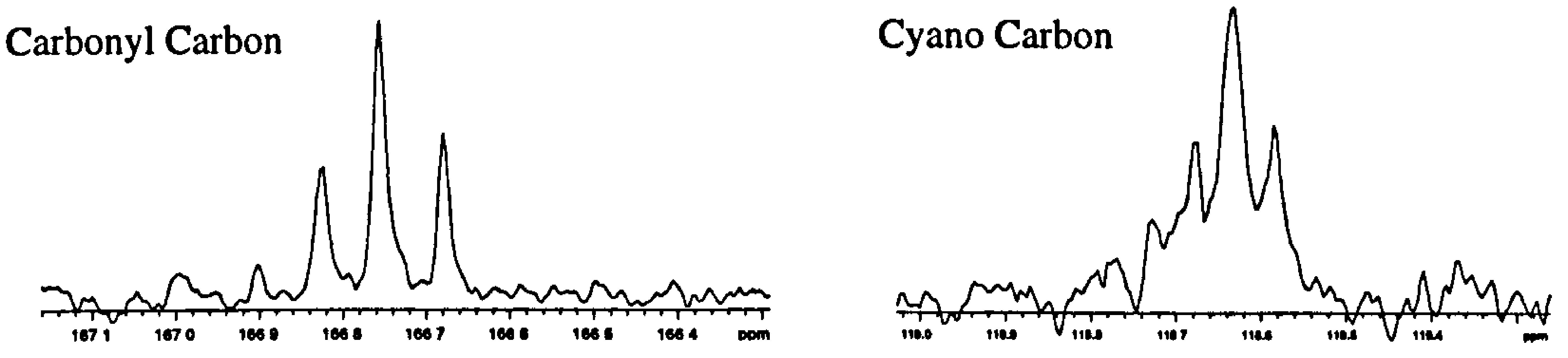


Figure 5-6 Carbonyl and cyano carbon peaks in the ^{13}C NMR spectrum of the polymer of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane

Without further work it is not possible to determine if the meso/meso or racemic/racemic peaks comes at higher field in the spectra.

5.3.2.2 Gel permeation chromatography

The samples were dissolved in chloroform and the resulting solutions analysed by gel permeation chromatography (GPC). The results are shown below.

Sample	Mn	Mw	Polydispersity
A	243 000	649 000	2.67
C	167 000	741 000	4.43
D	31 000	48 000	1.56
E	58 000	126 000	2.18
F	54 000	133 000	2.45
G	202 000	419 000	2.08
H	191 000	767 000	4.03

Table 5-4 GPC results for the polymer of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane (see experimental section and appendix 4.19)

Sample I, the product of bulk polymerisation, was not sufficiently soluble in chloroform to be analysed by GPC. By comparison of the data in Table 5-3 and Table 5-4, it can be seen that the highest molecular weight sample was produced under conditions A where the lowest amount of initiator relative to monomer was used. Comparison of runs C, E and F where the proportion of initiator was increased whilst other factors were held constant, showed that the molecular weight decreased although the difference between E and F was small. The effect of reaction time can be seen in runs C, H and G; the molecular weight was relatively unaffected whereas the yield was more significantly affected, more than doubling on increasing from 5 to 20 hours but without significant increase after that. This was as expected for a free-radical chain polymerisation where high molecular weight polymer is formed early in the reaction in the presence of monomer. As the reaction temperature was increased from run C to D, the molecular weight of the product decreased due to the increased rate of radical production from the AIBN generating a greater number of chains and lower molecular weight. Thus, although a detailed kinetic study has not been undertaken, in a qualitative sense this appears to be a normal free-radical polymerisation.

5.3.2.3 Thermogravimetry and differential scanning calorimetry

Thermogravimetry (TG) was performed to investigate mass loss on heating which provides information on the upper temperature working limit of the material. It was found that the polymers lost mass in two well-defined steps, the first beginning at

~183°C and the second at ~212°C. The first loss corresponds to ~31% of the mass and the second loss corresponds to ~18% mass loss. The residue stabilises at about 50% mass loss up to 300°C. See schematic below.

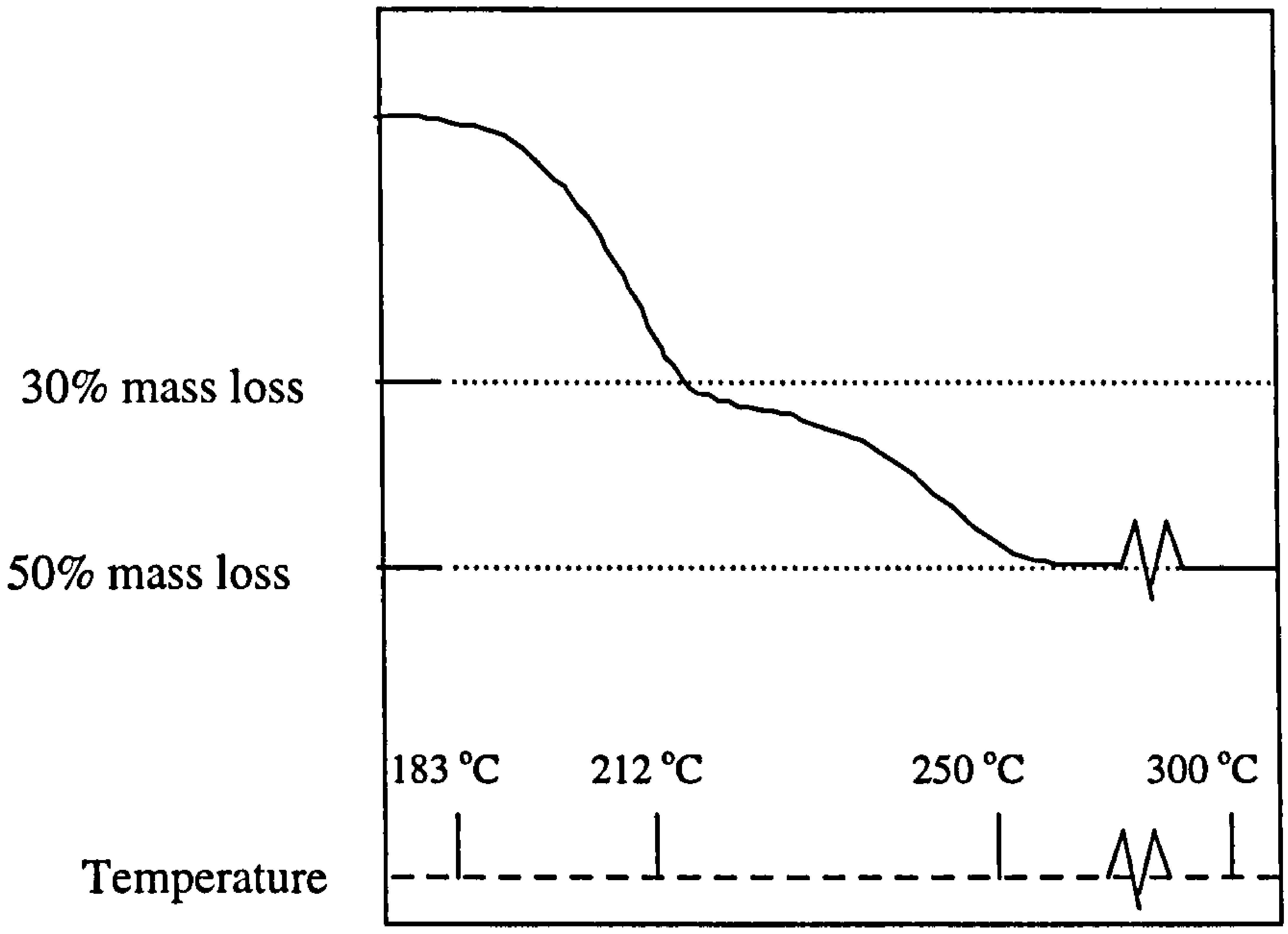
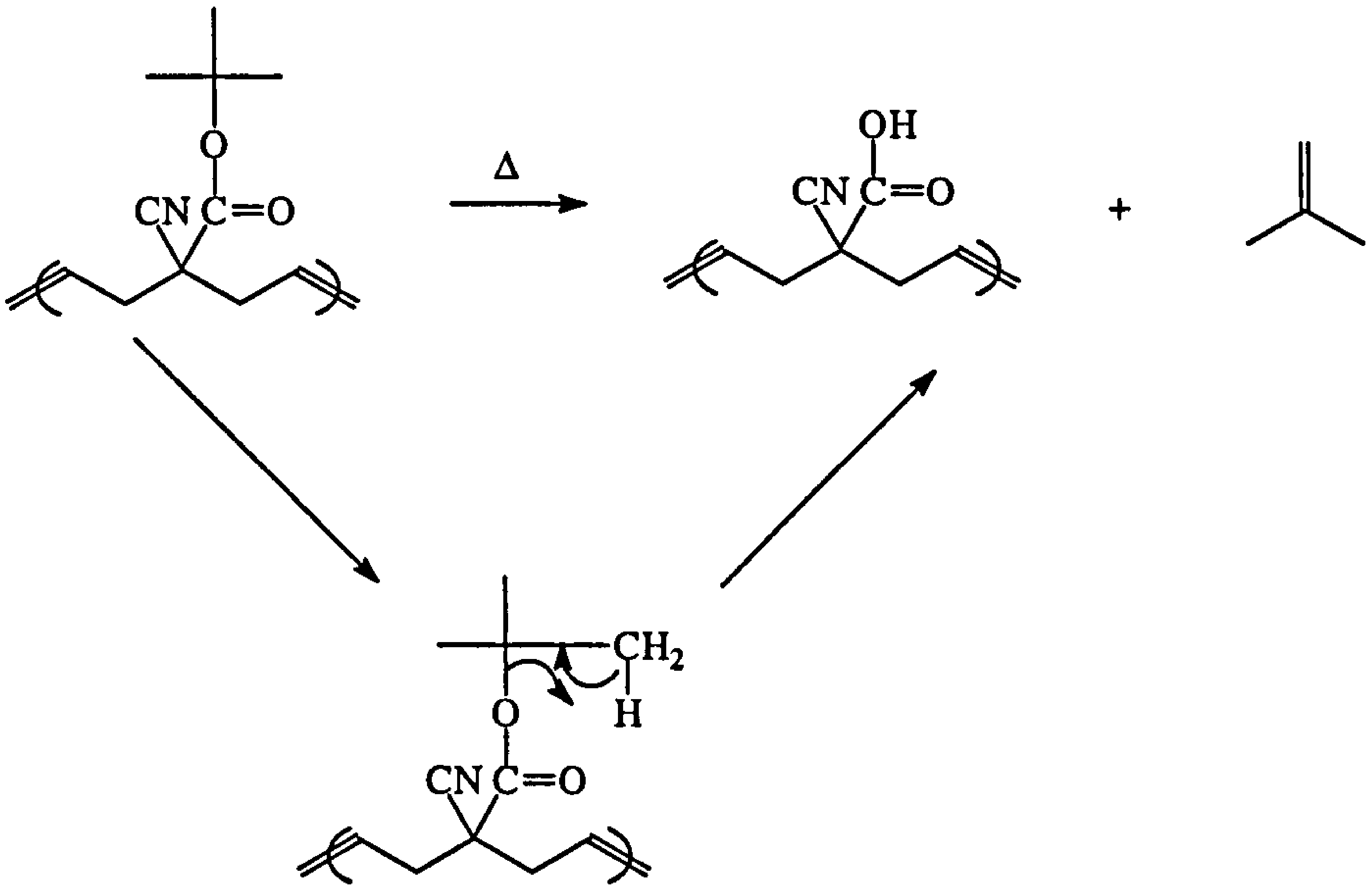
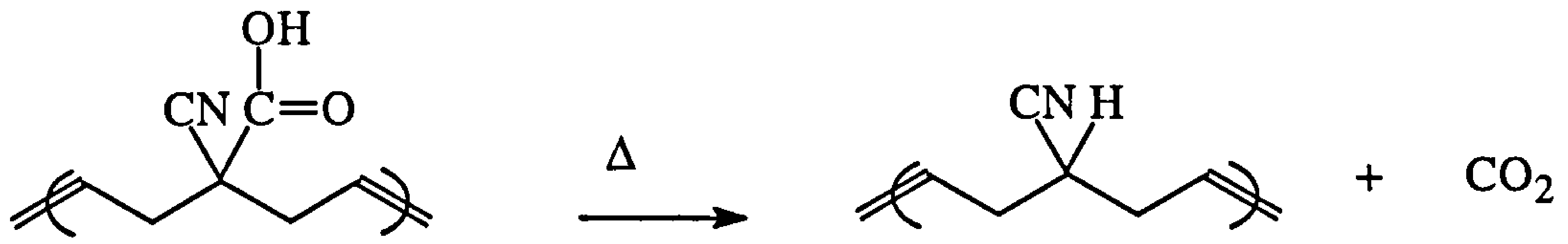


Figure 5-7 Schematic showing TGA trace

These losses can be explained in terms of two degradation steps. Firstly, isobutene is evolved as the *tert*-butyl ester cleaves via a six-membered cyclic transition as shown below.



The calculated percentage mass loss due to the formation of isobutene is 29% in agreement with the observed first weight loss step. The second mass loss corresponds primarily to the decarboxylation of the acid.



The calculated percentage mass loss due to the decarboxylation step is 22.8%. Therefore the total calculated mass loss due to these two processes is 51.8% which is in reasonable agreement with the observed mass losses. The slightly lower than expected mass loss in the decarboxylation step may be due to competition of decarboxylation and anhydride formation by dehydration.

The glass transition temperatures observed for each sample as the midpoint of the DSC transition are shown below.

Sample	T_g /°C
A	55.9
C	58.0
D	59.2
E	53.6
F	54.6
G	50.4
H	58.5

Table 5-5 Glass transition temperatures for the polymer of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane

The values display a scatter between 50.4°C and 59.2°C and there appears to be no sensible correlation with the molecular weight as measured by GPC. While some scatter is not unexpected, 9°C is rather large. These variations may be due to differences in the *cis*/*trans* ratio of the double bonds although this cannot be confirmed by NMR since it is not possible to observed the *cis* isomer peaks in the ^{13}C NMR.

A value was not obtained for sample I because there was concern that the residual monomer trapped within the sample would be evolved during heating and foul the DSC apparatus.

The glass transition temperatures obtained are significantly lower (~30°C) than those for the 1,1-dicyano-2-vinylcyclopropane polymer which is reasonable since the replacement of a cyano group by a *tert*-butyl ester group increases the disorder in the polymer.

5.3.2.4 Conclusion

These results show that 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane polymerises cleanly by radical 1,5-ring-opening polymerisation to produce a predominantly *trans*, atactic polymer. The Tg is above room temperature and therefore the required elasticity has not been achieved. However, the Tg has been lowered considerably by the replacement of a cyano group by a *tert*-butyl ester group. It was hoped that by increasing the length of the alkyl chain, the Tg would be lowered further and polymers which are elastomeric at room temperature would be produced. This work is reported in the following section.

5.3.3 Polymerisation of 1-cyano-1-butoxycarbonyl-2-vinylcyclopropane

The monomer was polymerised using AIBN as initiator and benzene as solvent under the following reaction conditions. See experimental section for full details.

	Temperature / °C	Time / hours	Initiator (% mol)	Yield %	Appearance
A	60	20	0.1	58	white rubbery solid
B	room temp	20	0.4	no polymer produced	
C	60	20	0.4	72	white rubbery solid
D	120	20	0.4	64	yellow rubbery solid
E	60	20	1.5	59	white rubbery solid
F	60	20	3.0	52	transparent rubbery solid
G	60	5	0.4	17	white rubbery solid
H	60	48	0.4	71	white rubbery solid
I*	60	20	0.4	53	clear, colourless gel

* - neat monomer

Table 5-6 Summary of the conditions and results of the homopolymerisation of 1-cyano-1-butoxycarbonyl-2-vinylcyclopropane

The reaction mixtures were precipitated into methanol. In the case of sample I where a gel was formed, it was not possible to dissolve the product although a range of solvents were tried (benzene, chloroform, acetone). Sample I was therefore dried and analysed as an unprecipitated gel.

The yields are similar to those obtained for the *tert*-butyl ester polymer. Again, the increase in reaction time from 5 hours (run G) to 20 hours (run C) lead to a large increase in the yield although the yield was not further increased on increasing the reaction time to 48 hours (run H). The increase in reaction temperature from run C to run D did not significantly affect the yield of product obtained.

5.3.3.1 Analysis

The analysis followed in a fairly straightforward manner from that established for the *tert*-butyl ester polymers.

The NMR spectra of the polymer samples dissolved in chloroform were all found to be identical with the exception of sample I. See appendix 4.22.

The simplicity of the spectra suggest that the monomer has undergone exclusively, 1,5-type ring-opening radical polymerisation. This is to due to the ability of the ester and cyano groups to stabilise the radical formed from 1,5-ring-opening.

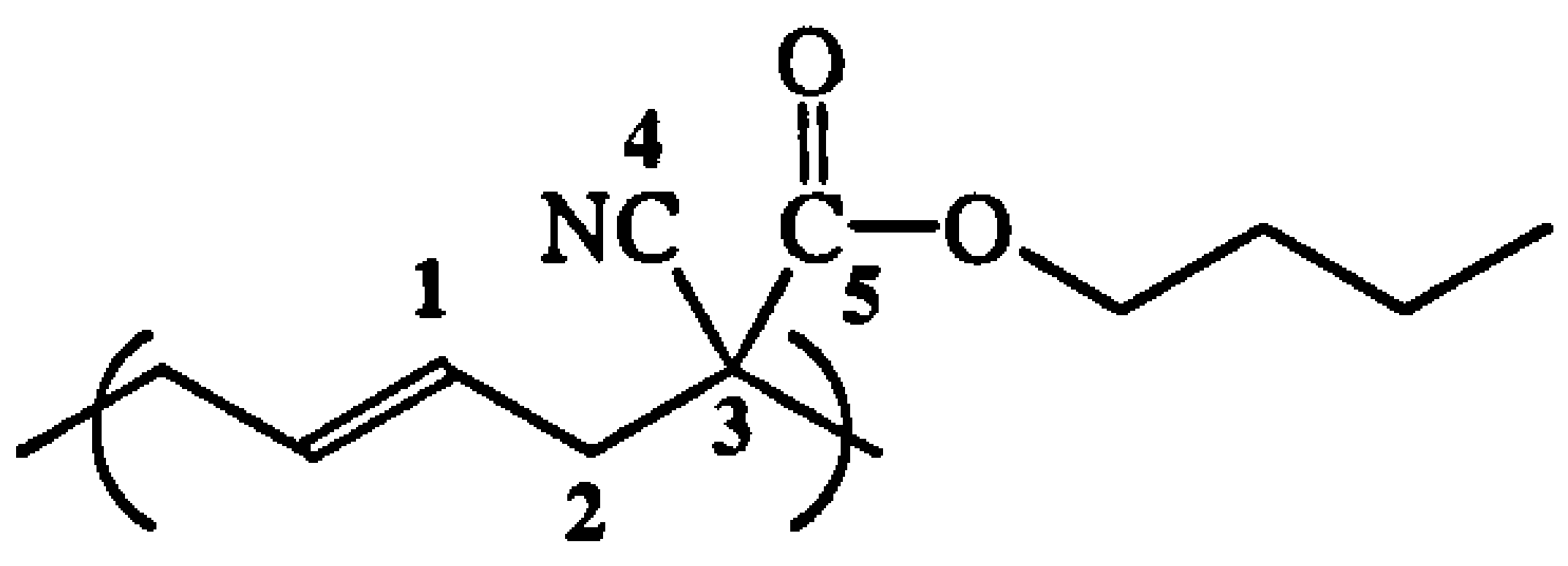
Sample I was analysed as a gel since it was not possible to reprecipitate the sample and it was found to contain residual monomer. During bulk polymerisation, the lack of solvent leads to gelation thus limiting stirring which in turn leads to unreacted monomer trapped within the polymer sample.

5.3.3.1.1 *Cis/trans* isomerism

The simplicity of the spectra also indicates that there is little *cis/trans* isomerism of the double bonds since there is no splitting of the olefinic hydrogen signal at ~ 5.6 ppm suggesting a unique environment.

The strong band at 974cm^{-1} in the infrared spectrum (appendix 4.21) indicates the presence of *trans* double bonds suggesting that the double bonds in the polymer chain are predominantly in the *trans* configuration. There is also a weak band at 726 cm^{-1} which could correspond to *cis* double bonds suggesting that the polymer may contain low numbers of *cis* double bonds.

^{13}C NMR showed clear isomer peaks on the carbonyl carbon (5), the olefinic carbon (1), the cyano carbon (4) and the saturated chiral carbon (3).



Carbons **3**, **4** and **5** will be affected by the configuration of the double bonds on either side. This therefore should lead to three peaks; one corresponding to a carbon between two *cis* double bonds, one corresponding to a carbon between two *trans* double bonds and one corresponding to a carbon situated between a *cis* and a *trans* double bond.

It can be seen that the **3**, **4** and **5** carbon peaks for the chiral, cyano and carbonyl carbons consist of a large peak with a small shoulder on the higher shift side.

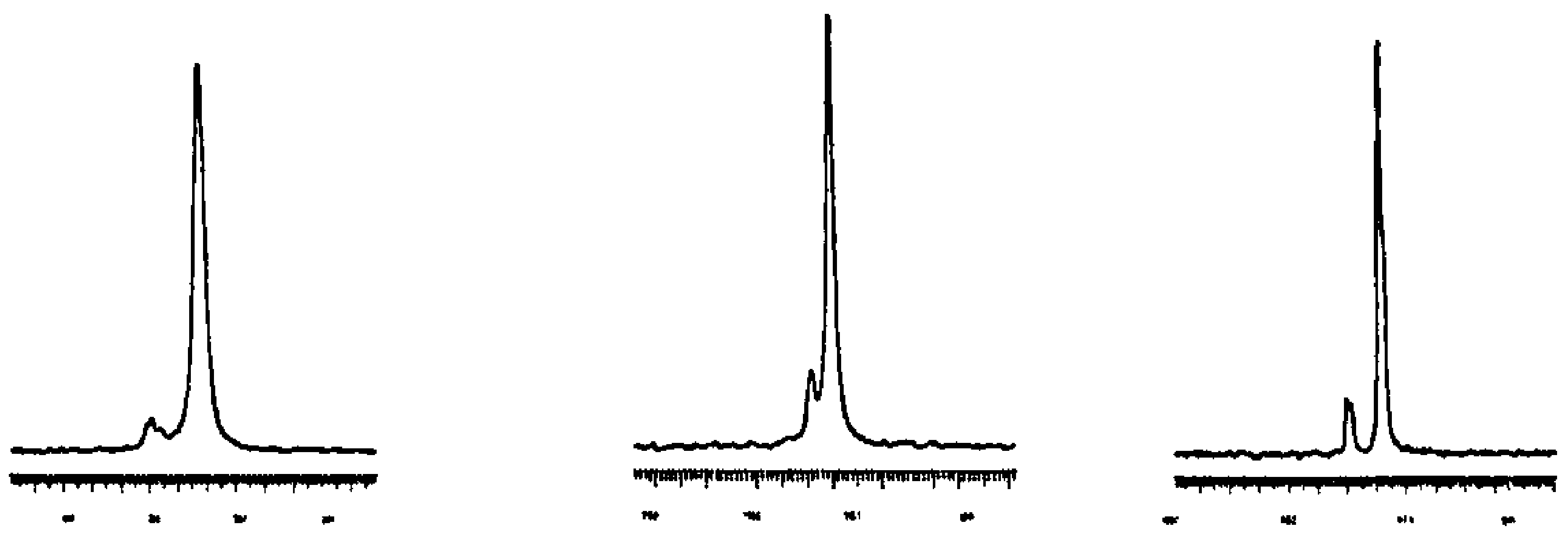


Figure 5-8 ^{13}C NMR peaks for the chiral, cyano and carbonyl carbons in the polymer of 1-cyano-1-butoxycarbonyl-2-vinylcyclopropane

The large peak in each case is the *trans/trans* configuration whilst the shoulder is the *cis/trans* and *trans/cis* configuration. The *cis/cis* peak is too small to be distinguished since the number of *cis* double bonds in the polymer is low.

The olefinic carbon is only affected by its own configuration and therefore was only expected to consist of two peaks; one for a *cis* double bond and one for a *trans* double bond. See below.

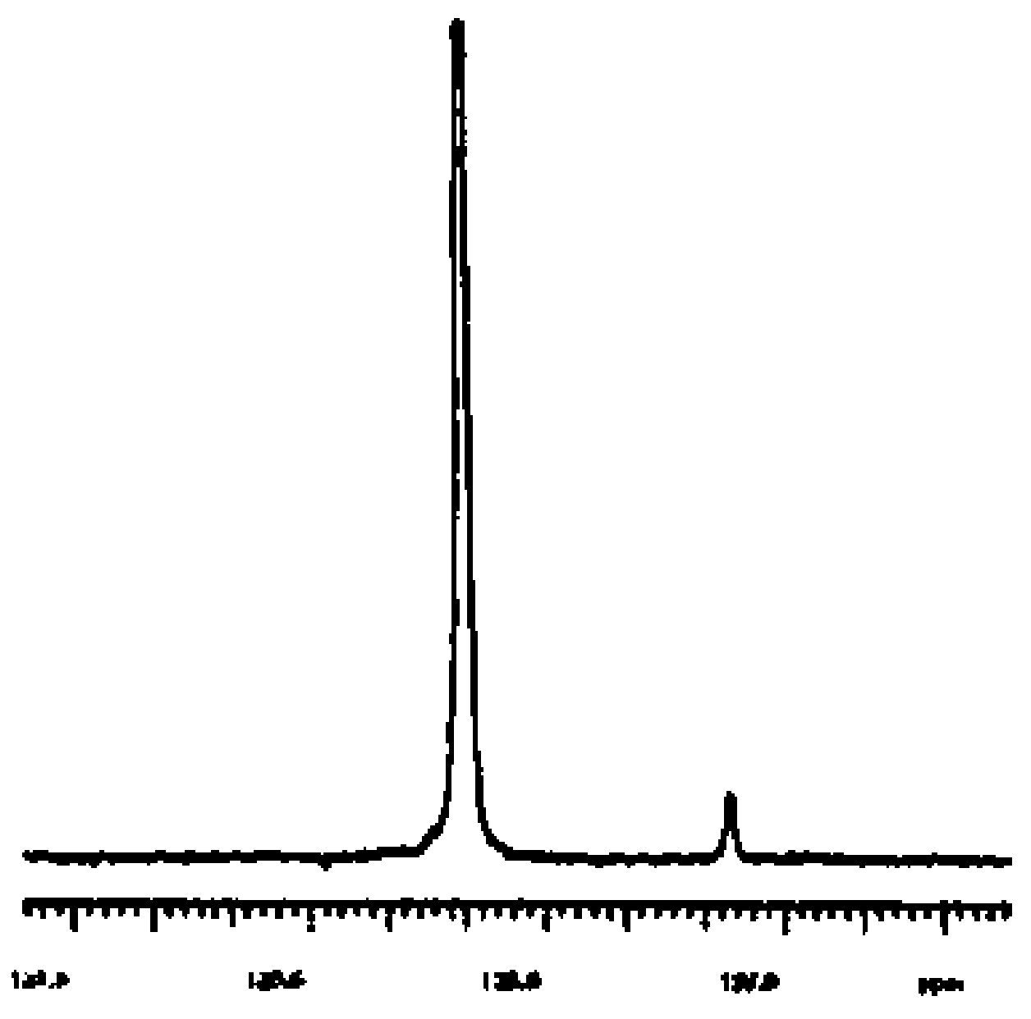


Figure 5-9 ^{13}C NMR peaks for the olefinic carbon in the polymer of 1-cyano-1-butoxycarbonyl-2-vinylcyclopropane

By comparing the relative intensities of the two peaks, it was possible to conclude that the double bonds in the polymer backbone are 93% *trans* in configuration.

5.3.3.1.2 Tacticity

The carbon peak corresponding to the methylene carbon showed a complex splitting pattern due to tacticity effects.

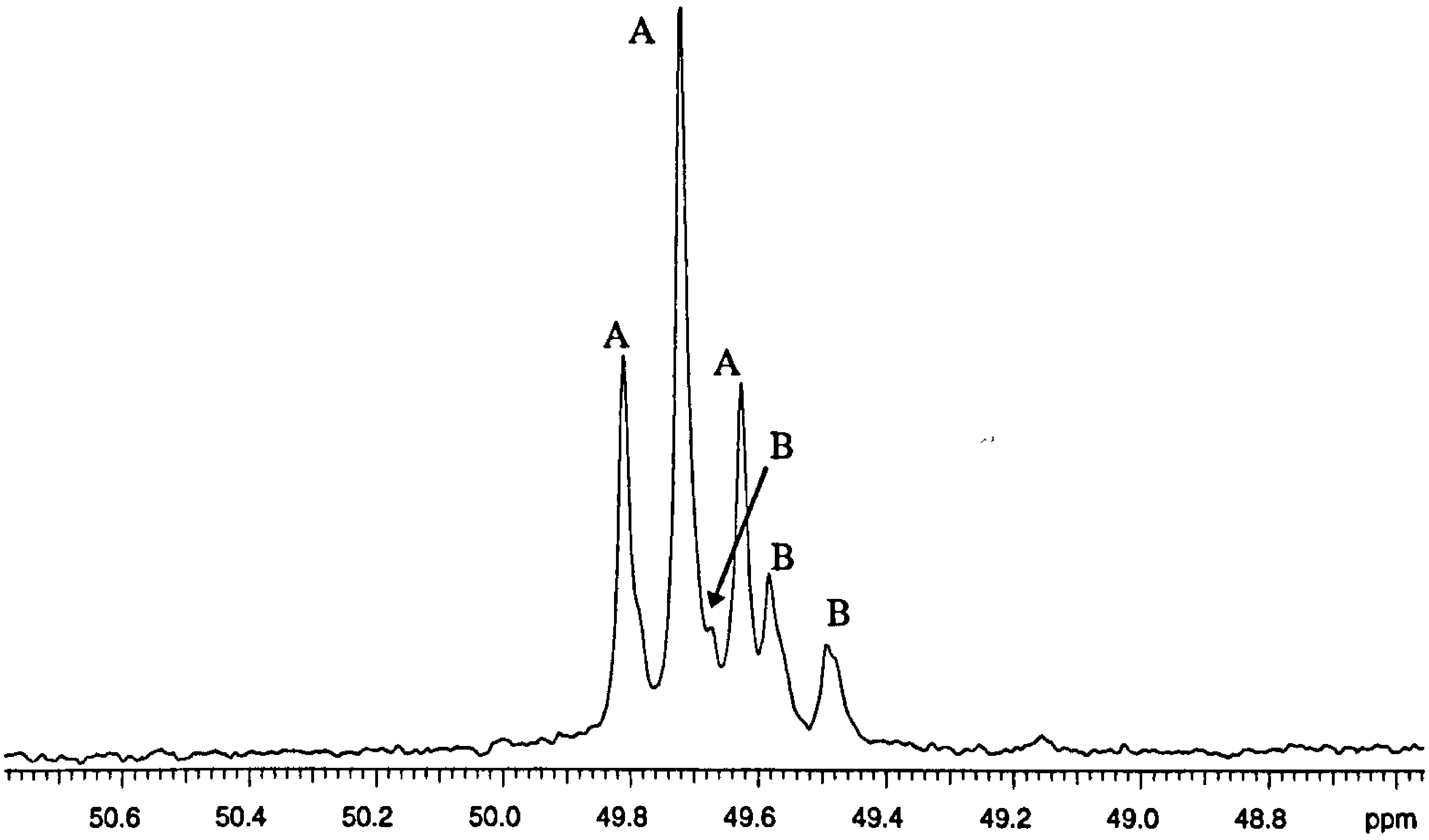


Figure 5-10 ^{13}C NMR spectrum showing the backbone methylene carbons polymer of 1-cyano-1-butoxycarbonyl-2-vinylcyclopropane

It can be seen that the splitting pattern consists of two triplets labelled A and B. Triplet A is corresponds to the carbon situated between two *trans* double bonds whereas triplet B corresponds to a carbon between a *cis* and *trans* double bond. There is no peak observed for a carbon between a two *cis* double bonds owing to the low frequency of occurrence of *cis* double bonds. The peaks appear as triplets due to the tacticity of the chiral carbons on either side of the methylene carbon. The methylene peak in this polymer appears to be susceptible to triad sequences, the centre peak of each triplet corresponding to the equivalent meso/racemic and racemic/meso triads and the two outer peaks corresponding to meso/meso and racemic/racemic triads. On this basis, the peak intensities are predicted to have a 1:2:1 relationship for an atactic polymer and since this appears to be the case, it can be concluded that the polymer is atactic.

5.3.3.2 Gel permeation chromatography

The samples were dissolved in chloroform and the resulting solutions analysed by gel permeation chromatography (GPC). The results are shown below.

Sample	**Mn**	**Mw**	**Polydispersity**
A	154 000	509 000	3.31
C	109 000	340 000	3.11
D	87 000	304 000	3.47
E	81 000	236 000	2.91
F	29 000	79 000	2.72
G	166 000	498 000	3.00
H	137 000	516 000	3.76

Table 5-7 GPC results for the polymer of 1-cyano-1-butoxycarbonyl-2-vinylcyclopropane (See experimental and appendix 4.24)

Sample I was not sufficiently soluble to obtain molecular weight information. The molecular weights measured show the same set of trends as observed for the *tert*-butyl ester polymers suggesting that this is a fairly standard free-radical chain polymerisation.

5.3.3.3 Differential scanning calorimetry

The glass transition temperatures observed for this set of samples as the mid-point in the DSC transition are shown below.

Sample	$T_g/^{\circ}C$
A	-1.3
C	-4.1
D	-4.7
E	-4.1
F	-5.1
G	-3.1
H	-3.7

Table 5-8 Glass transition temperatures of the polymer of 1-cyano-1-butoxycarbonyl-2-vinylcyclopropane

No glass transition temperature was recorded for sample I as the trapped monomer was evolved from the sample on heating and this was undesirable in the DSC apparatus. These glass transition temperatures are significantly lower than those obtained from the *tert*-butyl ester with a lower scatter.

5.3.3.4 Conclusion

These results show that 1-cyano-1-butoxycarbonyl-2-vinylcyclopropane polymerises cleanly by radical 1,5-ring-opening polymerisation to produce a predominantly *trans*, atactic polymer. The Tg was below room temperature and thus the required elasticity had been achieved. However, it was desirable to reduce the Tg further in order to extend the temperature range in which the polymer would be elastic. It was hoped that by increasing the length of the alkyl chain the Tg would be lowered even further. This work is reported in the following section.

5.3.4 Polymerisation of 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane

The monomer was polymerised in solution by free-radical polymerisation with AIBN as initiator and benzene as solvent under the following reaction conditions. See experimental section for full details.

	Temperature / °C	Time / hours	Initiator (% mol)	Yield %	Appearance
A	60	20	0.1	45	white rubbery solid
B	room temp	20	0.4	no polymer produced	
C	60	20	0.4	82	white rubbery solid
D	120	20	0.4	58	yellow rubbery solid
E	60	20	1.5	79	white rubbery solid
F	60	20	3.0	77	transparent rubbery solid
G	60	5	0.4	38	white rubbery solid
H	60	48	0.4	83	white rubbery solid
I*	60	20	0.4	85	clear, colourless gel

* - neat monomer

Table 5-9 Summary of the conditions and results of the homopolymerisation of 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane

The reaction mixtures were precipitated into methanol. In the case of sample I where a gel was formed, it was not possible to dissolve the product although a range of solvents were tried. Sample I was therefore dried and analysed as an unprecipitated gel.

The same set of trend in the yields was observed again with the yield increasing as the reaction time was increased from 5 hours (run G) to 20 hours (run C) but with no further increase on increasing the reaction time to 48 hours (run H).

5.3.4.1 Analysis

The samples were dissolved in chloroform and the resulting solutions analysed by ^{1}H and ^{13}C NMR. The NMR spectra of the polymer samples (excluding sample I), were all found to be identical.

The ^{1}H NMR spectra (appendix 4.27) indicated that the polymerisation had occurred by 1,5-ring-opening polymerisation and this again will be due to the stability of the radical formed by 1,5-ring-opened product.

5.3.4.1.1 *Cis/trans* isomerism

The simplicity of the spectra also indicates that there was little *cis/trans* isomerism of the double bonds since there is no splitting of the olefinic hydrogen signals suggesting a unique environment.

The strong band at 974 cm^{-1} in the infrared spectrum (appendix 4.26) indicates the presence of *trans* double bonds suggesting that the polymer chain is predominantly in the *trans* configuration. However, the presence of a weak band at 726 cm^{-1} suggests that the polymer backbone does contain some double bonds in the *cis* conformation.

^{13}C NMR showed the same effects as were observed in the carbon NMR of the n-butyl polymers. Peaks for the carbonyl, cyano and the chiral carbon show small shoulders due to the *cis/trans* sequence of double bonds with the main peak being due to the *trans/trans* sequence. The olefinic carbon again shows a distinct *cis* double bond peak and by comparing its intensity with that of the corresponding *trans* peak it was possible to conclude that the polymer was 96% *trans* in configuration.

5.3.4.1.2 Tacticity

Again, the methylene carbon displayed splitting due to tacticity effects as described earlier for the n-butyl ester polymers. It can be concluded that the polymer is atactic.

5.3.4.2 Gel permeation chromatography

The samples were dissolved in chloroform and the resulting solutions analysed by GPC. The results are shown below.

Sample	Mn	Mw	Polydispersity
A	388 000	973 000	2.51
C	266 000	681 000	2.56
D	65 000	182 000	2.80
E	75 000	184 000	2.46
F	35 000	106 000	2.99
G	123 000	272 000	2.21
H	98 000	309 000	3.15

Table 5-10 GPC results for the polymer of 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane (See experimental and appendix 4.29)

The molecular weights measured show the same set of trends as observed for the *tert*-butyl ester and n-butyl ester polymers suggesting that this too is a fairly standard free-radical chain polymerisation.

5.3.4.3 Differential scanning calorimetry

The glass transition temperature for each sample measured as the mid-point in the DSC transition are shown below.

Sample	T_g /°C
A	-23.1
C	-23.7
D	-22.3
E	-22.3
F	-22.2
G	-22.4
H	-23.1

Table 5-11 Glass transition temperatures for the polymer of 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane

These glass transition temperatures are lower than those obtained for the n-butyl polymer suggesting that the increase in the alkyl chain length creates more disorder within the polymer.

5.3.4.4 Conclusion

An increase in the alkyl chain of the ester from butyl to hexyl has caused a significant decrease in the glass transition temperature. It has been possible to synthesise a novel elastomeric polymer with a Tg of ~ - 23°C.

5.4 Summary

Three novel homopolymers have been synthesised. It has been shown that the replacement of a cyano group in the dicyano monomer with an ester group, increases solubility and decreases the glass transition temperature of the polymer obtained.

The polymers produced have been shown to be predominantly *trans* with the *tert*-butyl polymer being greater than 96% *trans*, the n-butyl ester being 93% *trans* and the hexyl ester being 96% *trans*.

The polymers are shown to be atactic. A difference between the bulky *tert*-butyl ester and the long chain esters is apparent. In the long chain esters, tacticity effects are only observed in the methylene carbon whereas in the *tert*-butyl ester, they are not apparent in the methylene carbon but can be clearly seen in the carbonyl, olefinic and cyano carbons. This difference is presumably due to steric effects but this is not clearly understood.

It has been shown that as the length of the ester chain increases, the glass transition temperature decreases and this can be attributed to the flexibility of the pendant ester. As the flexibility increases, the glass transition temperature is decreased. This has allowed us to produce two polymers with the required elasticity and solubility.

It remains to be seen whether these polymer will have the required polarity. The dielectric constant of the polymers produced in this chapter will be discussed in chapter seven.

5.5 Experimental

5.5.1 General

THF was dried prior to use by refluxing over sodium/benzophenone. Benzene was dried prior to use by stirring over calcium hydride and then distilled. All other reagents were used as supplied.

Infra red spectra were recorded on a Perkin Elmer 1600 series FTIR. The spectra were recorded as KBr discs or between sodium chloride discs. ^{1}H and ^{13}C NMR were recorded on a Varian VXR 400 NMR spectrometer and a Varian Gemini 200 NMR spectrometer. The solvent used was deuterated chloroform with TMS as internal reference or deuterated DMSO. Gel permeation chromatography was carried out in chloroform using a Knauer HPLC pump (model 64), Waters model R401 differential refractometer detector and 3 PLgel columns with pore sizes of 10^2, 10^3 and 10^5 Å (column packing PLgel 5μm mixed styrene-divinyl benzene beads). The sample solutions were filtered through a Whatman WTP type 0.2μm filter to remove any particulate before injection. The columns were calibrated using Polymer Laboratories polystyrene standards (162-770 000amu). Thermogravimetry (TG) was carried out using a Stanton Redcroft TG 760 series and differential scanning calorimetry (DSC) was performed using either a Perkin Elmer DSC 7 or a Pyris 1.

5.5.2 Synthesis of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane

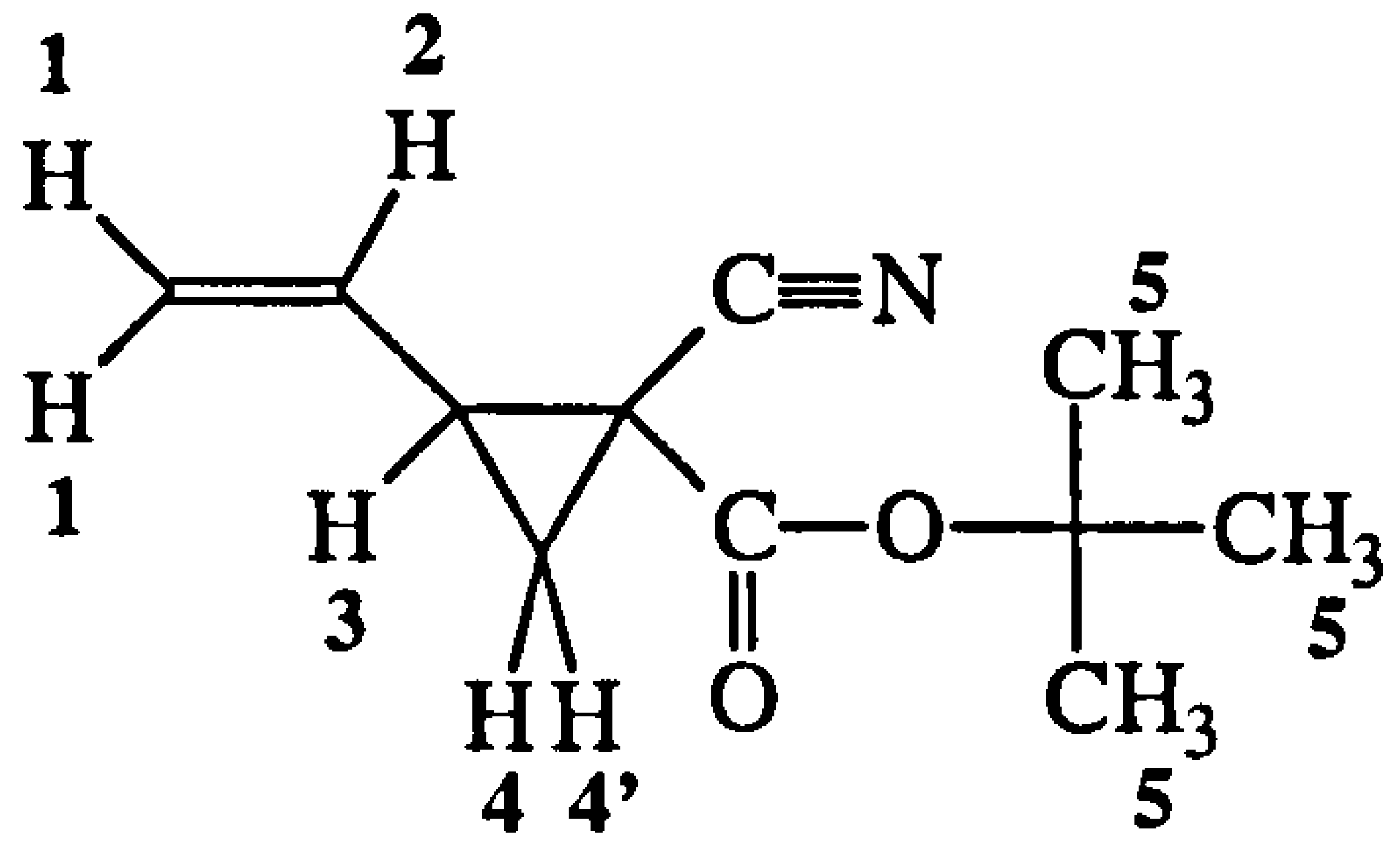
To a suspension of sodium hydride (5 g, 0.21 mol) in THF (200 cm^3), a mixture of tert-butyl cycnoacetate (9.87 cm^3, 0.069 mol) and *trans*-1,4-dibromobutene (15.42 g, 0.072 mol) in THF (150 cm^3), was added dropwise at room temperature under nitrogen. The reaction mixture was stirred for 48 hours at room temperature. The reaction mixture was poured into cold 10% hydrochloric acid and extracted with diethyl ether. The etheral layer was washed twice with saturated sodium hydrogen carbonate, once with saturated sodium chloride solution and dried using magnesium sulphate. The mixture was filtered and the solvent removed in vacuuo yielding a clear dark orange oil. This oil was distilled under vacuum to give 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane (8.23 g, 62%) as a clear colourless oil (b.p. = 61°C/0.6mmHg). Calculated for $C_{11}H_{15}NO_2$: C, 68.4%; H, 7.8%; N, 7.2%; Found : C, 68.2%; H, 7.9%; N, 6.9%.

5.5.2.1 Characterisation

Infra-Red Spectroscopy - See appendix 4.1

2981 cm^{-1} (aliphatic C-H stretch), 2244 cm^{-1} (CN stretch), 1729 cm^{-1} (CO ester stretch), 1640 cm^{-1} (C=C stretch), 1458 cm^{-1} (C-H bending in ring), 1153 cm^{-1} (C-O ester stretch), 987 and 924 cm^{-1} (out of plane terminal vinylic C-H deformation)

^{1}H NMR - See appendix 4.2



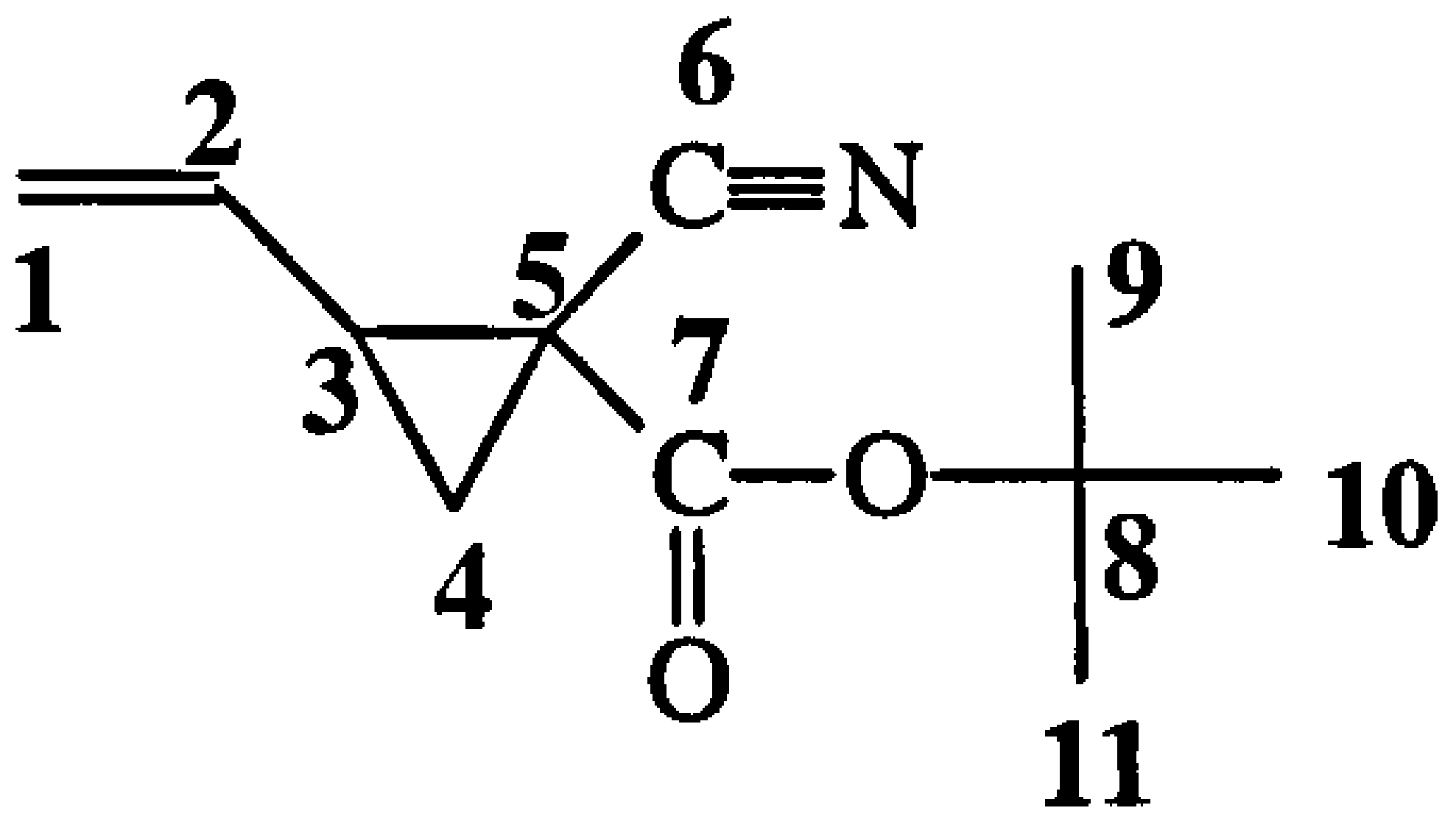
where **4'** is in the same plane as **3**

δ / ppm = 5.58 (m,**2**), 5.43 (m,**1**), 2.45 (m,**3**), 1.88 (m,**4'**), 1.56 (m,**4**), 1.49 (s,**5**)

Intensity ratio = 1:2:1:1:1:9

Carbon NMR - See appendix 4.3

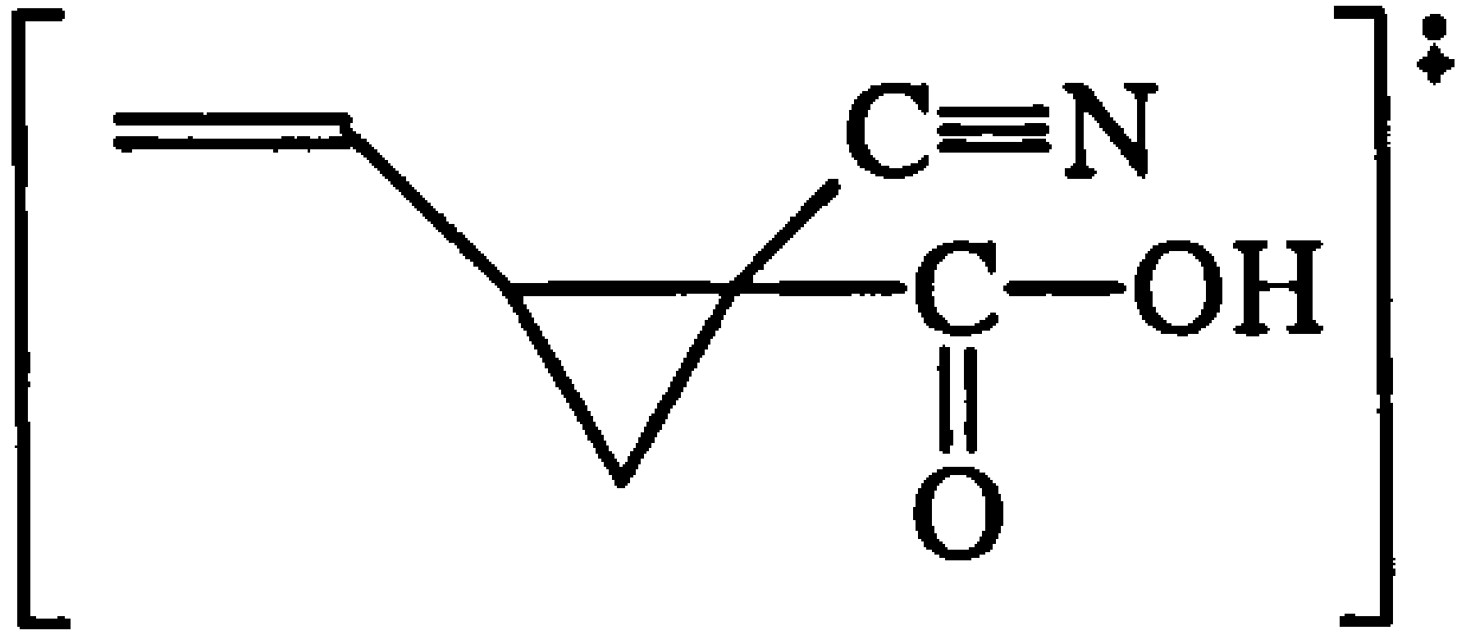
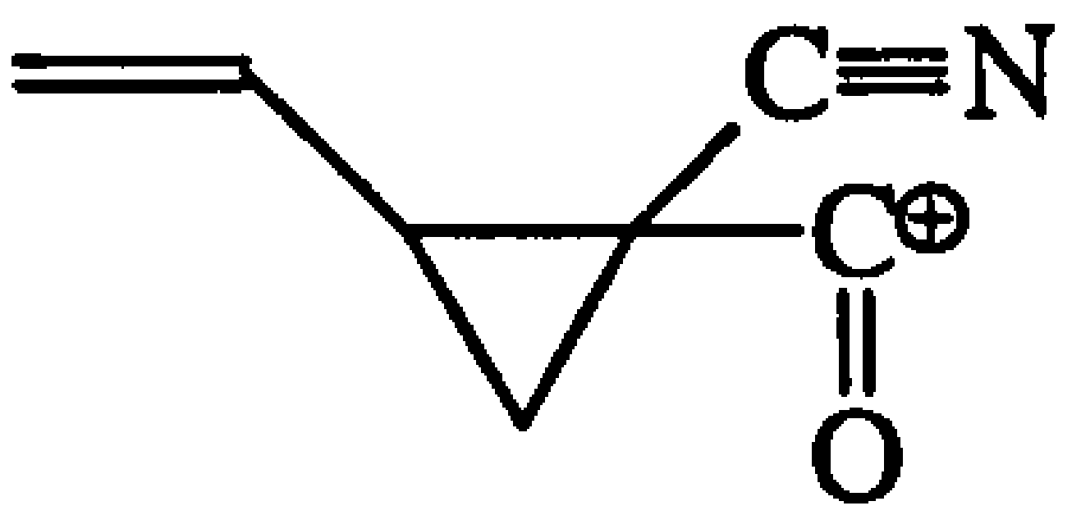
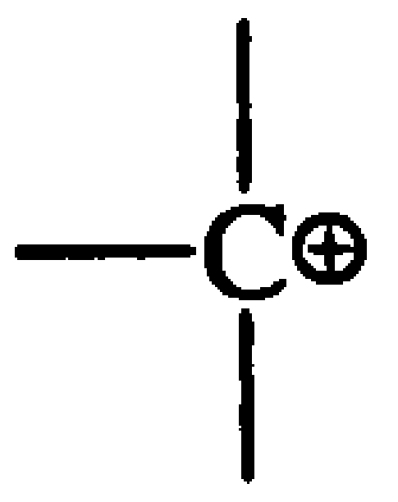
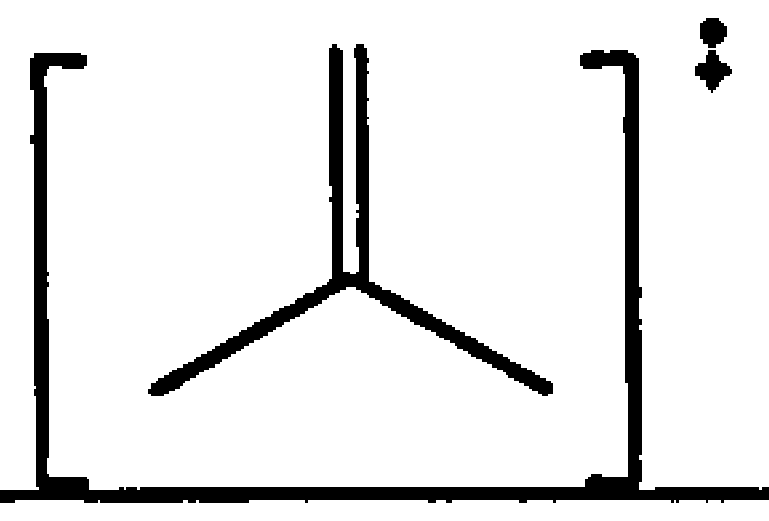
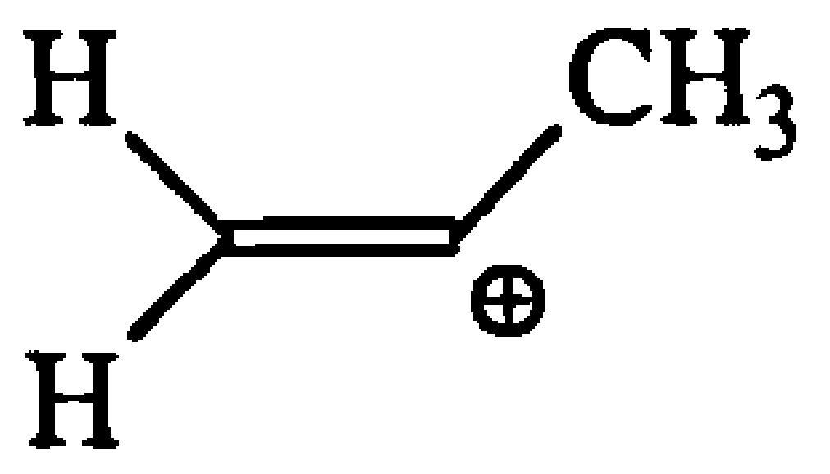
Assignments were made by comparison to the DEPT spectrum.



δ / ppm = 164.06 and 164.13 (**7**), 132.70 and 130.90 (**2**), 121.19 and 120.65 (**1**), 119.24 and 117.26 (**6**), 84.26 and 84.20 (**8**), 35.39 and 33.31 (**3**), 28.14 and 28.07 (**9,10,11**), 23.73 and 22.01 (**4**), 22.04 and 21.28 (**5**)

Assignments were made by comparison to the DEPT spectrum

Mass Spectrometry - See appendix 4.4

M/Z	**Assignment**
193	$M^{+\cdot}$
178	$[M - CH_3]^+$
137	
120	
57	
56	
41	
39	$H_2C{=}C{=}\overset{\oplus}{C}H$

5.5.3 Synthesis of 1-cyano-1-butoxycarbonyl-2-vinylcyclopropane

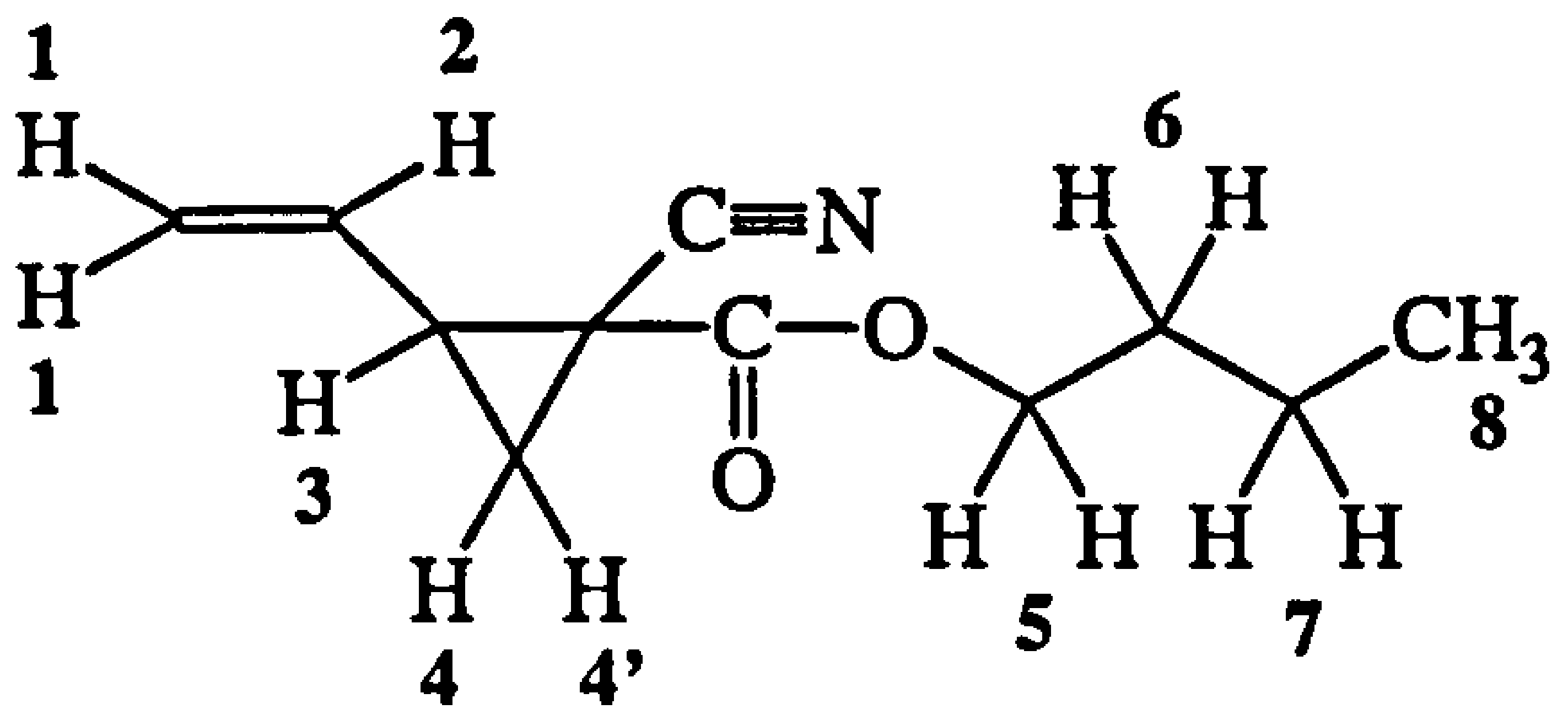
To a suspension of sodium hydride (5 g, 0.21 mol) in THF (200 cm^3), a mixture of n-butyl cycnoacetate (9.81 cm^3, 0.069 mol) and *trans*-1,4-dibromobutene (15.42 g, 0.072 mol) in THF (150 cm^3), was added dropwise at room temperature under nitrogen. The reaction mixture was stirred for 48 hours at room temperature. The reaction mixture was poured into cold 10% hydrochloric acid and extracted with diethyl ether. The etheral layer was washed twice with saturated sodium hydrogen carbonate, once with saturated sodium chloride solution and dried using magnesium sulphate. The mixture was filtered and the solvent removed in vacuuo yielding a clear dark orange oil. This oil was distilled under vacuum to give 1-cyano-1-butoxycarbonyl-2-vinylcyclopropane (8.03 g, 60%) as a clear colourless oil (b.p. = 78°C/0.6mmHg). Calculated for $C_{11}H_{15}NO_2$: C, 68.4%; H, 7.8%; N, 7.2%; Found : C, 68.2%; H, 8.1%; N, 7.0%.

5.5.3.1 Characterisation

Infra-Red Spectroscopy - See appendix 4.5

2957 cm^{-1} (aliphatic C-H stretch), 2245 cm^{-1} (CN stretch), 1736 cm^{-1} (CO ester stretch), 1640 cm^{-1} (C=C stretch), 1467 cm^{-1} (C-H bending in ring), 1171 cm^{-1} (C-O ester stretch), 923 cm^{-1} (out of plane terminal vinylic C-H deformation)

^{1}H NMR - See appendix 4.6

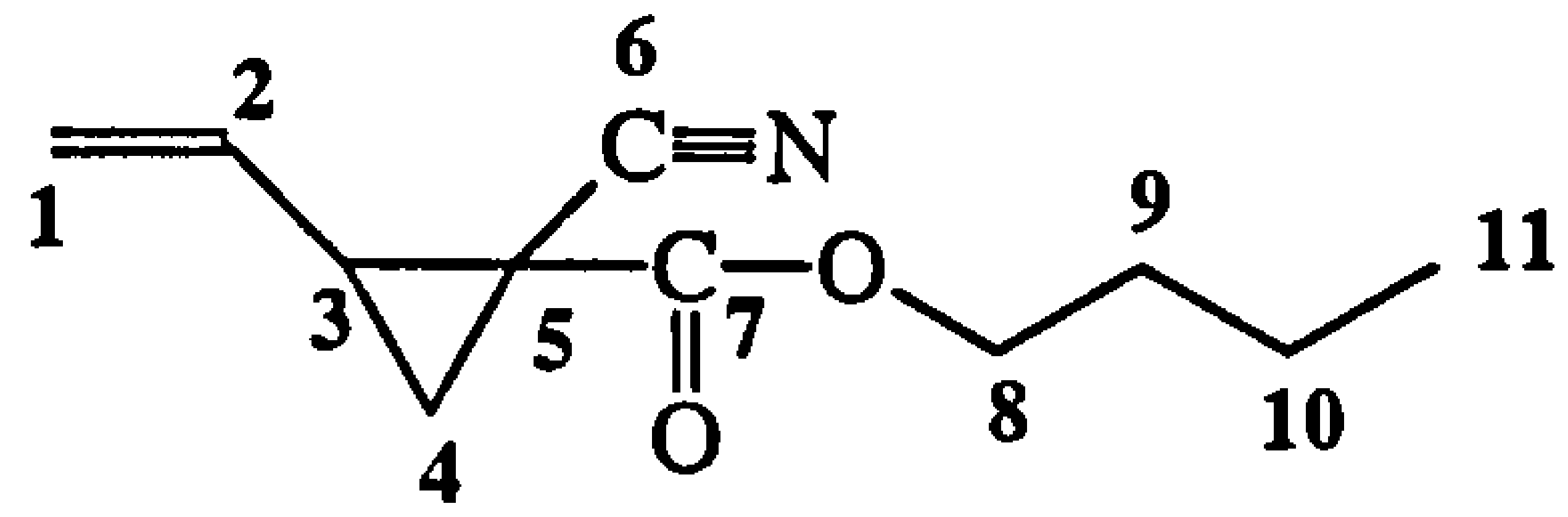


where **4'** is in the same plane as **3**

δ / ppm= 5.62 (m,2), 5.46 (m,1), 4.20 (m,5), 2.55 (m,3), 1.98 (4'), 1.67 (m, 4&6), 1.42 (m,7), 0.96 (m,8)

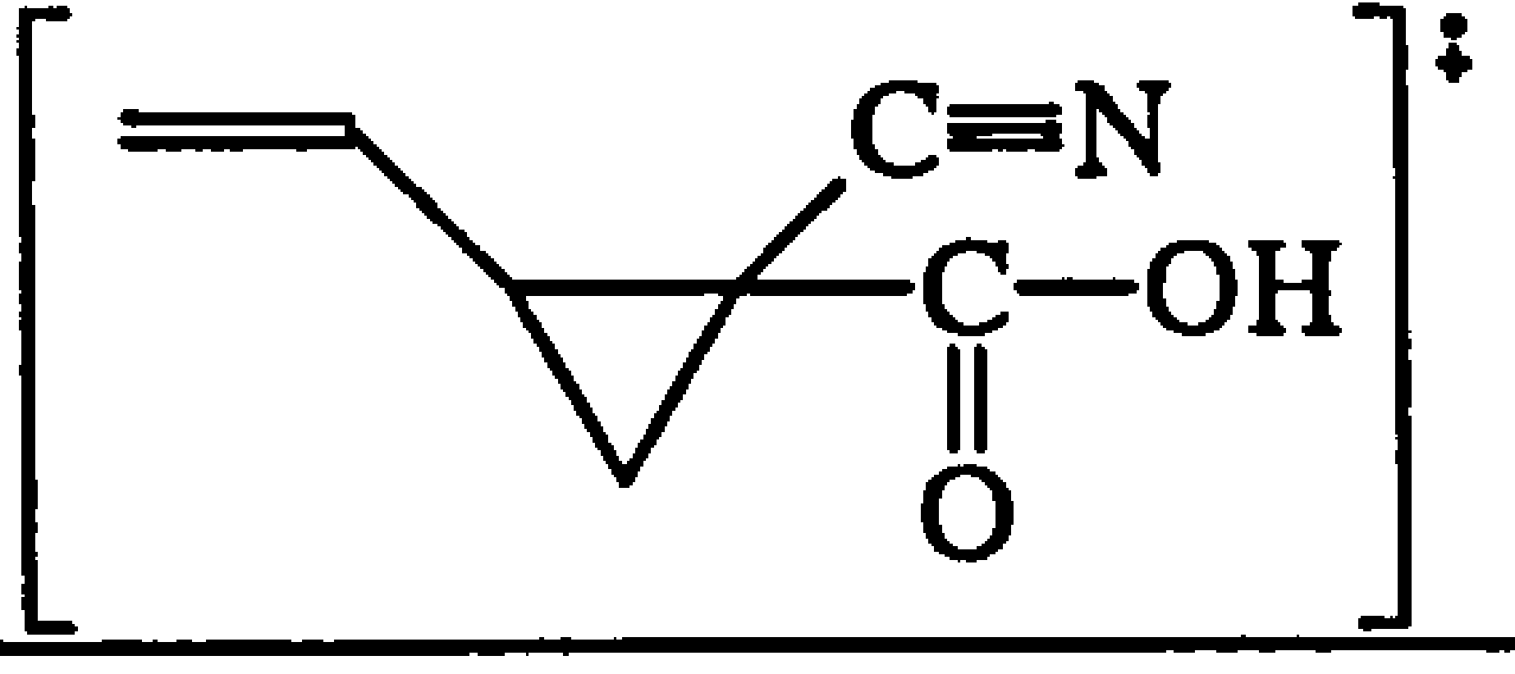
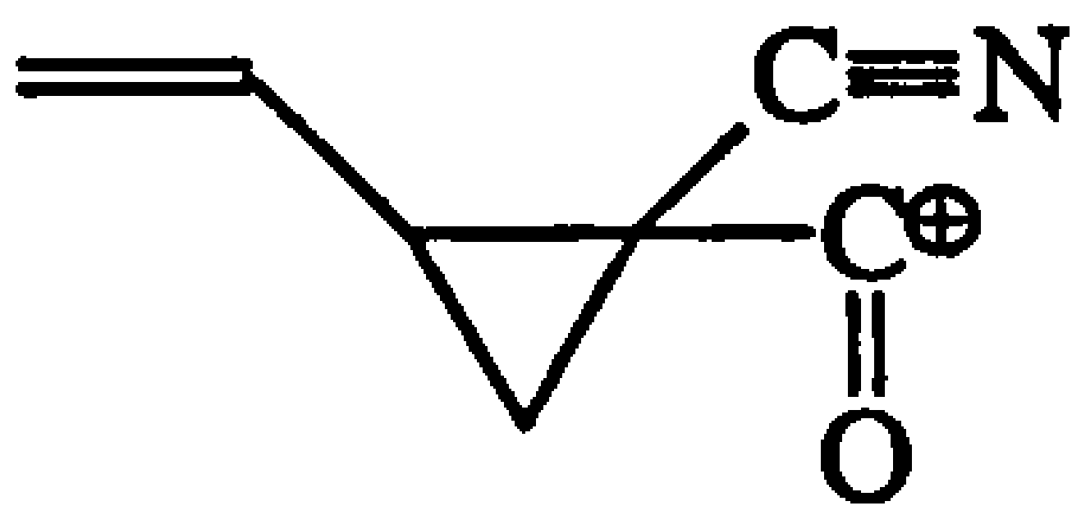
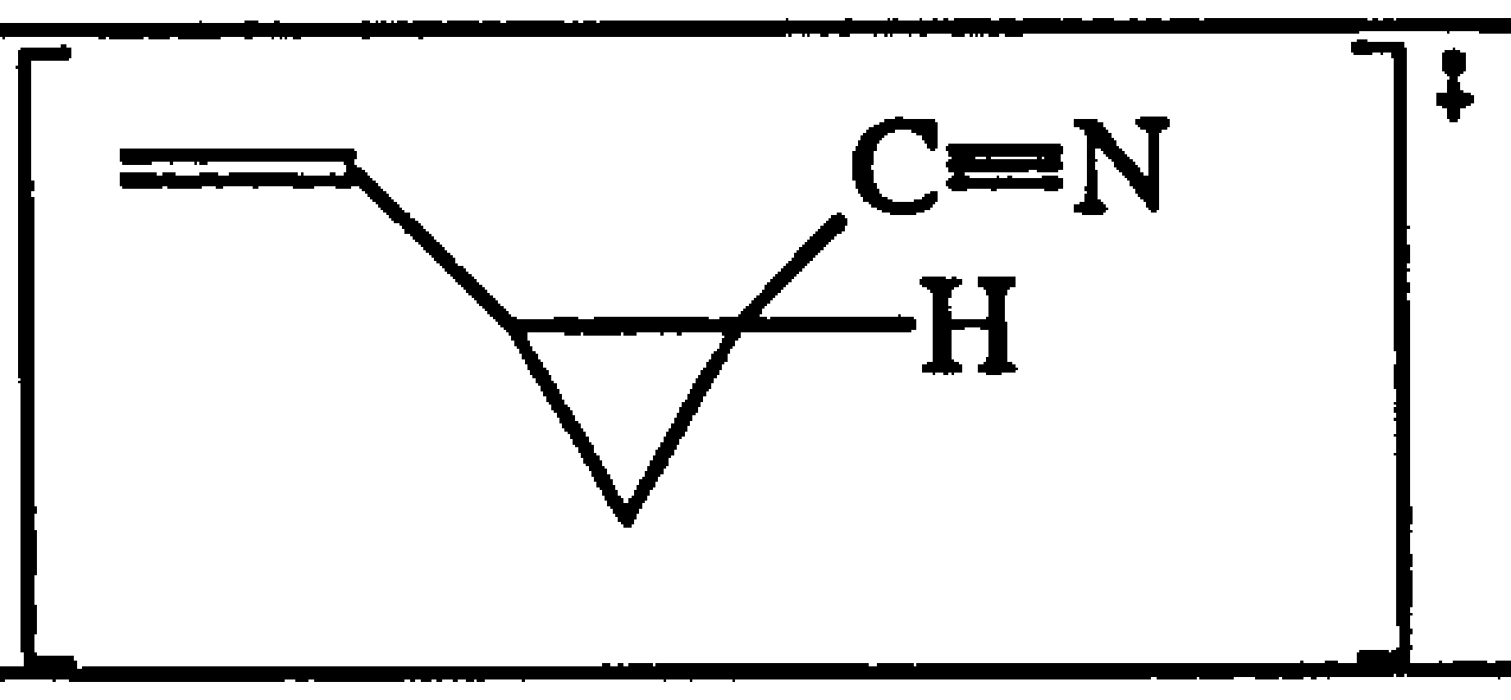
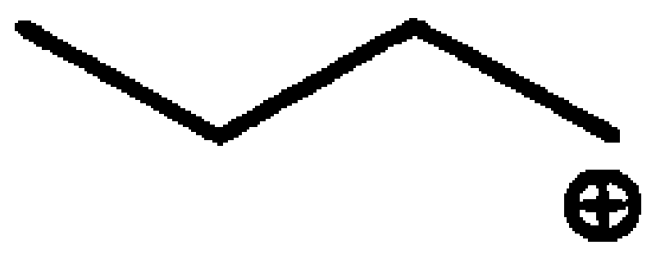
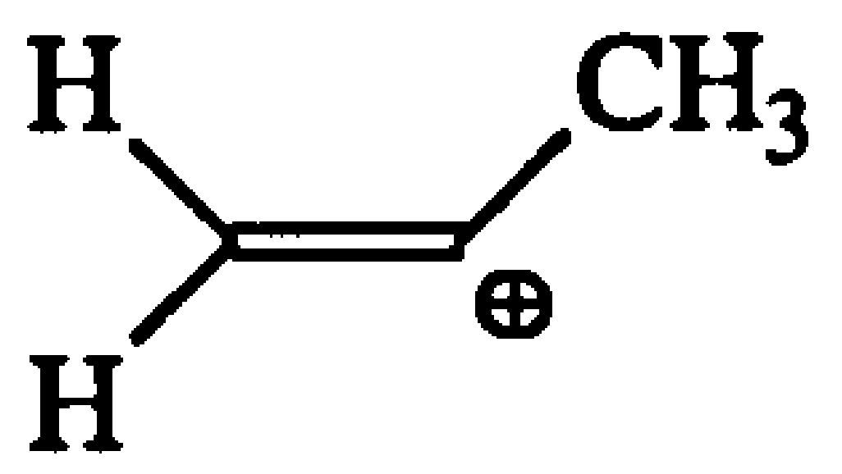
Intensity ratio = 1:2:2:1:1:3:2:3

Carbon NMR - See appendix 4.7



δ / ppm = 167.43 and 165.47 (**7**), 132.39 and 130.79 (**2**), 121.54 and 121.02 (**1**), 118.87 and 116.90 (**6**), 67.02 and 66.83 (**8**), 35.89 and 33.93 (**3**), 30.67 and 30.63 (**9**), 24.08 and 22.71 (**4**), 21.31 and 20.54 (**5**), 19.20 and 19.17 (**10**), 13.88 and 13.85 (**11**)

Mass Spectrometry - See appendix 4.8

M/Z	Assignment
137	
120	
93	
57	
41	
39	$H_2C{=}C{=}\overset{\oplus}{C}H$

5.5.4 Synthesis of hexyl cyanoacetate

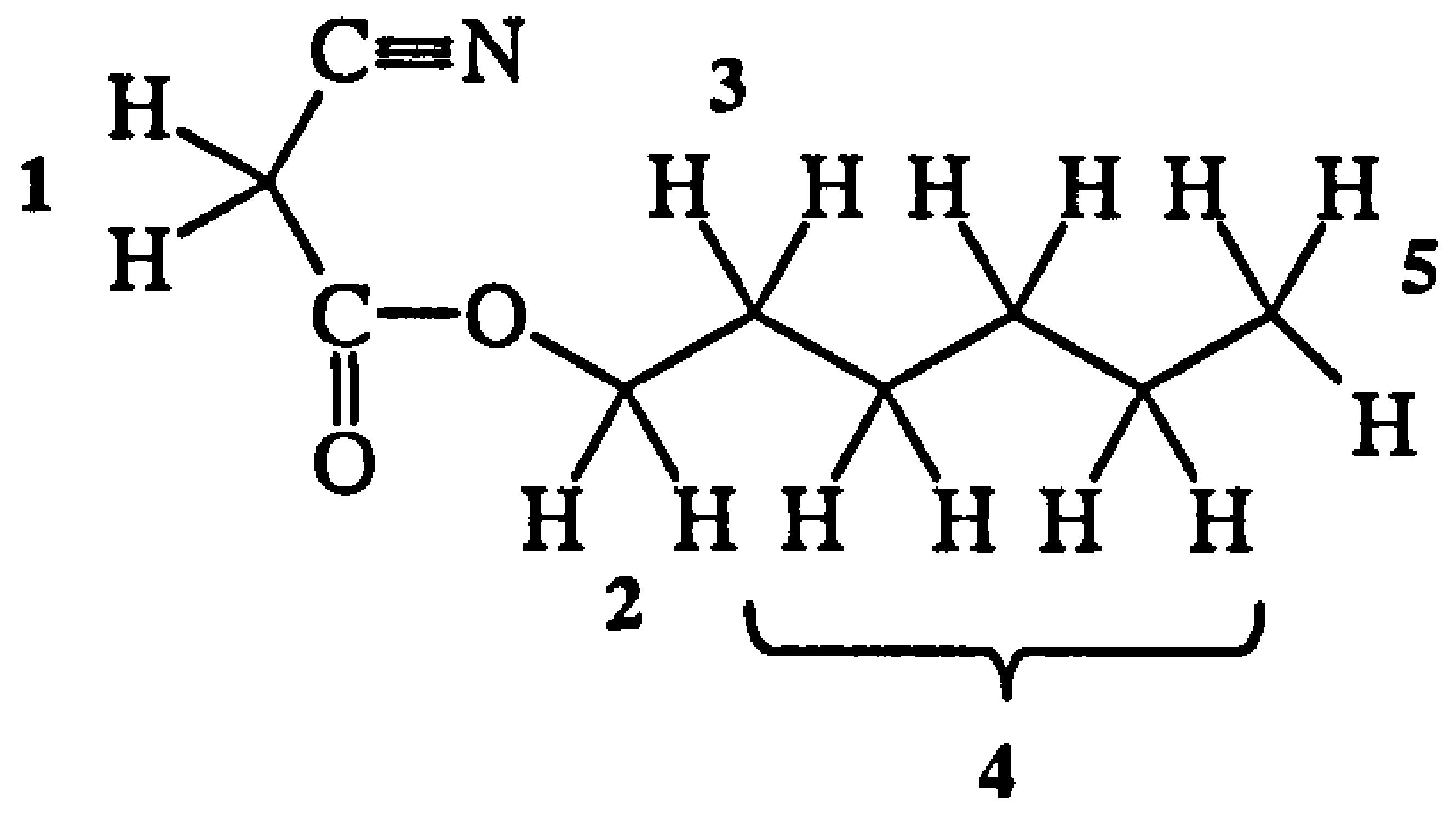
Cyanoacetic acid (45 g, 0.486 mol), hexanol (47 g, 0.46 mol) and concentrated sulphuric acid (1.0 cm^3) were refluxed in 100 cm^3 of benzene for three hours with the azeotrophic removal of water (8.3 cm^3, 0.46 mol). After cooling, the reaction mixture was concentrated by the removal of benzene in vacuuo to leave a clear yellow oil. This was distilled under vacuum to give hexyl cyanoacetate (71.1 g, 93%) as a clear colourless oil (b.p. = 82°C at 0.6mm/Hg). Calculated for C_9H_{15} : C, 63.9%; H, 8.9%; N, 8.3%; Found : C, 63.7%; H, 9.0%; N, 8.2%.

5.5.4.1 Characterisation

Infra-Red Spectroscopy - See appendix 4.9

2932 cm^{-1} (aliphatic C-H stretch), 2265 cm^{-1} (C-N stretch), 1748 cm^{-1} (CO ester stretch), 1468-1189 cm^{-1} (C-H bending in alkane), 997 cm^{-1} (C-C stretch in alkane)

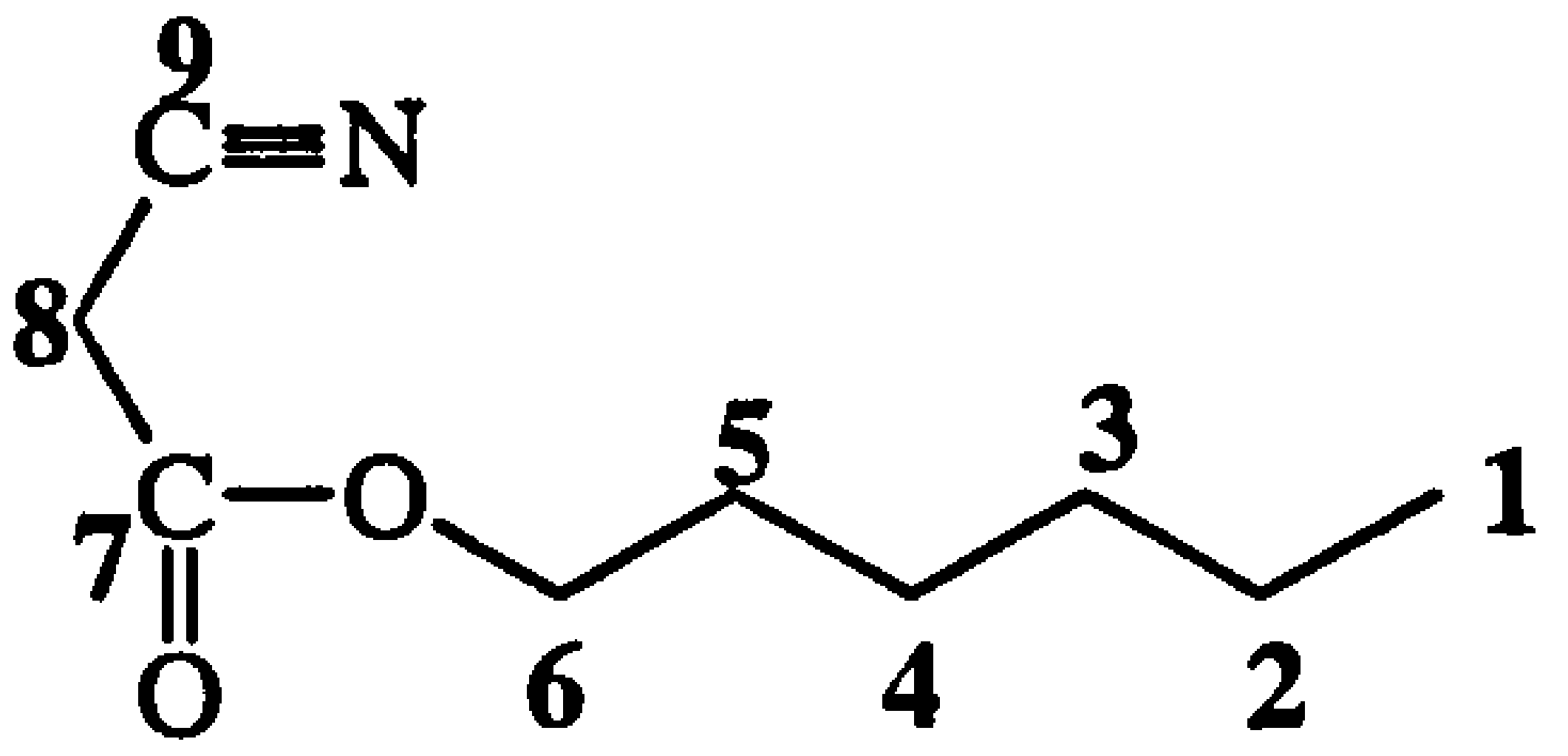
^{1}H NMR - See appendix 4.10



δ / ppm = 4.17 (m,2), 3.45 (m,1), 1.64 (m,3), 1.28 (m,4), 0.86 (m,5)

Intensity ratio 2:2:2:6:3

Carbon NMR - See appendix 4.11



δ / ppm = 163.03 (7), 113.06 (9), 66.97 (8), 31.14 (6), 28.11 (5), 25.19 (4), 24.61 (3), 22.32 (2), 13.80 (1)

5.5.5 Conversion of hexyl cyanoacetate to vinylcyclopropane derivative

To a suspension of sodium hydride (5 g, 0.21 mol) in THF (200 cm^3), a mixture of hexyl cyanoacetate (11.68 g, 0.069 mol) and *trans*-1,4-dibromobut-2-ene (15.40 g, 0.072 mol) in THF (150 cm^3), was added dropwise at room temperature under nitrogen. The reaction mixture was stirred overnight at room temperature. The reaction mixture was poured into cold 10% hydrochloric acid and extracted with diethyl ether. The etheral layer was washed twice with saturated sodium hydrogen carbonate, once with saturated sodium chloride solution and dried using magnesium sulphate. The mixture was filtered and the solvent removed in vacuuo yielding a brown oil. Distillation of this oil gave 1-cyano-1-hexoxycarbonyl-2-

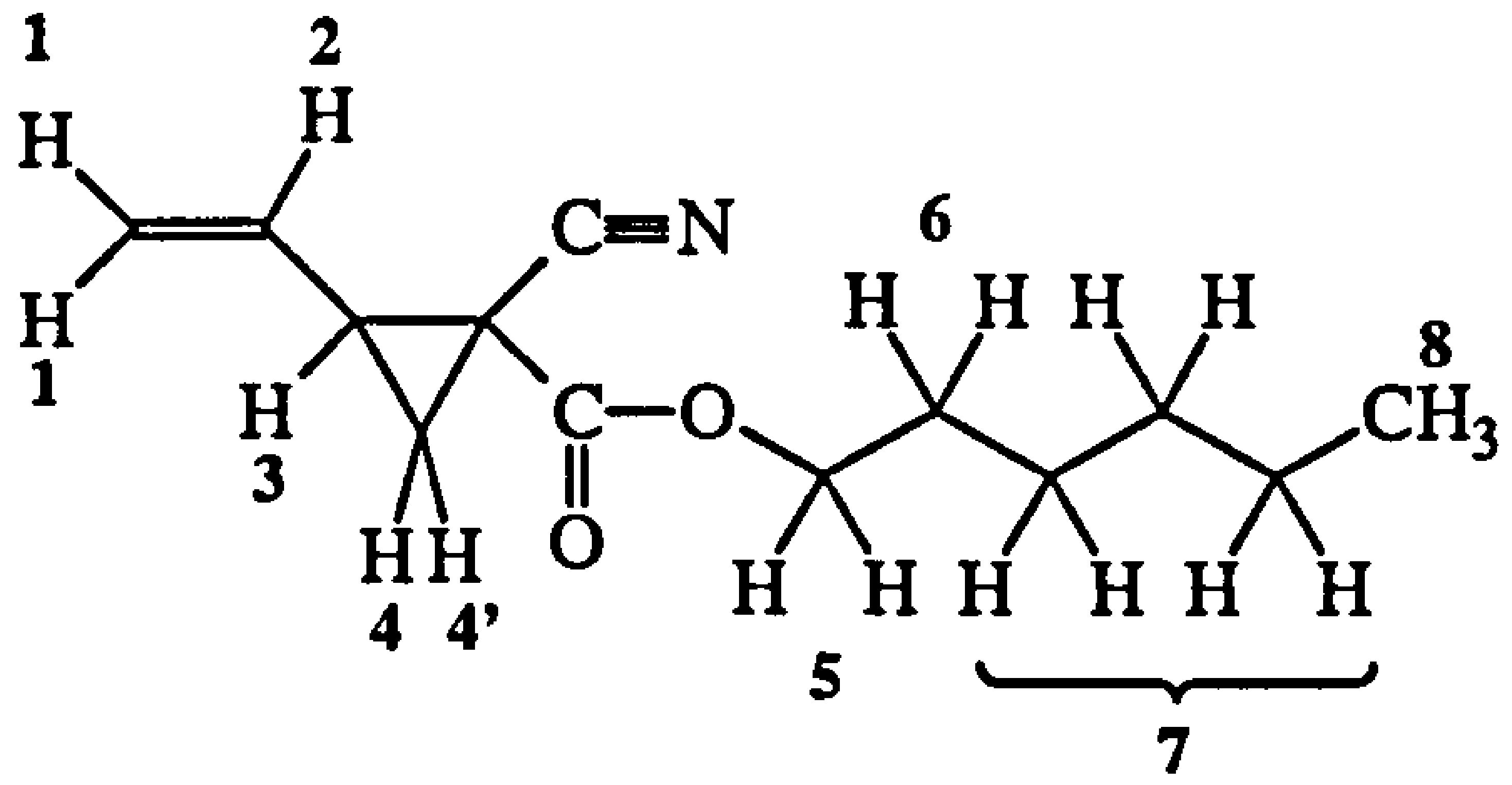
vinylcyclopropane (9.05 g, 59 %) as a clear colourless liquid (b.p. = 78°C at 0.2 mm/Hg). Calculated for $C_{13}H_{19}NO_2$: C, 70.6%; H, 8.7%; N, 6.3%; Found : C, 70.3%; H, 8.8%; N, 6.2%.

5.5.5.1 Characterisation

Infra-Red Spectroscopy - See appendix 4.12

2957 cm^{-1} (aliphatic C-H stretch), 2245 cm^{-1} (CN stretch), 1736 cm^{-1} (CO ester stretch), 1640 cm^{-1} (C=C stretch), 1467 cm^{-1} (C-H bending in ring), 1171 cm^{-1} (C-O ester stretch), 923 cm^{-1} (out of plane terminal vinylic C-H deformation)

^1H NMR - See appendix 4.13

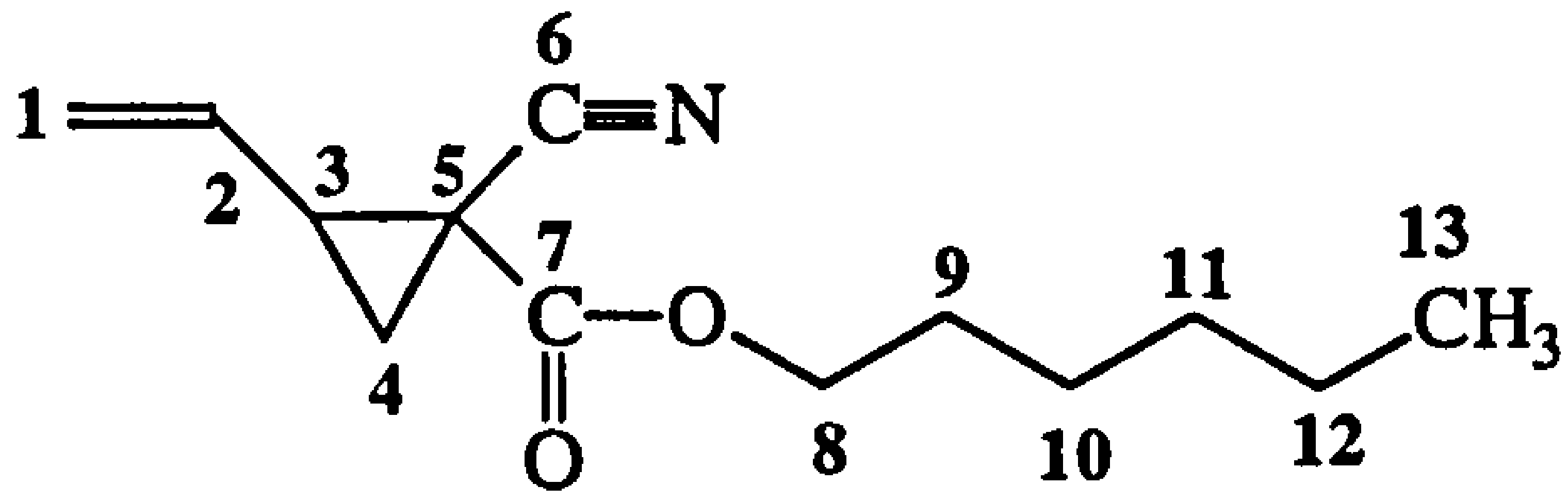


where 4' is in the same plane as 3

δ / ppm = 5.61 (m,2), 5.45 (m,1), 4.18 (m,5), 2.53 (m,3), 1.97 (m,4'), 1.67 (m,4&6) 1.30 (m,7), 0.89 (m,8)

Intensity ratio = 1:2:2:1:1:3:6:3

Carbon NMR - See appendix 4.14

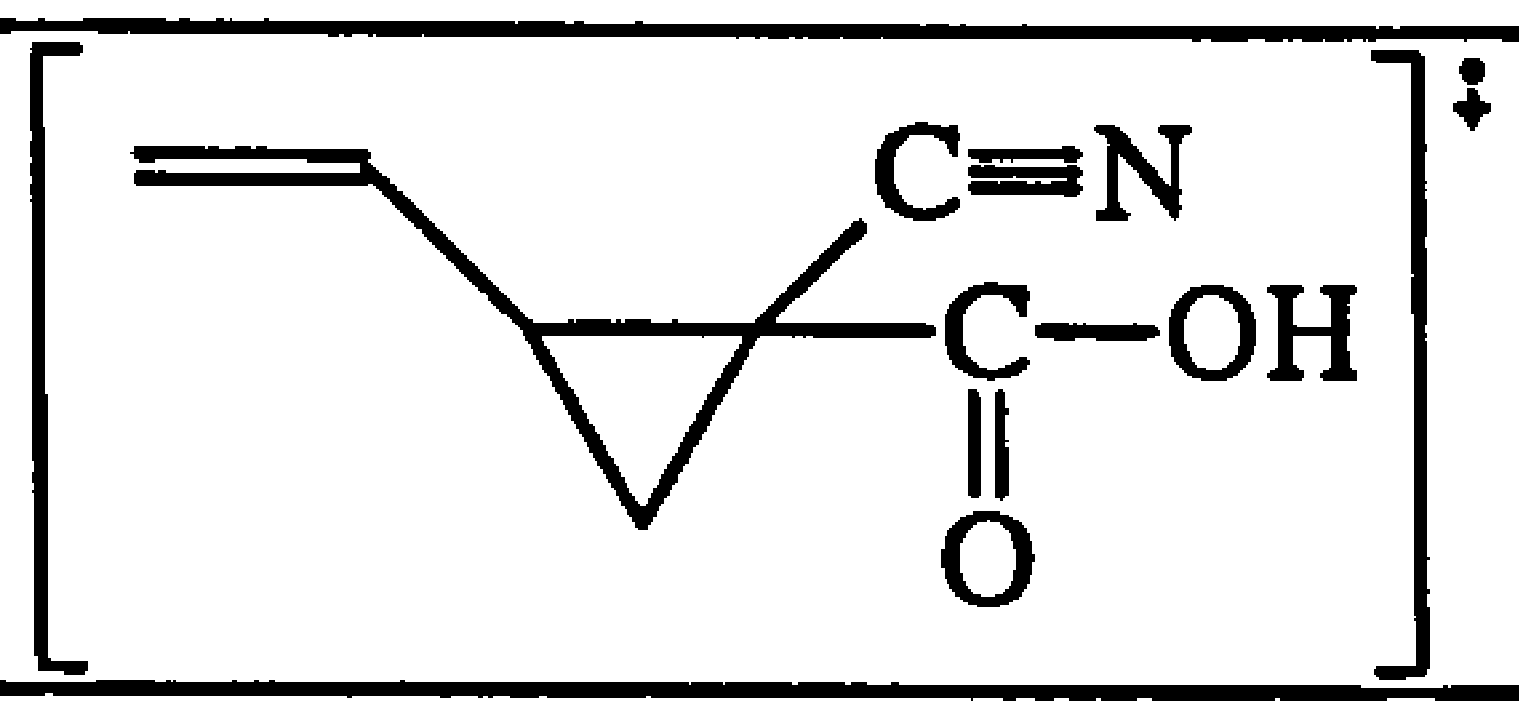
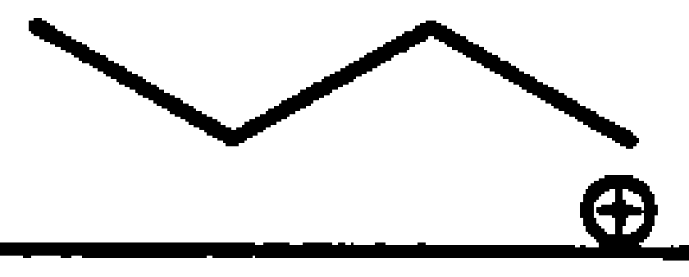


δ / ppm = 167.45 and 165.48 (7), 132.39 and 130.80 (2), 121.58 and 121.05 (1), 118.90 and 116.92 (6), 67.35 and 67.15 (8), 35.91 and 33.96 (3), 31.55 and 31.53 (9), 28.62 and 28.56 (4), 25.60 and 25.59 (10), 24.11 (11), 22.69 (12), 14.19 (13)

Assignments were made by comparison to the DEPT spectrum.

Mass Spectrometry - See appendix 4.15

M/Z	Assignment

137	
57	
43	

5.5.6 Typical Polymerisation

The monomer (3 mmol) was weighed into an ampoule. The required amount of initiator (see tables 5-3, 5-6 and 5-9) and dry solvent (5 cm^3) if required, were added. The contents of the ampoule were frozen and degassed by the freeze/thaw method. The ampoule was left under vacuum and placed in an oil bath at the required temperature for the desired length of time.

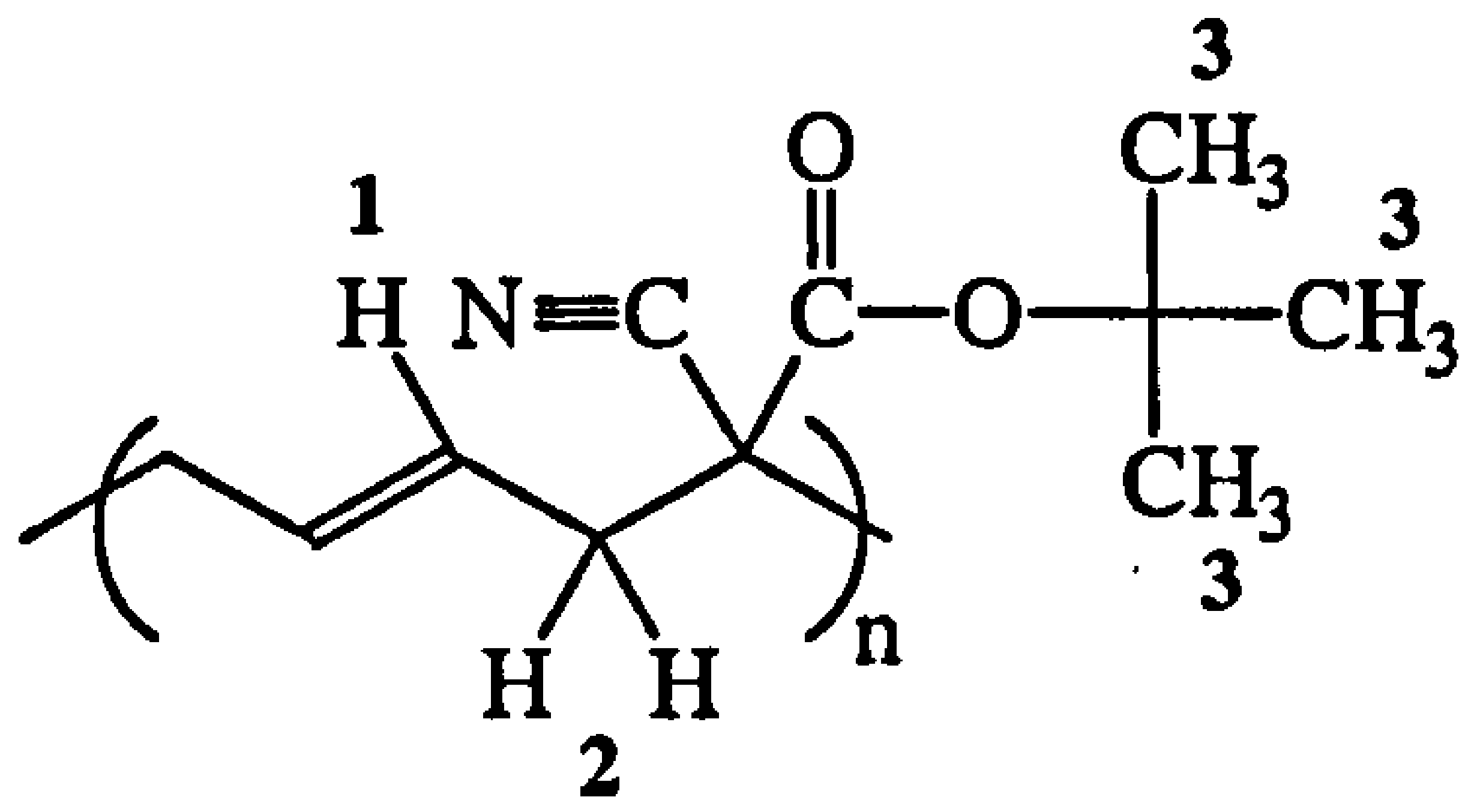
5.5.6.1 Characterisation of *tert*-Butyl Polymers

Infra-Red Spectroscopy - All spectra were indistinguishable. The spectrum of sample A is shown as a typical spectrum. See appendix 4.16

2979 cm^{-1} (aliphatic C-H stretch), 2243 cm^{-1} (CN stretch), 1734 cm^{-1} (CO ester stretch), 1370 cm^{-1} (C-H bend of *tert*-butyl group), 1155 cm^{-1} (C-O ester stretch), 973 cm^{-1} (C=C *trans* stretch)

No IR spectrum was gained for sample I

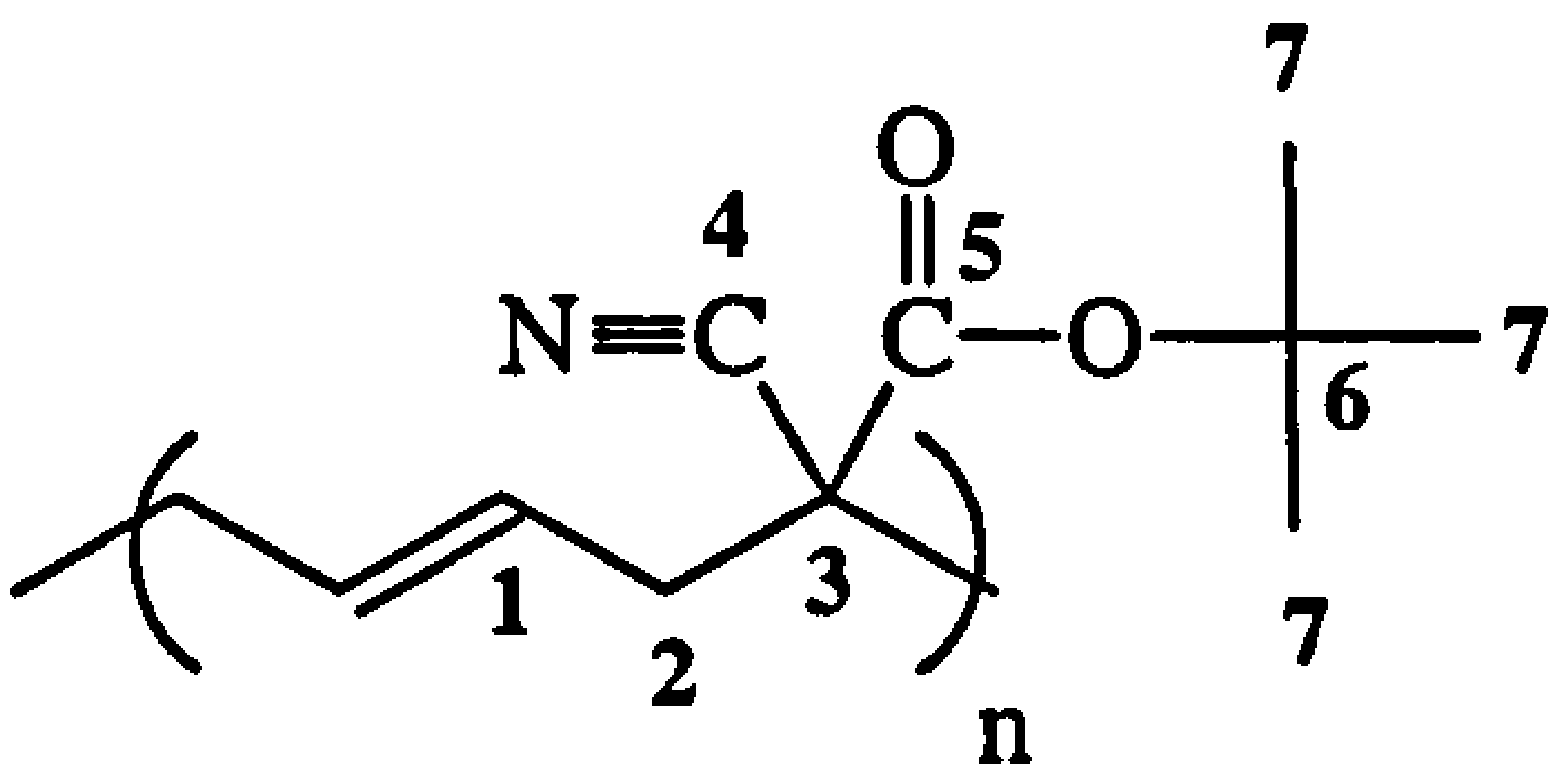
^{1}H NMR - All spectra were indistinguishable. The spectrum of sample H is shown as a typical spectrum. See appendix 4.17.



δ / ppm = 5.67 (m,1), 2.61 and 2.49 (m,2), 1.50 (s,3)

Intensity ratio = 2:4:9

Carbon NMR - All spectra were indistinguishable. The spectrum of sample E is shown as a typical spectrum. See appendix 4.18.



δ / ppm = 166.76 (5), 128.90(1), 118.63 (4), 84.62 (6), 50.12 (2), 39.65 (3), 28.12 (7)

Gel Permeation Chromatography - See appendix 4.19 for the GPC trace of sample G which was typical of the GPC traces produced.

Sample	Mn	Mw	Polydispersity
A	243 000	649 000	2.67
C	167 000	741 000	4.43
D	31 000	48 000	1.56
E	58 000	126 000	2.18
F	54 000	133 000	2.45
G	202 000	419 000	2.08
H	191 000	767 000	4.03

Differential Scanning Calorimetry - See appendix 4.20 for the DSC trace of sample F which was typical of the DSC traces produced.

Sample	T_g /°C
A	55.9
C	58.0
D	59.2
E	53.6
F	54.6
G	50.4
H	58.5

Elemental Analysis

		Found							
	Calculated	A	C	D	E	F	G	H	I
C%	68.4	68.3	67.7	67.7	68.2	68.1	68.3	68.1	67.3
H%	7.8	7.8	7.8	7.9	8.1	7.9	8.1	7.9	7.8
N%	7.2	7.0	7.2	7.2	7.3	7.2	7.2	7.1	7.1

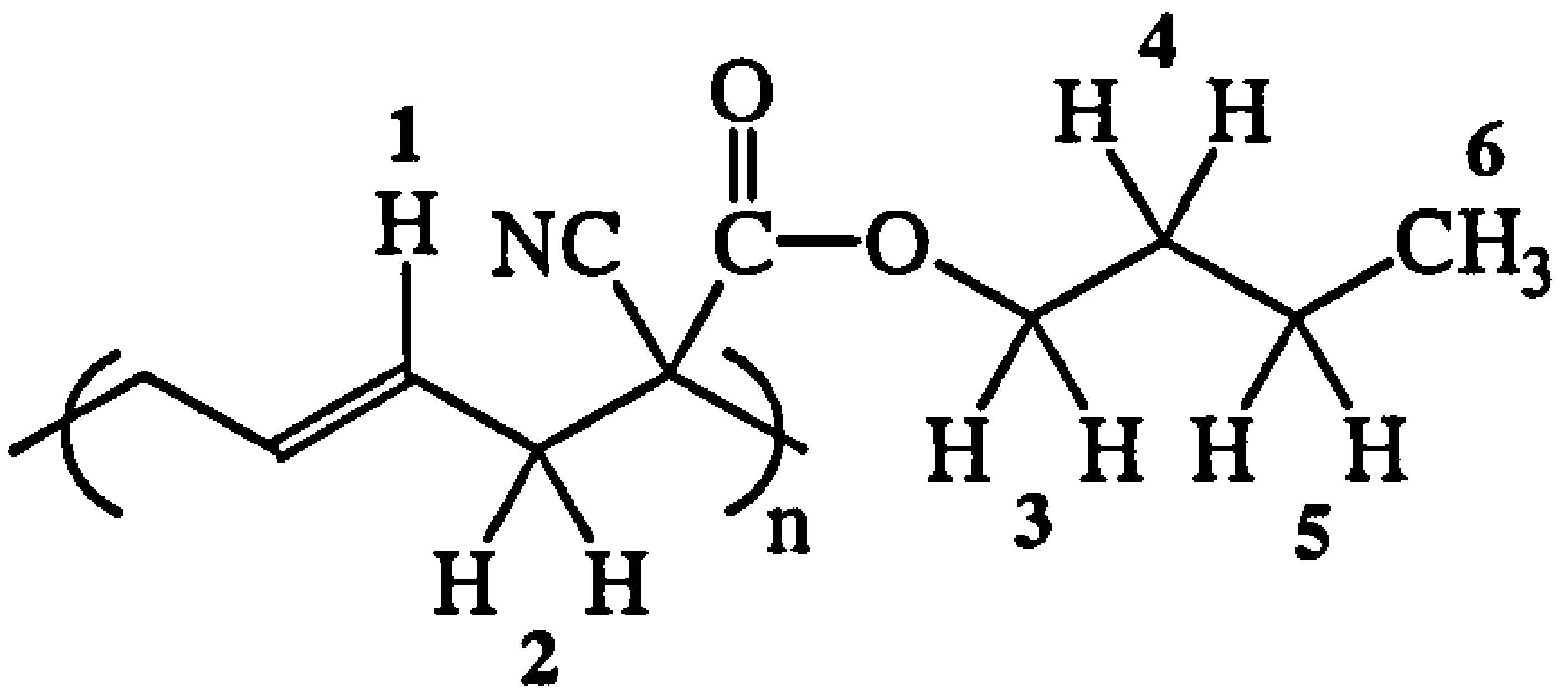
5.5.6.2 Characterisation of n-Butyl Polymers

Infra-Red Spectroscopy - All spectra were indistinguishable. The spectrum of sample A is shown as a typical spectrum. See appendix 4.21

2934 cm^{-1} (aliphatic C-H stretch), 2244 cm^{-1} (CN stretch), 1741 cm^{-1} (CO ester stretch), 1213 cm^{-1} (C-O ester stretch), 974 cm^{-1} (C=C *trans* stretch), 726 cm^{-1} (C=C *cis* stretch)

No IR spectrum was gained for sample I

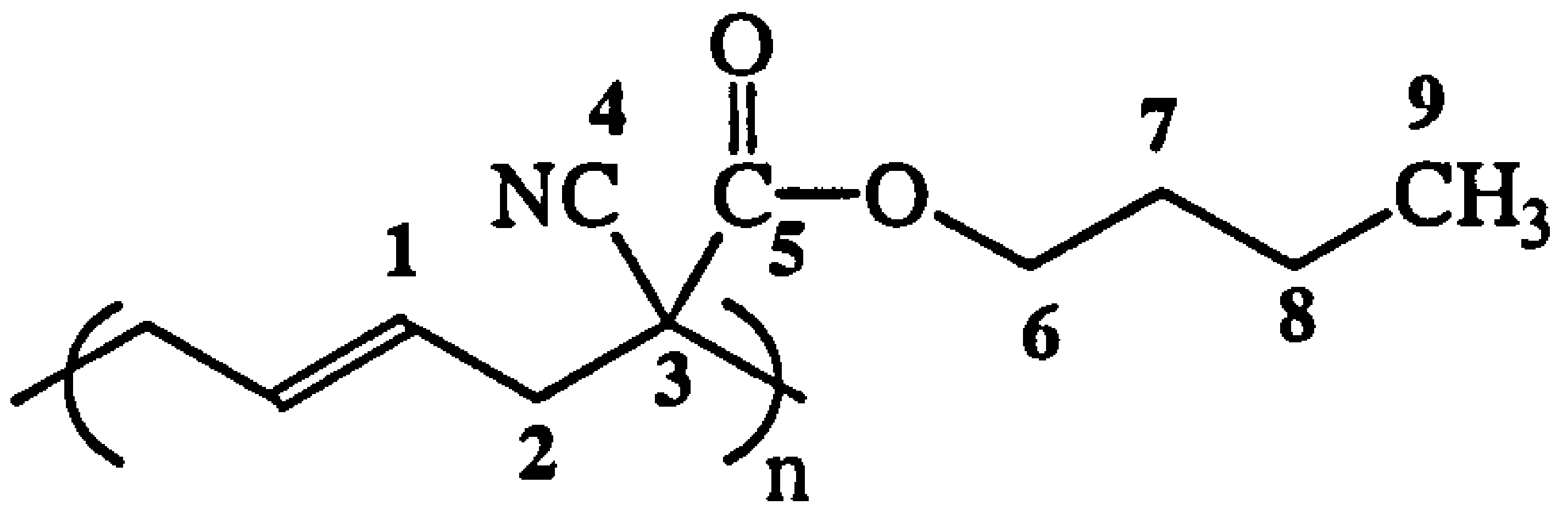
^{1}H NMR - All spectra were indistinguishable. The spectrum of sample F is shown as a typical spectrum. See appendix 4.22.



δ / ppm = 5.63 (s,1), 4.19 (t,3), 2.59 and 2.51 (m,2), 1.64 (m,4), 1.40 (m,5), 0.94 (m,6)

Intensity ratio = 2:2:4:2:3

Carbon NMR - All spectra were indistinguishable. The spectrum of sample D is shown as a typical spectrum. See appendix 4.23.



δ / ppm = 167.76 (5), 129.02 (1), 118.31 (4), 67.03 (6), 49.71 (2), 39.45 (3), 30.60 (7), 19.21 (8), 13.89 (9)

Gel Permeation Chromatography - See appendix 4.24 for the GPC trace of sample C which was typical of the GPC traces produced.

Sample	Mn	Mw	Polydispersity
A	154 000	509 000	3.31
C	109 000	340 000	3.11
D	87 000	304 000	3.47
E	81 000	236 000	2.91
F	29 000	79 000	2.72
G	166 000	498 000	3.00
H	137 000	516 000	3.76

Differential Scanning Calorimetry - See appendix 4.25 for the DSC trace of sample F which was typical of the DSC traces produced.

Sample	T_g /°C
A	-1.3
C	-4.1
D	-4.7
E	-4.1
F	-5.1
G	-3.1
H	-3.7

Elemental Analysis

		Found							
	Calculated	A	C	D	E	F	G	H	I
C%	68.4	68.3	68.2	68.3	68.4	68.3	68.3	68.5	67.9
H%	7.8	7.8	7.8	7.8	7.9	7.8	7.9	7.9	7.8
N%	7.2	7.0	7.1	7.2	7.3	7.3	7.3	7.3	7.1

It can be seen that sample I is not pure and this will be due to the trapped monomer.

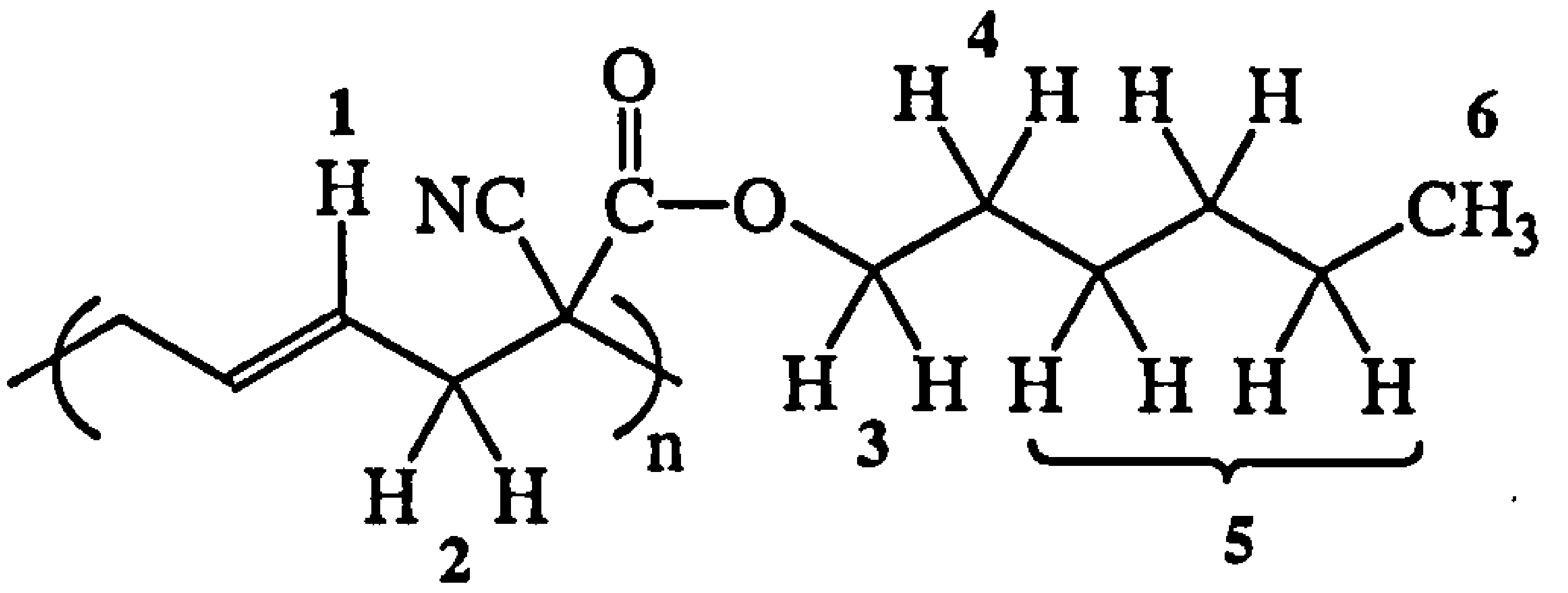
5.5.6.3 Characterisation of Hexyl Polymers

Infra-Red Spectroscopy - All spectra were indistinguishable. The spectrum of sample A is shown as a typical spectrum. See appendix 4.26

2930 cm^{-1} (aliphatic C-H stretch), 2245 cm^{-1} (CN stretch), 1741 cm^{-1} (CO ester stretch), 1213 cm^{-1} (C-O ester stretch), 974 cm^{-1} (C=C *trans* stretch), 726 cm^{-1} (C=C *cis* stretch)

No IR spectrum was gained for sample I

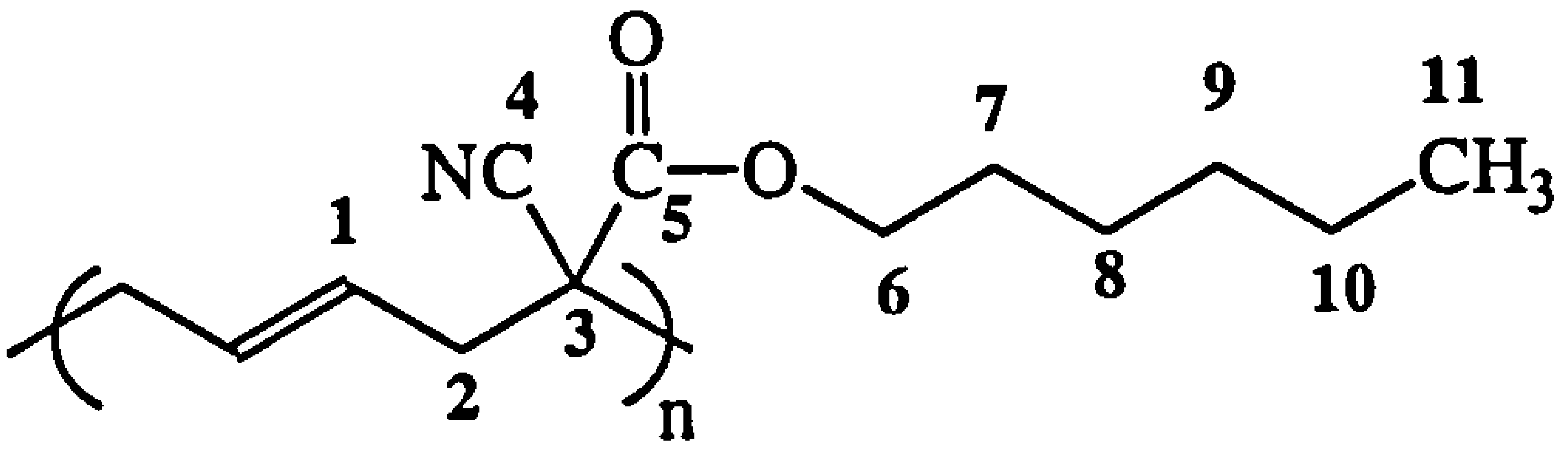
^{1}H NMR - All spectra were indistinguishable. The spectrum of sample H is shown as a typical spectrum. See appendix 4.27



δ / ppm = 5.63 (s,1), 4.17 (t,3), 2.59 and 2.50 (m,2), 1.65 (m,4), 1.31 (m,5), 0.89 (t,6)

Intensity Ratio = 2:2:4:2:6:3

Carbon NMR - All spectra were indistinguishable. The spectrum of sample A is shown as a typical spectrum. See appendix 4.28



δ / ppm = 167.51 (5), 128.77 (1), 118.03 (4), 67.08 (6), 49.47 (2), 39.23 (3), 31.29 (7), 28.31 (8), 25.36 (9), 22.48 (10), 13.98 (11)

Gel Permeation Chromatography - See appendix 4.29 for the GPC trace of sample D which was typical of the GPC traces produced.

Sample	Mn	Mw	Polydispersity
A	388 000	973 000	2.51
C	266 000	681 000	2.56
D	65 000	182 000	2.80
E	75 000	184 000	2.46
F	35 000	106 000	2.99
G	123 000	272 000	2.21
H	98 000	309 000	3.15

Differential Scanning Calorimetry - See appendix 4.30 for the DSC trace of sample H which was typical of the DSC traces produced.

Sample	T_g /°C
A	-23.1
C	-23.7
D	-22.3
E	-22.3
F	-22.2
G	-22.4
H	-23.1

Elemental Analysis

		Found							
	Calculated	A	C	D	E	F	G	H	I
C%	70.6	70.5	70.6	70.8	70.4	70.4	70.7	70.7	70.7
H%	8.7	8.7	8.9	8.9	8.7	8.7	8.8	8.9	8.9
N%	6.3	6.2	6.5	6.6	6.2	6.4	6.5	6.4	6.2

5.6 References

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Chapter 6

Copolymerisation of 1,1-dicyano-vinylcyclopropane and 1-cyano-1-hexoxycarbonyl-vinylcyclopropane

6. Free-radical copolymerisation of 1,1-dicyano-2-vinylcyclopropane and 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane

6.1 Introduction

In chapter three, the polymerisation of 1,1-dicyano-2-vinylcylopropane was described. The product was an insoluble polymer with a Tg of ~77°C. Attempts to incorporate this monomer into a copolymer in order to obtain a soluble polar polymer with a lower glass transition temperature failed. Neither solution nor emulsion copolymerisation of this monomer with butyl acrylate were successful.

In chapter five an attempt to produce soluble elastomers by replacing one of the cyano groups in the 1,1-dicyano-2-vinylcyclopropane monomer with a series of ester groups was reported. This work was successful; when the ester alkyl group was butyl or hexyl ester, polymers with a Tg below room temperature were obtained.

There was concern that the replacement of a cyano group by an ester group would lead to a large decrease in the polarity of the polymer so it was decided to attempt the copolymerisation of 1,1-dicyano-2-vinylcyclopropane with 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane. It was hoped that the incorporation of the dicyano monomer would increase the polarity of the hexyl ester polymer whilst the long alkyl chain of the ester would allow the polymer to retain the solubility and low glass transition temperature required.

6.2 Copolymerisation of 1,1-dicyano-2-vinylcyclopropane and 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane

The copolymerisations were carried out using the various ratios of the two monomers shown below.

	Mass of hexyl ester monomer X / g	Mass of dicyano monomer Y / g	Molar % of hexyl ester monomer X	Molar % of dicyano monomer Y
A	1.5	0.5	62	38
B	1.0	1.0	35	65
C	0.5	1.5	15	85

Table 6-1 Ratios of monomers used in the copolymerisation of 1,1-dicyano-2-vinylcyclopropane and 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane

The copolymerisations were carried out at 60°C in benzene using 1.5 mole% AIBN as initiator. For full details, see experimental section.

After 24 hours, samples A and B were clear, pale yellow viscous solutions. The products were precipitated by pouring the reaction mixtures into excess methanol, recovered by decantation and dried under vacuum for 24 hours. The methanol used to precipitate the polymers was reduced in vaccuo and the resulting residues were analysed by NMR. The residues were found to be a mixture of the two monomers suggesting that they have similar reactivities.

After 24 hours, sample C had set to a soft yellow gel which could not be dissolved in chloroform even after prolonged warming and stirring. The gel was therefore washed with chloroform and allowed to dry. After drying it was ground using a pestle and mortar to give a white powdery solid which was washed several times with methanol and then dried overnight under vacuum.

The yields and appearances of the polymers obtained are shown below.

Sample	Yield / %	Appearance
A	51	Clear, colourless, rubbery solid
B	61	White, stiff, rubbery solid
C	51	White powder

Table 6-2 Results of the copolymerisation of 1,1-dicyano-2-vinylcyclopropane and 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane

These yields are comparable to those achieved for the hexyl ester homopolymer and are greatly improved from those obtained for the dicyano homopolymer.

6.2.1 Analysis of percentage composition

The incorporation of each monomer into the homopolymer was investigated by analysis of elemental analysis and ^{13}C NMR spectroscopic data.

6.2.1.1 Elemental analysis

The calculated elemental analysis results for the two homopolymers are shown below along with the experimental values obtained for the three copolymers.

	%C	%H	%N
Hexyl ester homopolymer X	70.56	8.65	6.33
Dicyano homopolymer Y	71.17	5.12	23.71
Copolymer A	70.56	8.21	9.30
Copolymer B	70.78	7.50	12.44
Copolymer C	70.70	6.36	17.30

Table 6-3 Experimental elemental analysis data for the copolymers

By comparing the experimental percentage nitrogen and percentage hydrogen values of the copolymers with the theoretical values for the two homopolymers, it was possible to calculate the percentages of the two monomers present in the copolymers. The calculations for copolymer A using the percentage nitrogen values are shown below.

Let the percentages of monomer X and Y equal x and y respectively.

$$x + y = 1 \quad \Rightarrow \quad x = 1 - y$$

$$6.33x + 23.71y = 9.30 \quad \Rightarrow \quad 6.33 - 6.33y + 23.71y = 9.30$$

$$y = 0.17 \quad \text{and} \quad x = 0.83$$

The values obtained for the percentages of monomers in the copolymers are shown below.

	% Hexyl Ester monomer residue		% Dicyano monomer residue	
	from N	from H	from N	from H
A	83	88	17	12
B	65	67	35	33
C	37	35	63	65

Table 6-4 Percentages of monomer residues incorporated in copolymers as calculated from elemental analysis data

Within the likely error limits of the elemental analyses, these results show that there is more of the ester monomer in the copolymer than is present in the feed. This is reasonable and in line with the earlier observation that the ester monomers were quantitatively more easily polymerised than the dicyano monomer. The data is insufficient in quantity and quality to derive reactivity ratios.

6.2.1.2 ^{13}C NMR spectroscopic data

In an alternative approach, ^{13}C NMR spectroscopic analyses were used to establish the percentages of the monomer residues in the copolymers by integrating the carbon peaks associated with the cyano carbons in the spectra recorded under quantitative conditions. There are two peaks for the cyano carbons, one for each monomer residue and these appear at ~ 118 ppm and ~114 ppm, the peak at higher shift corresponding to the cyano carbon in the hexyl ester containing monomer unit. By comparing the intensity of these two peaks, it was possible to calculate the relative percentages of the two monomer residues present in the copolymer. It was taken into account that, in the dicyano monomer, there are two cyano carbons and this will double the peak intensity. It was therefore necessary to compare the ratio of the intensity of the 118 ppm peak with half the intensity of the 114 ppm peak. The incorporation ratios are tabulated below.

	% Hexyl ester monomer residue	% Dicyano monomer residue
A	76	24
B	52	48
C	24	76

Table 6-5 Percentages of monomer residues incorporated in copolymers as calculated from ^{13}C NMR data

Whilst there is not exact agreement between the values obtained from analysis of the NMR data with those obtained from elemental analysis data, both methods show that the cyanoester monomer is more readily incorporated into the copolymer chain than the dicyano monomer.

6.2.2 NMR analysis

The ^1H NMR spectra were recorded for chloroform solutions of samples A and B. Sample C was not sufficiently soluble in chloroform and was therefore analysed as a solution in DMSO.

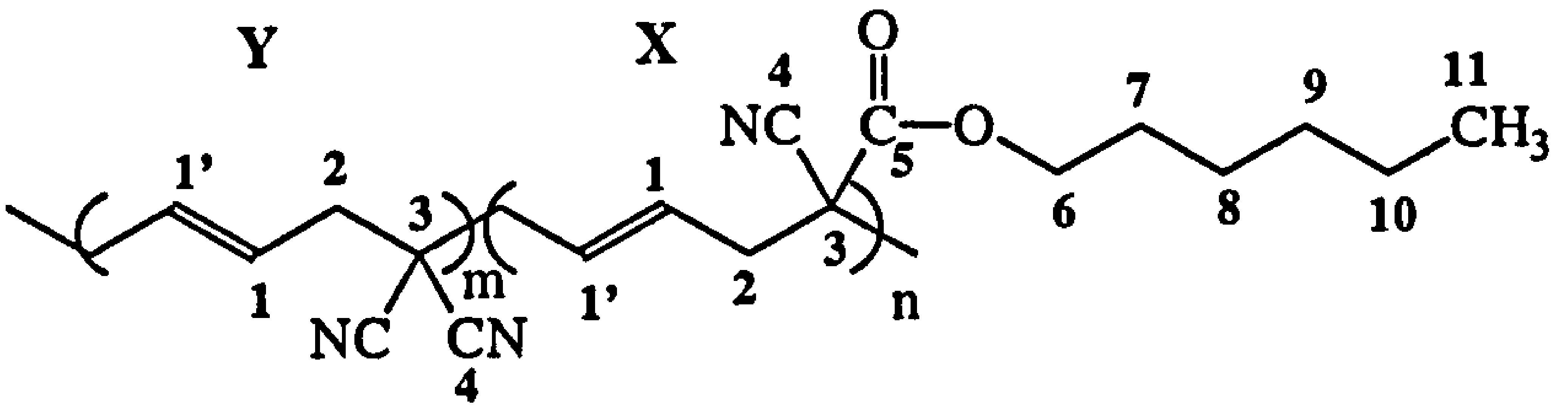
Peaks for the hydrogens on the ester chain were observed as broad, mainly unresolved mulitplets. The hydrogens situated on the backbone of the chain gave more complex peaks. This complexity arises from several sources; tacticity, *cis/trans* isomerism, inequivalence in certain situations and from copolymer sequence distribution.

Analysis of the IR spectra showed a strong band at 975 cm^{-1} corresponding to *trans* double bonds and a weak band at 731 cm^{-1} corresponding to *cis* double bonds. This analysis along with the conclusions drawn earlier about the double bond conformation in the homopolymers leads to the conclusion that the copolymers contain predominantly *trans* double bonds.

Resolution was not sufficient in either the ^1H or ^{13}C NMR spectra for conclusions to be made about the tacticity of the copolymers.

The ^{13}C NMR spectra were recorded for chloroform solutions of copolymers A and B and a hot DMSO solution of copolymer C.

Samples A and B both showed the same peak positions and by comparison with the peak positions obtained for the two fully characterised homopolymers, it was possible to assign the peaks as shown below.



δ / ppm = 167.78 (5), 131.60, 129.26 and 127.11 (X&Y 1&1'), 118.28 (X4), 114.84 (Y4), 67.49 (6), 49.61 (X2), 39.67 (Y2), 39.10 (X3), 37.59 (Y3), 31.53 (7), 28.54 (8), 25.60 (9), 22.73 (10), 14.25 (11)

Sample C showed the same set of peaks although at slightly different shifts, as expected.

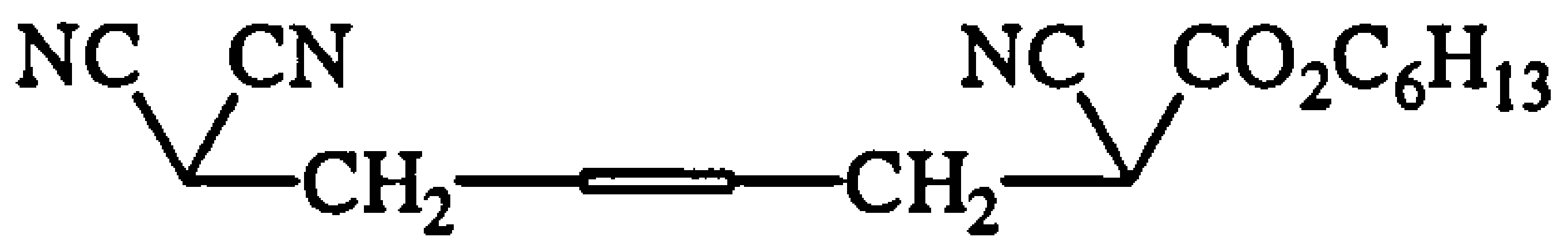
The peaks for the olefinic carbons (1 and 1') show a complex splitting pattern and this is due to several factors including copolymer sequence distribution.

6.2.3 Copolymer sequence distribution

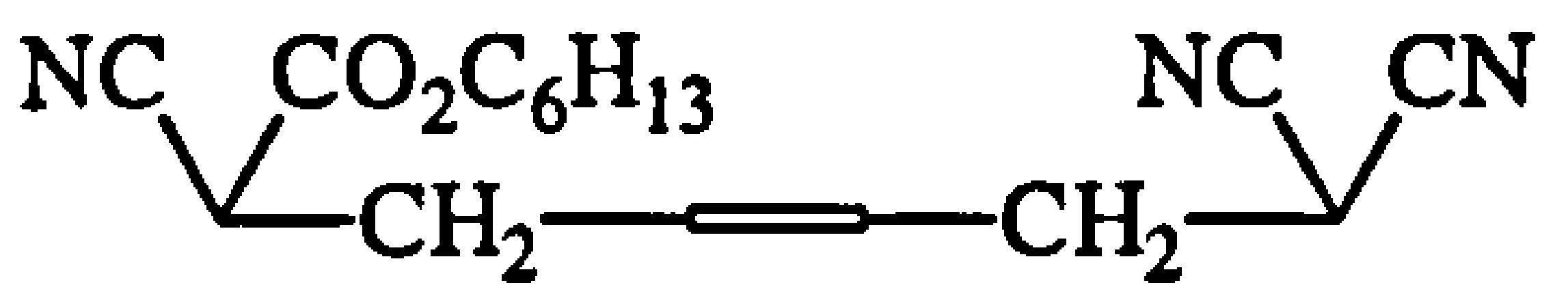
For two adjacent monomer residue units, there are four different arrangements possible. These can be represented as -X-X-, -Y-Y-, -X-Y- and -Y-X-.

The environments of the hydrogens on the double bond are affected by which monomer residue is situated next to them. There are four possibilities (ignoring chirality effects);

YY



YX

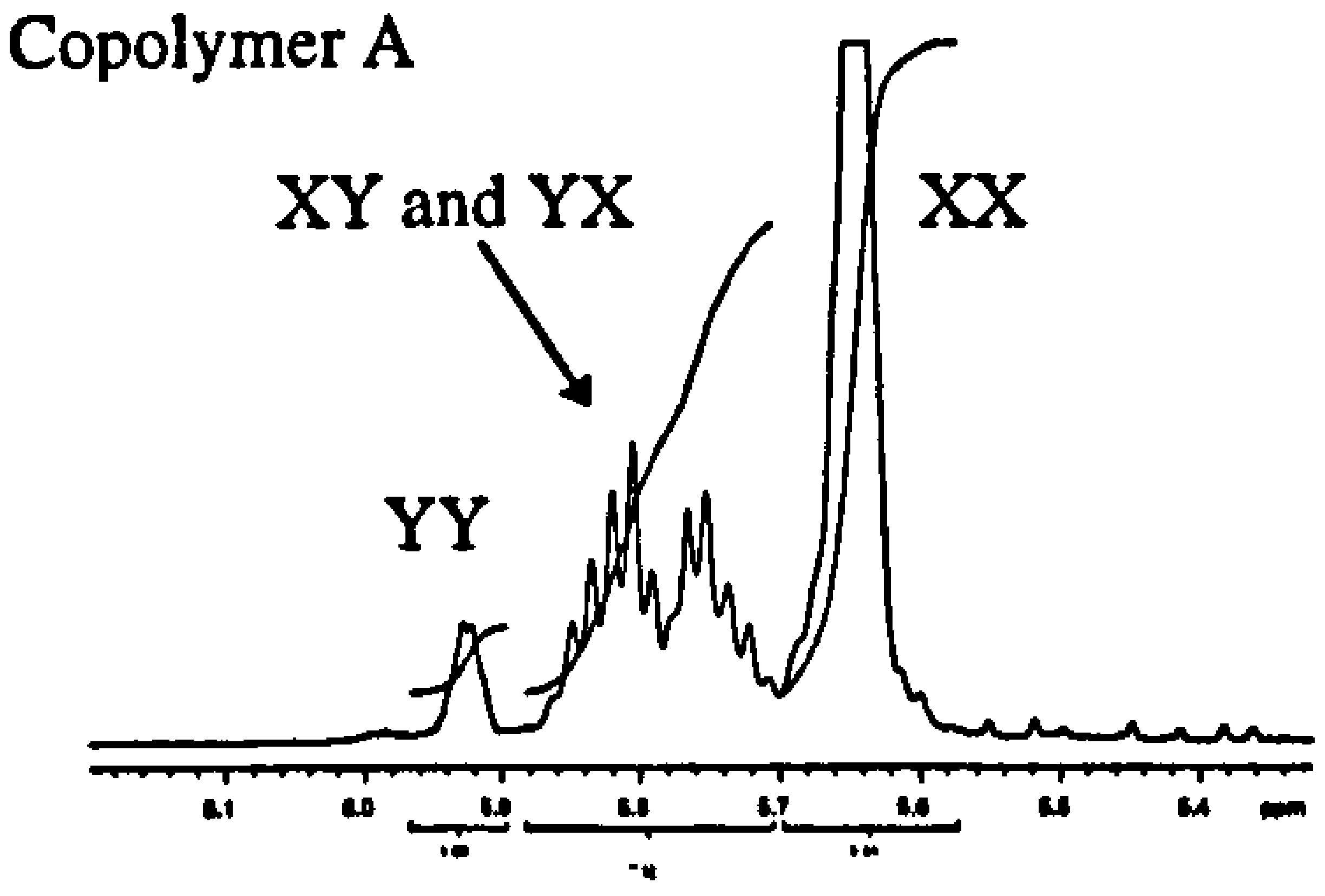


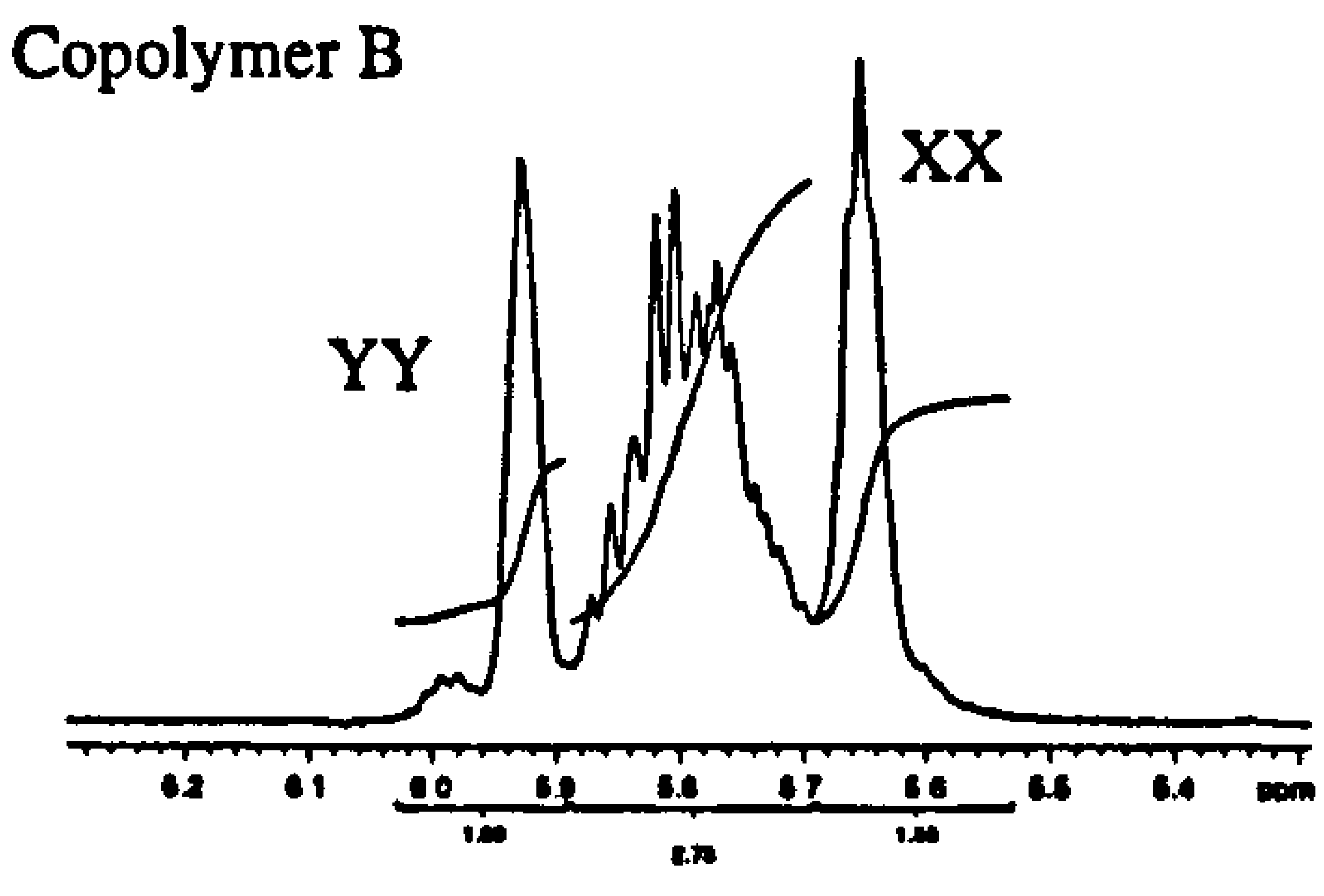
XY

XX

The ^{1}H NMR spectra for the olefinic regions are fairly complex and in the XY and YX cases, the two olefinic hydrogens are inequivalent and therefore it can be seen that for one of these hydrogens the monomer sequence XY is not the same as YX. Since the two olefinic hydrogens are inequivalent, splitting arises in the XY and YX peaks complicating the spectrum to an even greater extent.

The peaks corresponding to the olefinic hydrogens are shown below. The assignments follow straightforwardly from the known copolymer compositions and the fully assigned homopolymer spectra.





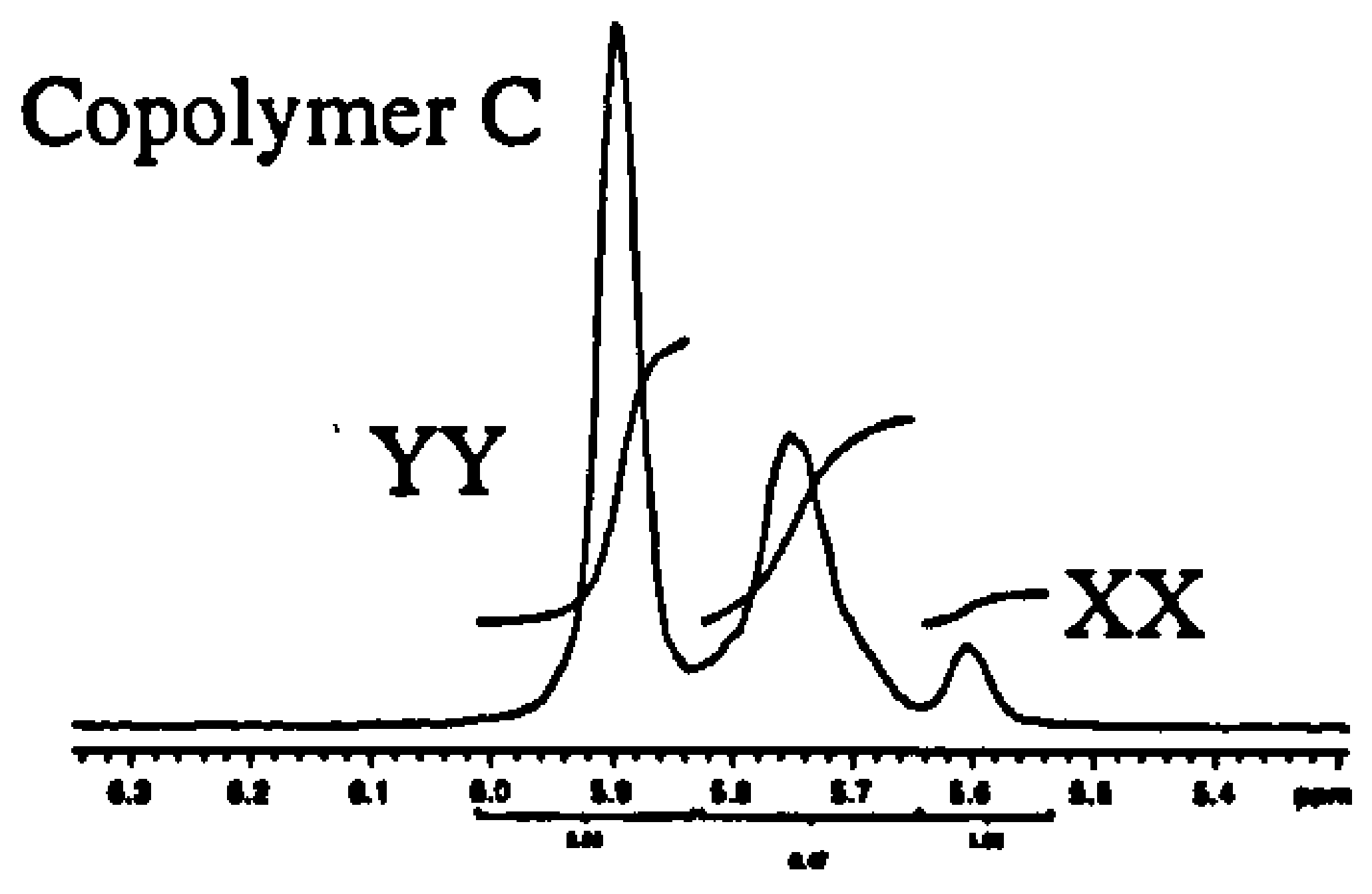


Figure 6-1 ^{1}H NMR peaks for the olefinic carbons in the copolymers

It can be seen that the XY and YX peaks overlap and it was not possible to completely assign these peaks. The different monomer residues can be detected but the resolution is insufficient to give quantitative information on the distribution.

The methylene hydrogens are subject to splittings caused by the same factors as the olefinic hydrogen splittings. In the ^{1}H NMR spectra of samples A and B, the peaks for the methylene hydrogens were poorly resolved and could not be completely assigned. In the ^{1}H NMR of sample C, the resolution was improved but again it was not possible to fully assign each peak.

In the ^{13}C NMR, the olefinic carbons will be subject to the same splitting effects as the hydrogens *i.e.* tacticity, *cis/trans* isomerism, inequivalence and copolymer sequence distribution.

It is possible to work out the relative intensities of the peaks corresponding to XX, YY, XY and YX residues assuming that the polymer is a statistical copolymer. If the experimental observations deviate from these predictions we have to assume that the copolymer does not contain a statistical distribution. There are several other types of copolymer as shown below.

Statistical	-X-Y-X-Y-Y-X-Y-X-X-Y-X-Y-
Alternating	-X-Y-X-Y-X-Y-X-Y-X-Y-X-Y-
Block	-X-X-X-X-X-X-Y-Y-Y-Y-Y-Y-

In a statistical copolymer, it is assumed that all sequences are equally probable and that there is no preference for any particular sequence. Statistical analysis can be used to calculate the expected relative intensities of the peaks corresponding to the various sequences.

For example, in copolymer A there was 38 mole% of monomer Y and 62 mole% of monomer X in the feed. If we assume ideal statistical copolymerisation, at an active polymer end there a greater probability that an X unit will add to the chain.

The exact probability for each sequence is shown below.

Probability of X = 0.62 Probability of Y = 0.38

Probability of XX = 0.62 x 0.62 = 0.3844

Probability of YY = 0.38 x 0.38 = 0.1444

Probability of XY = 0.38 x 0.62 = 0.2356

Probability of YX = 0.38 x 0.62 = 0.2356

XX:XY:YX:YY = 2.7 : 1.6 : 1.6 : 1

This means therefore that, if it is a statistical copolymer, there should be four peaks with the relative intensities 2.7:1.6:1.6:1 for the olefinic carbon in the ^{13}C NMR spectrum of copolymer A.

This ratio has been calculated using the ideal statistical incorporation values based on the percentages of the monomers present in feed. It has been shown, however, that the actual percentages of the monomer residues in the copolymer does not reflect that in the feed. It was necessary to calculate the expected intensities of the peaks based on the percentage of the monomer residues as calculated by the ^{13}C and elemental analysis data. In practice, it was observed that the ^{13}C NMR peaks for XY and YX came at the highest and lowest shifts with the peaks for XX and YY overlapping as a central peak leading to a triplet. The expected intensities of these triplets are tabulated below.

	mixed : XX/YY : mixed		
Copolymer	from N elemental analysis %	from H elemental analysis %	from NMR % (^{13}C of CN groups)
A	1 : 5.2 : 1	1 : 7.4 : 1	1 : 3.5 : 1
B	1 : 2.3 :1	1 : 2.5 : 1	1 : 2.3 : 1
C	1 : 2.3 : 1	1 : 2.4 : 1	1 : 3.5 : 1

Table 6-6 Calculated integrated intensities for the olefinic carbons in the ^{13}C NMR spectra of the copolymers using monomer incorporation percentages obtained from elemental analysis and cyano ^{13}C NMR data

The observed ratios are tabulated below.

Copolymer	Observed Ratio
A	1 : 3.0 : 1
B	1 : 2.0 : 1
C	1 : 3.0 : 1

Table 6-7 Observed ratio of peaks for the olefinic carbon in the ^{13}C NMR spectra of copolymers

The relevant section of the ^{13}C NMR spectrum for copolymer B is shown below.

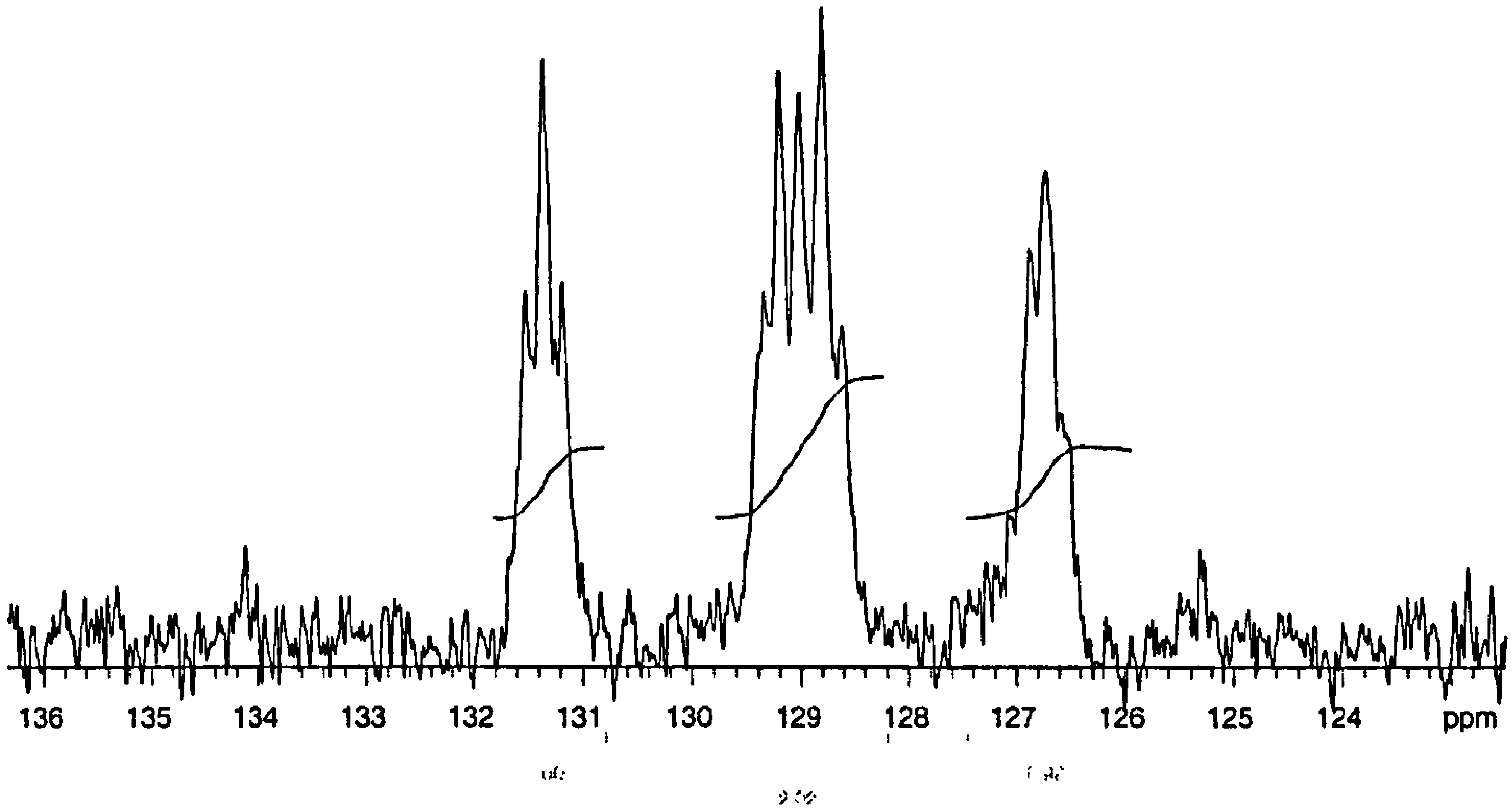


Figure 6-2 Olefinic carbon peaks in the ^{13}C NMR spectrum of copolymer B showing the 1:2:1 splitting pattern

Comparison of the observed ratios with those calculated using the monomer percentages obtained by elemental analysis and cyano group ^{13}C NMR spectroscopic analysis shows reasonably good agreement for copolymers B and C. The elemental analysis data for copolymer A does not correlate with this analysis and may be in error. However, to a first approximation, there is no significant deviation between the calculated and observed values of the intensity ratios suggesting that the sequence distribution in the copolymers is statistical.

6.2.4 Differential scanning calorimetry

The glass transition temperatures of the copolymers were measured and are shown below.

Sample	Tg /°C
A	-10.8
B	-0.9
C	37.4

Table 6-8 Glass transition temperatures of the copolymers

A single transition was observed for the copolymers which is consistent with the suggestion that the copolymers are statistical in sequence distribution since a blocky polymer could lead to glass transitions observed for each of the blocks.

It can be seen that as the percentage of dicyano monomer in the polymer increases, the glass transition temperature increases.

It is possible to calculate the theoretical value expected for the glass transition temperature using the Fox equation[1] shown below,

$$\frac{1}{Tg} = \frac{Wx}{Tgx} + \frac{Wy}{Tgy}$$

where Wx is the weight fraction of monomer X (hexyl ester) and Tgx is the glass transition temperature (in K) of the hexyl ester homopolymer

Glass transition temperature of dicyano homopolymer = 77°C = 350K

Glass transition temperature of hexyl ester homopolymer = -23°C = 250 K

The calculation is shown below for copolymer A assuming that the percentages of the monomer residues present are those calculated from ^{13}C NMR data.

$$\mathrm{Wx} = \frac{0.76\,x\,221.30}{(0.76\,x\,221.30) + (0.24\,x\,118.14)} = 0.86 \text{ and } \mathrm{Wy} = 0.14$$

$$\frac{1}{Tg} = \frac{0.86}{250} + \frac{0.14}{350} = 0.00385 \quad \Rightarrow \quad \mathrm{Tg} = 260.4\,^{\circ}\mathrm{K} = -12.6\,^{\circ}\mathrm{C}$$

Calculated values for the other copolymers are shown in the table below;

	Calculated Tg / °C	Observed Tg / °C
Copolymer A	-12.6	-10.79
Copolymer B	3.0	-0.9
Copolymer C	31.9	37.4

Table 6-9 Comparison of the observed glass transition temperatures with those calculated using the Fox equation

It can be seen that there is close agreement between the calculated and the observed glass transition temperatures for copolymers A and B confirming that the percentages of each monomer in the copolymers is close to the values obtained from ^{13}C NMR spectroscopic analysis. There is a greater deviation between the calculated and observed values for copolymer C. The DSC transition in copolymer C was weak and as a result it was difficult to locate the midpoint of the transition. This probably lead to an error in the DSC glass transition temperature observed.

6.2.5 Gel permeation chromatography

Sample	$\overline{Mn}$	$\overline{Mw}$	Polydispersity
A	53 000	147 000	2.75
B	32 000	84 000	2.62

Table 6-10 GPC data obtained for copolymers

Sample A and B were dissolved in chloroform and the resulting solutions analysed by GPC. It was not possible to gain molecular weight information for sample C owing to its limited solubility.

It can be seen that the molecular weights are relatively low but this is desirable for this work. The dicyano homopolymer was found, in the work described in chapter three, to be insoluble in all common solvents with the exception of hot DMSO. There was concern that the incorporation of dicyano groups into the hexyl ester polymer would decrease solubility. It was therefore decided to use a 1.5% molar ratio of initiator to monomer to produce lower molecular weight polymer that might be expected to have improved solubility over a high molecular weight sample.

6.3 Summary

Three copolymers have been synthesised. It was observed that as the percentage of the dicyano monomer increased, the glass transition temperature was raised and the solubility was decreased such that copolymer C resembled the homopolymer of the dicyano monomer and could only be analysed in DMSO. In contrast, copolymers A and B were found to be soluble polymers with glass transition temperatures below room temperature. The copolymers were found to have a statistical distribution and contain predominantly *trans* double bonds.

A study of the dielectric properties of copolymers A and B is described in chapter seven.

6.4 Experimental

6.4.1 General

Benzene was dried prior to use by stirring over calcium hydride and then distilled. All other reagents were used as supplied. The monomers were synthesised as described in the experimental sections of chapters three and five.

Infra red spectra were recorded on a Perkin Elmer 1600 series FTIR. The spectra were recorded as KBr discs or between sodium chloride discs. ^{1}H and ^{13}C NMR were recorded on a Varian VXR 400 NMR spectrometer and a Varian Gemini 200 NMR spectrometer. The solvent used was deuterated chloroform with TMS as internal reference or deuterated DMSO. Gel permeation chromatography was carried out in chloroform using a Knauer HPLC pump (model 64), Waters model R401 differential refractometer detector and 3 PLgel columns with pore sizes of 10^2, 10^3 and 10^5 Å (column packing PLgel 5μm mixed styrene-divinyl benzene beads). The sample solutions were filtered through a Whatman WTP type 0.2μm filter to remove any particulate before injection. The columns were calibrated using Polymer Laboratories polystyrene standards (162-770 000amu). Thermogravimetry (TG) was carried out using a Stanton Redcroft TG 760 series and differential scanning calorimetry (DSC) was performed using either a Perkin Elmer DSC 7 or a Pyris 1.

6.4.2 Typical copolymerisation

The required amounts of two monomers (see Table 6-1) were weighed into an ampoule. The required amount of initiator (see table below) and dry solvent (5cm^3) were added. The contents of the ampoule were frozen and degassed by the freeze/thaw method. The ampoule was left under vacuum and placed in an oil bath at 60°C and the contents stirred for 24 hours.

	Mass AIBN / g
A	0.027
B	0.032
C	0.037

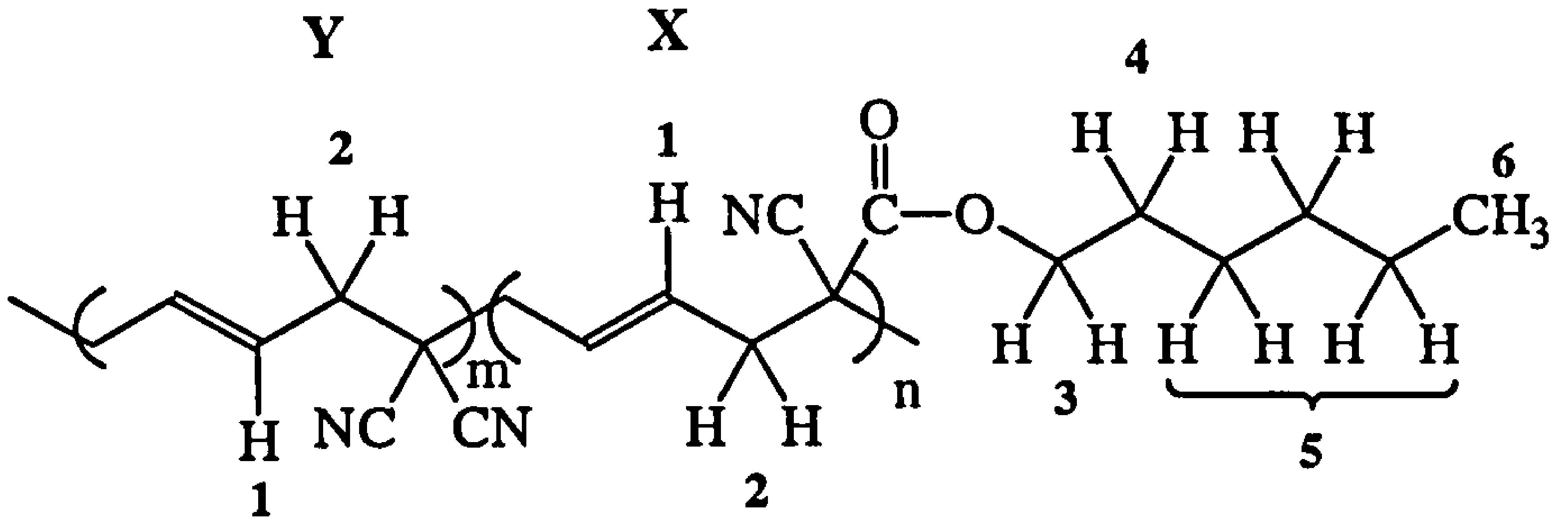
Table 6-11 Mass of AIBN used in copolymerisation experiments

6.4.2.1 Characterisation of copolymers

Infra-Red Spectroscopy - All spectra were indistinguishable. See appendix 5.1 for spectrum of copolymer A which was typical.

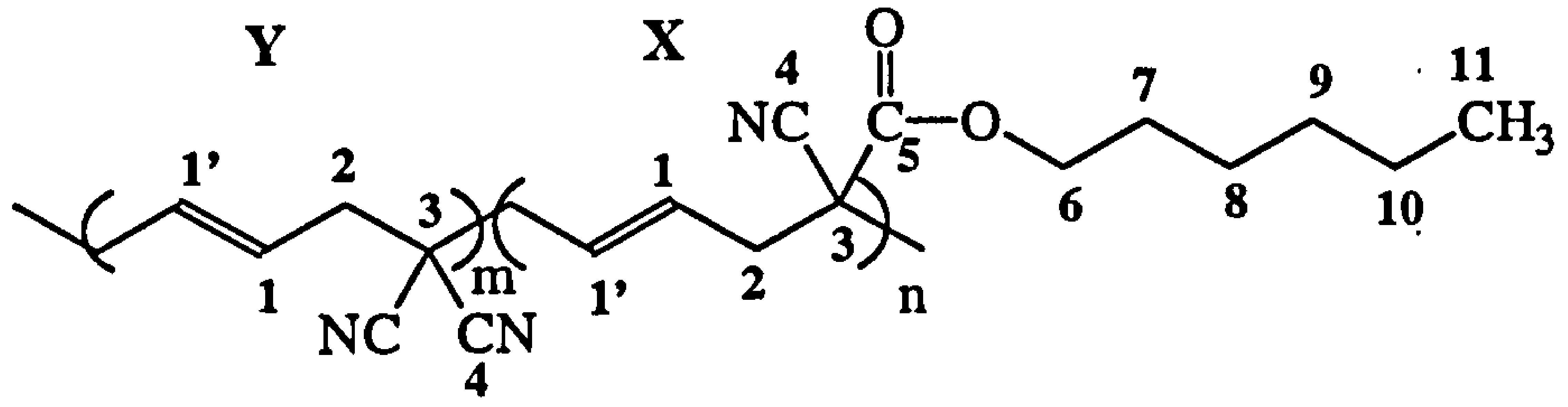
2930 cm^{-1} (aliphatic C-H stretch), 2247 cm^{-1} (CN stretch), 1740 cm^{-1} (CO ester stretch), 1219 cm^{-1} (C-O ester stretch), 975 cm^{-1} (C=C *trans* stretch), 731 cm^{-1} (C=C *cis* stretch) - wave numbers for copolymer A

^{1}H NMR - See appendix 5.2 - 5.4



δ / ppm = 5.80 (m,Y1), 5.65 (s,X1), 4.18 (m,3), 2.68(m,X&Y2), 1.66 (m,4), 1.31 (m,5), 0.89 (m,6) - shift values for copolymer A

^{13}C NMR - See appendix 5.5 - 5.7



δ / ppm = 167.50 (X5), 131.34, 128.76 and 126.40 (X&Y 1&1'), 118.03 (X4), 114.56 (Y4), 67.08 (6), 49.32 (X2), 39.45 (Y2), 38.88 (X3), 37.42 (Y3), 31.27 (7), 28.29 (8), 25.35 (9), 22.46 (10), 13.98 (11) - shift values for copolymer A

In copolymer **C**, the peaks for **Y2** and **X3** appear under the solvent peak.

Gel Permeation Chromatography - see appendix 5.8 - 5.9

Copolymer	Mn	Mw	Polydispersity
A	53 000	147 000	2.75
B	32 000	84 000	2.62

Differential Scanning Calorimetry - see appendix 5.10 -5.12

Copolymer	T_g /°C
A	-10.8
B	-0.9
C	37.4

Elemental Analysis

Found	Copolymer **A**	C: 70.6%	H: 8.2%	N: 9.3%
	Copolymer **B**	C: 70.8%	H: 7.5%	N: 12.4%
	Copolymer **C**	C: 70.7%	H: 6.4%	N: 17.3%

6.5 Reference

[1] Fox, *Bull. Am. Phys. Soc.* **1**,123 (1956)

Chapter 7

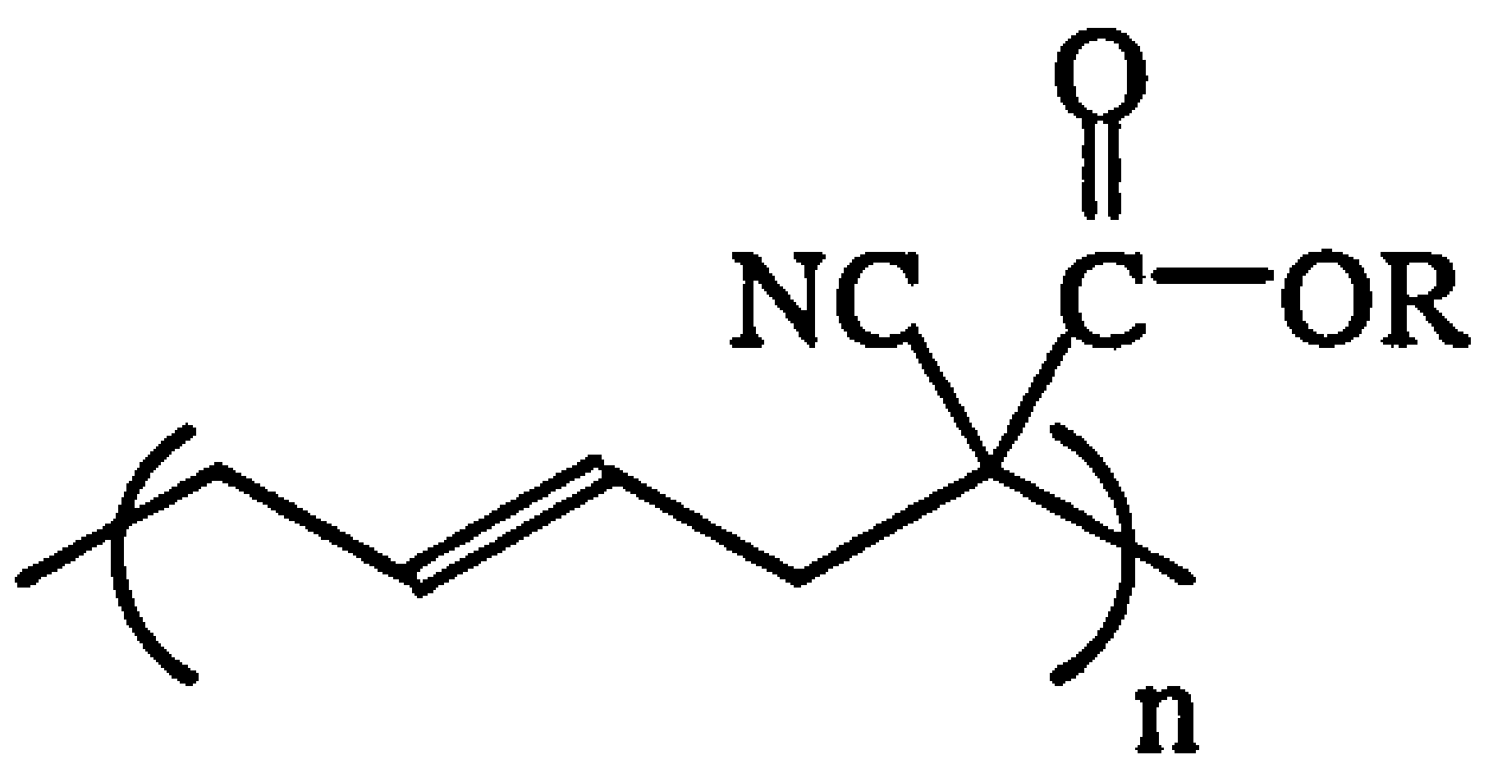
Dielectric analysis of polymers

7. Dielectric analysis of polymers

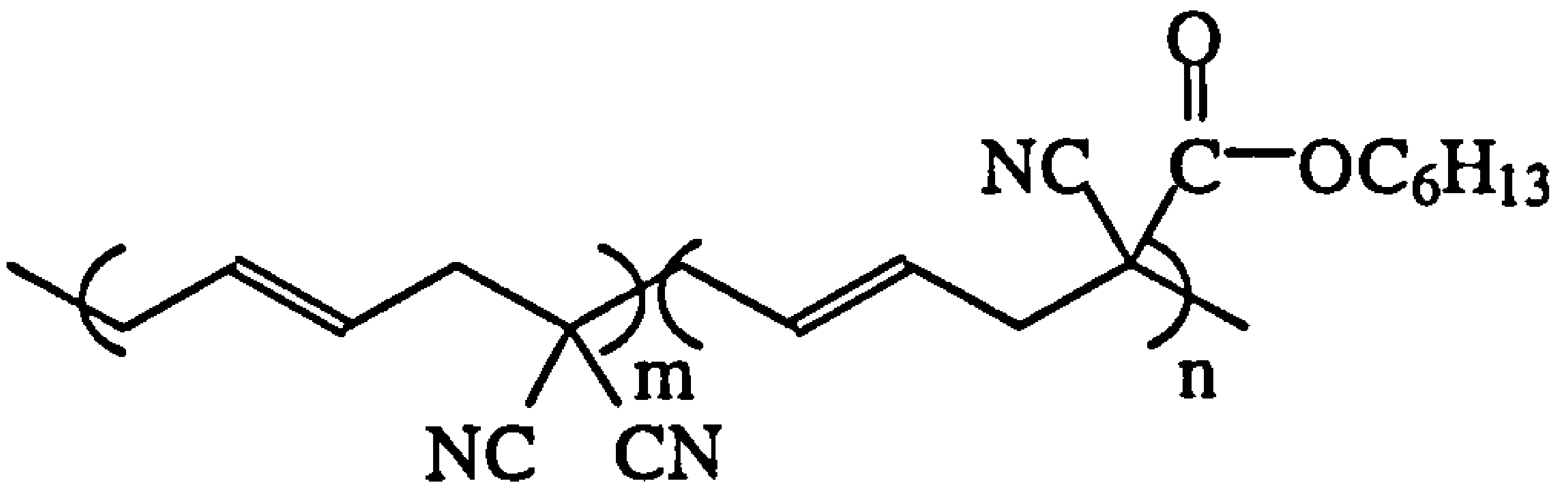
7.1 Introduction

The experimental work described in this chapter was carried out by Professor G.R. Davies and P.L. Carr in the Interdisciplinary Research Centre for Polymer Science and Technology at the University of Leeds. It involved the investigation of the dielectric properties of the polymers produced in the work described in chapters 5 and 6.

The polymers that have been studied are shown below.



where R = *tert*-butyl
n-butyl
hexyl



Two samples of the copolymer were studied with the percentage of dicyano monomer incorporated equal to 24% and 48% corresponding to copolymers A and B described in chapter 6.

The aim of this study was to determine the effect on the dielectric properties of the pendant ester chain length and the percentage of dicyano monomer incorporation in the copolymers. After a general introduction to the physics of this area, the results obtained by the Leeds group are summarised and briefly discussed in this chapter.

The polyurethane referred to in this chapter is supplied by ICI and is described as a block copolymer with soft segments of polyethylene butylene polyester and hard segments of methylene di-p-phenol di-isocyanate (MDI) and 1,4-butane diol.

7.2 Definition of permittivity

If two conductors are enclosed within a vacuum and charged by the application of a potential difference, V, across them, the conductors will carry equal and opposite charges +q and -q. The charges are related to V by the expression

$$q = CV \tag{1}$$

where C is the capacitance of the system measured in Farads (F).

For a parallel plate capacitor in which two plates of area A are separated by a distance d,

$$C = \frac{\varepsilon_o A}{d} \tag{2}$$

where ε_o is the dielectric permittivity of free space and equal to 8.85×10^{-12} Fm^{-1}. The electric field, E, between the plates is given by

$$E = \frac{V}{d} \tag{3}$$

If the vacuum separating the plates is replaced by an insulator or a dielectric material, the amount of charge stored on the plates for a given potential difference is increased such that

$$C = \frac{\varepsilon\varepsilon_o A}{d} \tag{4}$$

where ε is the relative permittivity or the dielectric constant of the material. The table below shows the permittivity for various dielectrics.

Material	Permittivity
vacuum	1.00000
air	1.00054
polyethylene	2.3
polystyrene	2.6
Bakelite	4.8
titanium dioxide	100

Table 7-1 Permittivity of various dielectrics at audio frequencies[1]

The permittivity of a material reflects the extent to which an applied field can polarise the localised charge distribution within a sample. There are three components of molecular polarisation; electronic, atomic and orientational.

7.3 Molecular polarisation

Electronic polarisation occurs when the applied electric field causes a slight displacement of the electrons of each atom with respect to the positive nucleus. This shift is quite small because the applied field is usually weak relative to the intra-atomic field at an electron due to the nucleus. Electronic polarisation can however respond at very high frequencies.

Atomic polarisation occurs when the applied electric field causes a distortion in the arrangement of partially charged atomic nuclei in a molecule or lattice. The movement of heavy nuclei is more sluggish than electrons so that atomic polarisation cannot occur at such high frequencies as electronic polarisation. The origin of atomic polarisation in molecules is thought to be due to bending motions in the molecule rather than stretching since vibrational spectroscopy has shown that the force constants involved in bending are smaller than those involved in stretching motions. The magnitude of atomic polarisation is usually quite small, often only one-tenth of that for electronic polarisation. However, there are exceptions. For example, ionic compounds can sometimes display a large atomic polarisation effect resulting from a relative shift of all the positive ions with respect to the negative ones.

If the molecule already possesses a permanent dipole, there is a tendency for this to align with the applied field to give a net polarisation in that direction. This is termed orientational polarisation. This effect can be large in magnitude but may be slow to develop and is therefore not seen at high frequencies. Only when the frequency of the applied electric field is sufficiently slow for the dipole orientation to attain equilibrium will the maximum polarisation, corresponding to the relaxed permittivity, ε_R, be realised in a material.

The fact that these three different types of polarisation occur at different frequencies means that the permittivity of a material is dependent on frequency and varies as shown in the diagram below.[2]

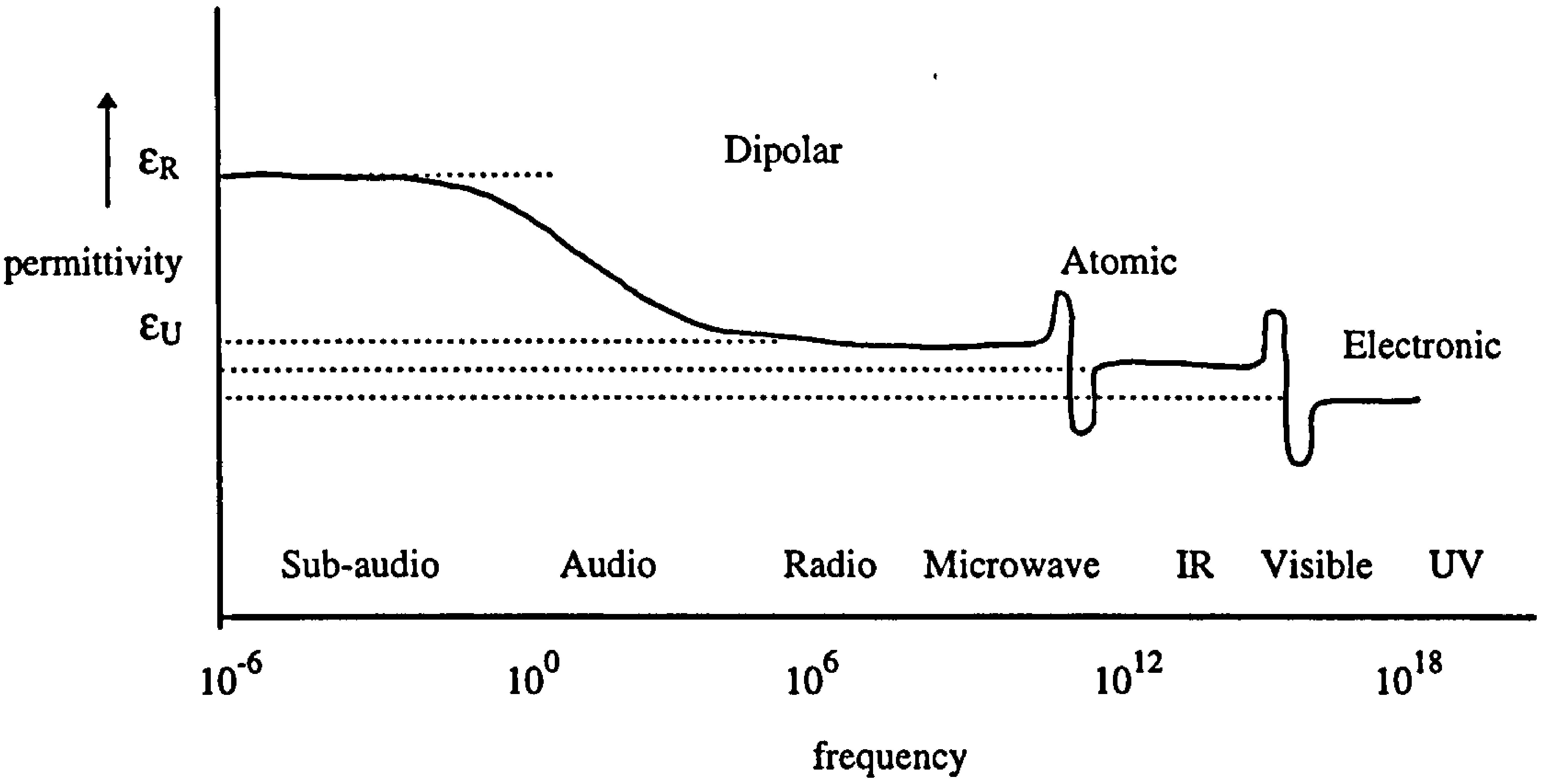


Figure 7-1 Graph showing frequency dependence of permittivity

At high frequencies, the permittivity will be low (ε_U) and due to atomic and electronic effects alone since the dipole moments are not able to align quickly enough for orientational polarisation to occur. This value, ε_U, is termed the unrelaxed permittivity. As the frequency decreases, the observed permittivity will begin to increase until the maximum, relaxed permittivity (ε_R) is reached when the dipoles are able to reach maximum alignment.

Resonances are observed at the points where the frequency corresponds exactly to the frequencies of the atomic and electronic components of the molecular polarisation.

7.4 Summary of the physics of dielectric relaxation

A relaxation is a process by which a system which has been perturbed returns to its equilibrium position. Such a process does not require a 'restoring force' but can be entropy driven. For example, if one considers a gas of diatomic, dipolar molecules in which all the molecules have been aligned and then allowed to relax, the average orientation of the molecules would decay as a result of random collisions. This relaxation process does not minimise the internal energy of the gas but it does increase the entropy and minimise the free energy of the gas.

The simplest model for a dielectric is one of weakly interacting dipoles as in the dipolar gas described previously. In the absence of an electric field, the equilibrium polarisation (P_{eq}), which is defined as the dipole moment per unit volume, is zero. If the system is perturbed by briefly applying an external field then the system is in a non-equilibrium state characterised by the instantaneous value of the polarisation (P). The greater the deviation from equilibrium polarisation value (P_{eq}) the greater the rate of change of polarisation (dP/dt) as shown in the schematic below.

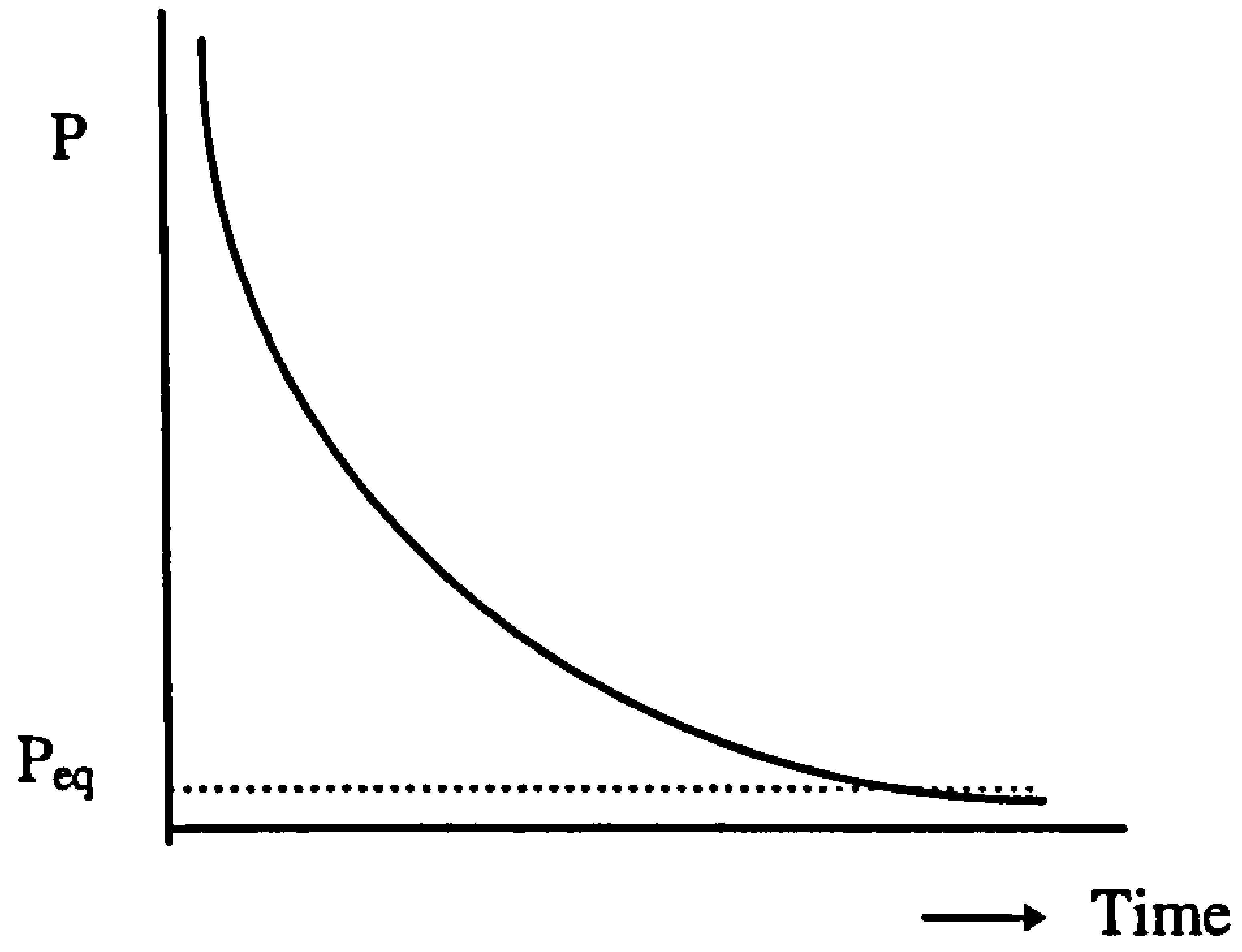


Figure 7-2 Graph showing exponential decay of polarisation

This relationship between the instantaneous polarisation (P) and the time from the start of relaxation can be expressed in an equation (5) which is taken as the starting point for this discussion of dielectric relaxation.

$$\frac{dP}{dt} = -\frac{P}{\tau} \qquad (5)$$

This equation predicts that the polarisation (P) decays exponentially towards the equilibrium polarisation value (P_{eq}) characterised by a 'relaxation time' τ. This relaxation time gives an indication of the rate at which the orientation of the dipoles and hence the instantaneous polarisation returns to the equilibrium state. It varies with temperature and also with the state of the system; the relaxation time is short for gases because the molecules can move freely unlike in solids where the dipoles are restricted by the intermolecular interactions and therefore a long relaxation time is observed.

Dielectric measurements are made by applying a field (E) and measuring the polarisation, (P). For small fields P is proportional to E and the ratio P/E is known as the susceptibility, χ. In SI units $\chi = \varepsilon_0 \chi_r$ where χ_r is the dimensionless relative susceptibility and ε_0 is the permittivity of free space.

$$\chi = P/E = \varepsilon_0\chi_r \qquad (6) \qquad \Rightarrow \qquad P = \chi E \qquad (7)$$

At equilibrium in a static field, the polarisation is given by $P_{eq} = \chi_{eq}E$ and the instantaneous departure from equilibrium of the polarisation (P) arising from perturbation is given by $P - P_{eq}$ or $P - \chi_{eq}E$. Substituting this value into equation (5) gives

$$\frac{dP}{dt} = -\frac{(P - \chi_{eq}E)}{\tau} \qquad (8)$$

where the rate of change of polarisation is still proportional to the departure from equilibrium but now the equilibrium polarisation (P_{eq}) depends upon the applied static field.

If the applied field is oscillatory such that $E = E_0 \cos(\omega t)$ where E_0 is the magnitude of the field and ω is the angular frequency, then the polarisation will take the form

$$P = P_0 \cos(\omega t - \delta) \qquad (9)$$

where $P_0 = \chi_0 E_0$. Equation (9) indicates that the polarisation varies at the same frequency as the oscillating field but lags behind the field by an angle δ owing to the time taken for the dipoles to respond to the field. At low frequencies, the phase angle δ will tend to zero as the dipoles are able to keep up with the oscillating field whereas at high frequencies δ is finite as the dipoles cannot move sufficiently quickly.

It then becomes difficult to define the susceptibility by the ratio of P/E since this now varies with time.

$$\frac{P}{E} = \frac{P_0 \cos(\omega t - \delta)}{E_0 \cos(\omega t)} \qquad (10)$$

It is therefore necessary to write a different definition of susceptibility in oscillatory fields.

The expression for P may be written in terms of variables P' and P" rather than P_0 and δ as shown below in equation (11)

$$\begin{aligned} P_0\cos(\omega t - \delta) &= P_0\cos(\omega t)\cos(\delta) + P_0\sin(\omega t)\sin(\delta) \\ &= P'\cos(\omega t) + P''\sin(\omega t) \end{aligned} \qquad (11)$$

P' is the magnitude of the component of polarisation in phase with the applied field and P'' is the magnitude of the component 90 out of phase with the applied field.

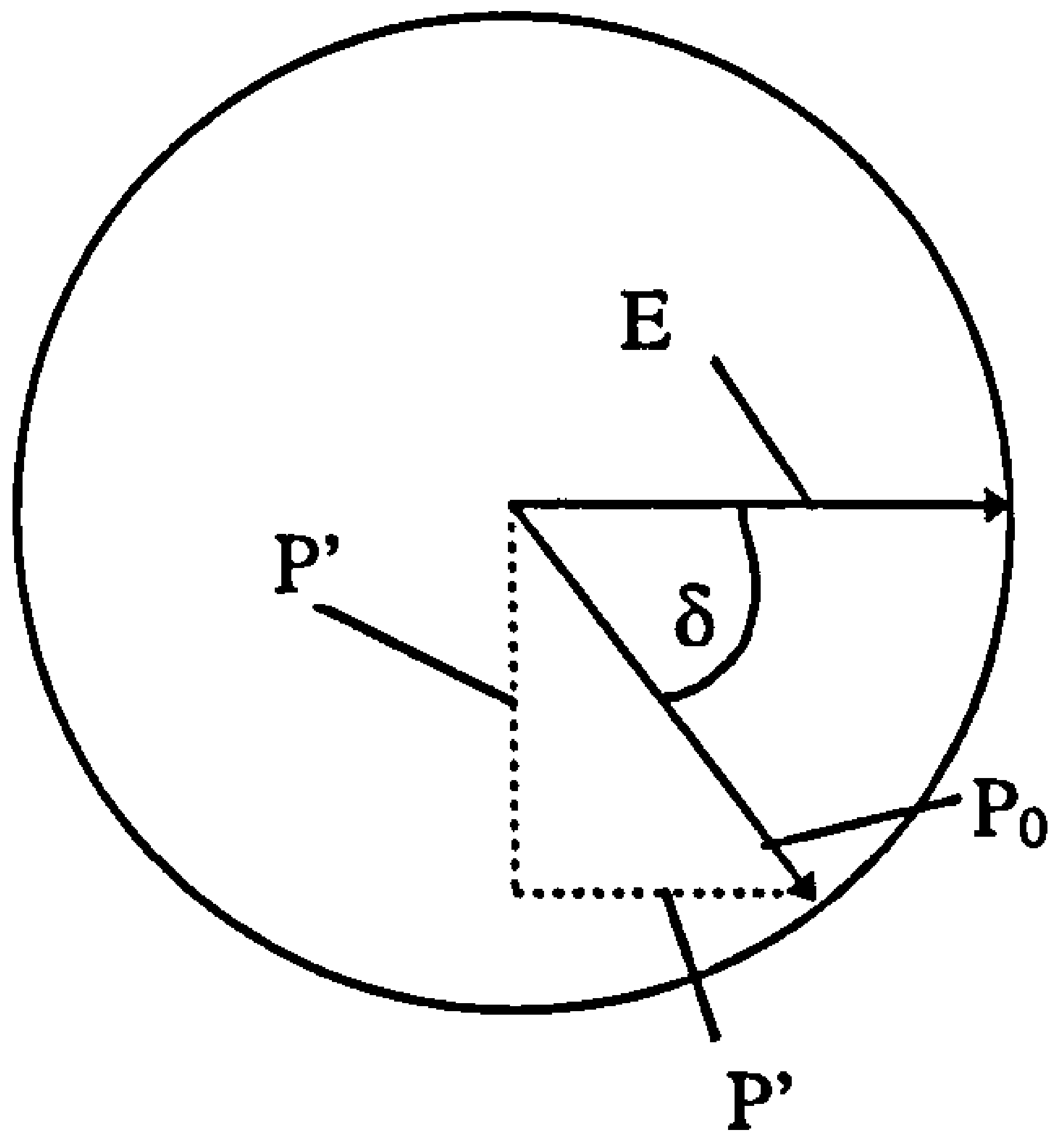


Figure 7-3 Schematic showing components of the polarisation in an oscillating field

It can be seen from equation (11) and Figure 7-3 that

$$P' = P_0 \cos(\delta) \quad \text{and } P'' = P_0 \sin(\delta) \qquad (12)$$

In dynamic fields, $P = \chi_{eq} E$ is replaced by

$$P' = \chi' E_0 \text{ and } P'' = \chi'' E_0 \qquad (13)$$

to define two components of the susceptibility, χ' and χ''. Trial substitution in differential equation (8) shows that the variation of χ' and χ'' with frequency is then given by

$$\chi' = \frac{\chi_{eq}}{1+\omega^2\tau^2} \text{ and } \chi'' = \frac{\chi_{eq}\omega\tau}{1+\omega^2\tau^2} \qquad (14)$$

This result can also be obtained by considering the field (E) as the real part of a complex quantity, E* and the polarisation (P) as the real part of a complex polarisation, P*. The following definitions can be written

$$E^* = E_0\exp(i\omega t) \qquad (15)$$

$$P^* = P_0\exp(i(\omega t - \delta)) \qquad (16)$$

where i is the imaginary value $\sqrt{-1}$. The complex susceptibility χ^* is then defined by

$$\chi^* = P^*/E^* = \chi' - i\chi'' \qquad (17)$$

χ' is thus referred to as the real part of the susceptibility and χ'' as the imaginary part. In physical terms, χ' is proportional to the maximum energy stored per cycle and χ'' is proportional to the energy dissipated as heat per cycle.

Experimental data is usually quoted in terms of the complex relative permittivity, ε_r^*. This is defined in SI units as

$$\varepsilon_r^* = \varepsilon_r' - i\varepsilon_r'' = \chi_r^* + 1 = \chi^*/\varepsilon_0 + 1 \qquad (18)$$

The above discussion has only considered the dipolar contribution to the susceptibility; atomic and electronic contributions have not been included. These latter two contributions occur extremely rapidly compared with the maximum frequencies used for direct dielectric measurements and can hence be represented by a constant addition to the real part of the susceptibility or permittivity since they are always in phase with the applied field.

The equations for the complex permittivity are therefore usually written as

$$\varepsilon_r' = \frac{\varepsilon_R - \varepsilon_U}{1+\omega^2\tau^2} + \varepsilon_U \qquad (19)$$

$$\varepsilon_r'' = \frac{(\varepsilon_R - \varepsilon_U)\omega\tau}{1+\omega^2\tau^2} \qquad (20)$$

where ε_U, the unrelaxed permittivity, is the permittivity at frequencies high enough for dipolar contributions to be absent but low enough to allow atomic and electronic polarisation mechanisms to occur. At sufficiently low frequencies for the dipolar contribution to be fully developed, the relaxed permittivity ε_R can be obtained as shown in Figure 7-4 below.

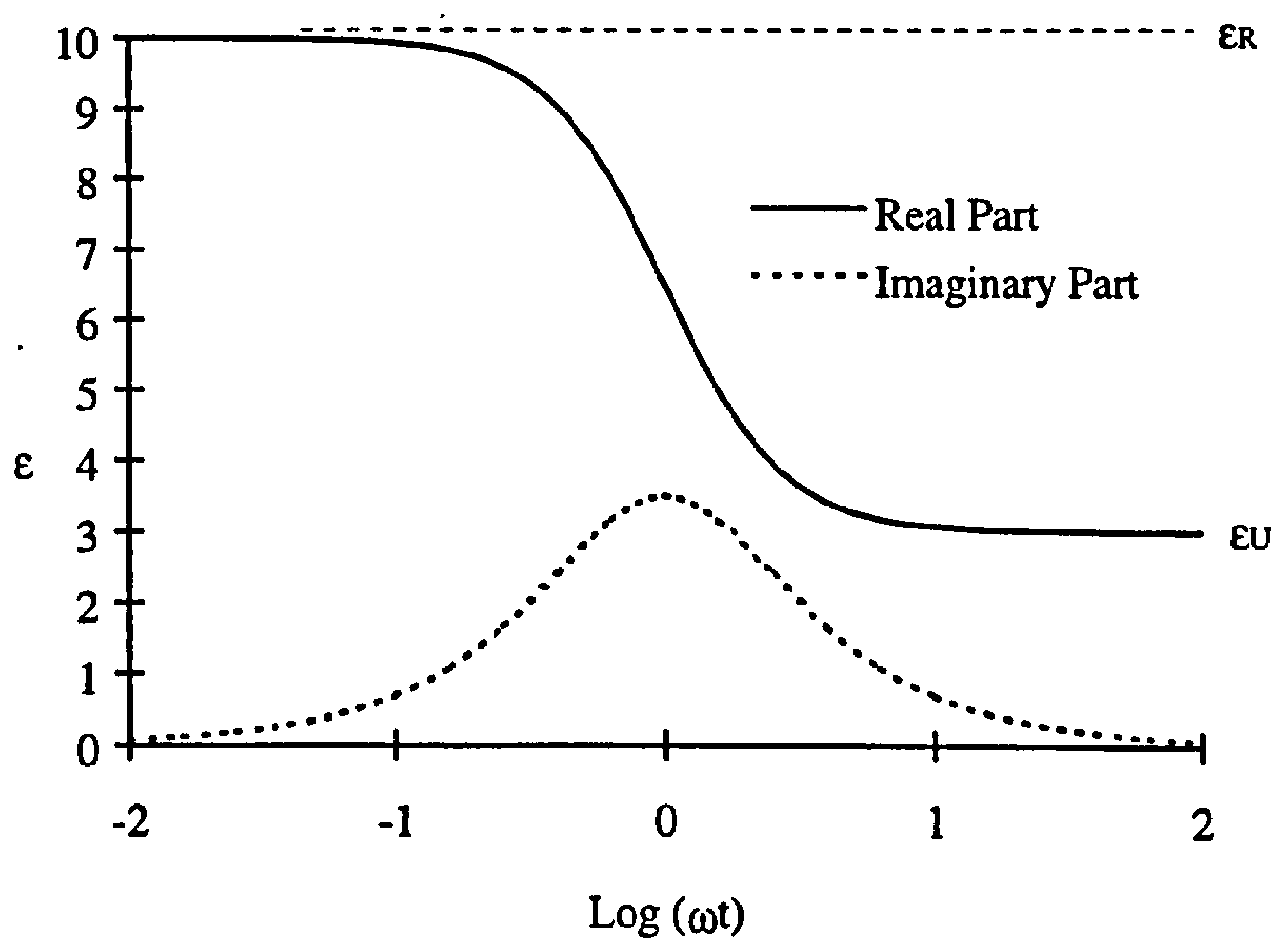


Figure 7-4 The characteristic frequency dependence of the permittivity for a single relaxation time (Debye) model

The two basic parameters for a relaxation are its strength (ε_R - ε_U) and relaxation time, τ. The strength is measured from the step in ε', and the relaxation time is obtained from the frequency at which ε'' is a maximum since$\tau = 1/\omega_{max}$.

The strength of the relaxation is related to the concentration and dipole moment of the mobile, polar entities in the material through the Onsager equation[3] written below.

$$\frac{(\varepsilon_R - \varepsilon_U)(2\varepsilon_R + \varepsilon_U)}{\varepsilon_R(\varepsilon_U + 2)^2} = \frac{n\mu^2}{9\varepsilon_0 kT} \qquad \textbf{(21)}$$

where n is the number of polar entities per unit volume and μ is their mean square dipole moment.

7.5 Relaxation processes

Several distinct dielectric relaxation processes are usually present in a solid polymeric sample. As the frequency is decreased, molecular mobilities of various types become successively energised and available for dipolar segments of the main chain.

By convention, the relaxation processes are labelled α, β and so on beginning at the low frequency end. The high frequency β relaxations are characteristically very broad as the activation energy for the processes are small, typically 50 kJmol^{-1}. The mechanism of a β-type process may be one of several different types depending on the nature of the dipole group concerned and its position on the polymer chain. Among the most important mechanisms for a β process are rotation of a side group about a C-C bond, conformational flip of a cyclic group and local motion of a segment.

The α relaxation process corresponds to the glass transition temperature, Tg, when the polymer chains are able to move freely within the sample. The logarithm of the frequency of maximum ε'' is frequently plotted as a function of inverse temperature to display the temperature dependence of the relaxation time. A straight line in this plot is characteristic of an Arrhenius process where τ is a simply activated function of the form: $\tau = \tau_0 \exp(E/kT)$. This is obtained for processes which involve activation over a constant energy barrier. The glass transition process, however, gives a curved locus in this plot and the temperature at which this locus occurs indicates the glass transition temperature which is well represented by the Williams-Landel-Ferry (WLF) equation.[4]

$$\log(\tau / \tau_0) = -\frac{C_1(T-T_0)}{C_2+(T-T_0)} \qquad (22)$$

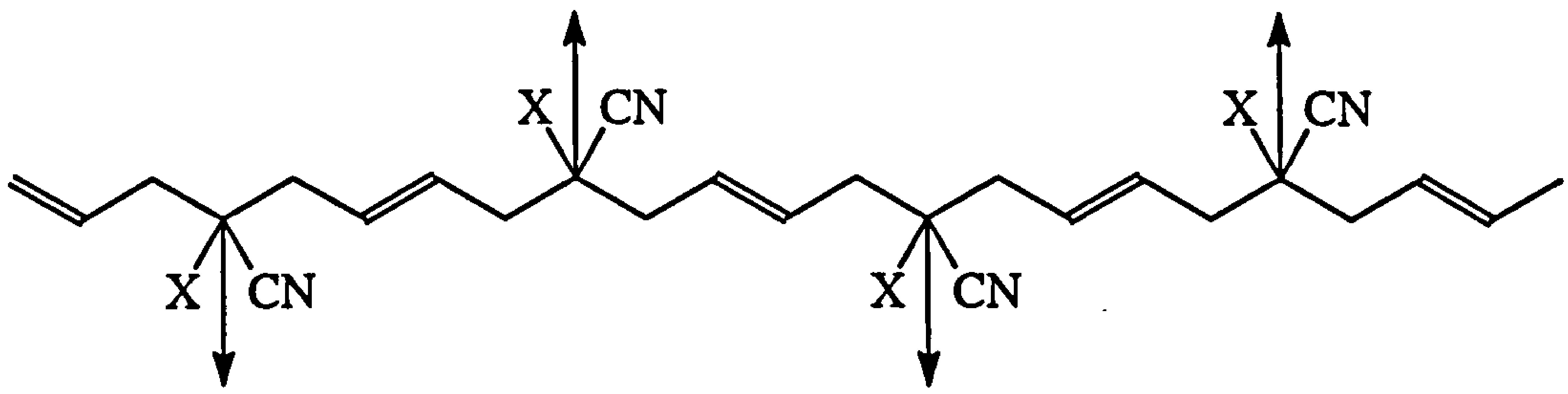
where T_0 is an arbitrary reference temperature at which the relaxation time is τ_0 and C_1 and C_2 are independent fitting parameters.

7.6 Polar polymers

When permanent dipole moments are present in a polymer, there are two different situations that can exist. It is possible that the whole polymer backbone along with its polar groups are rigidly fixed in a single conformation as in the crystalline state. If a polymer is held in this fixed state, the resulting moment of the complete molecule will depend on whether the moments of the individual segments reinforce or compensate each other. For example, in polytetrafluoroethylene, the high dipole moments of the alternate CF_2 groups balance each other exactly giving the polymer a low dielectric constant. In contrast, the C-Cl dipole moment in poly(vinylchloride) are additive in the preferred planar zig-zag conformation so that the dielectric constant of the polymer is high.

Usually polymers will not be in a single fixed conformation and the observed dipole moment is an average over many different conformations. In a real situation this depends principally on the constraints of chemical bonding, steric factors and upon dipole-dipole interaction along the chain.

When the structure of the polymers formed in the work described in chapters 5 and 6 are drawn out in a zig-zag arrangement they appear to cancel each other out.



However, several of these polymers are elastomeric at room temperature and are therefore not fixed into a rigid crystalline structure. It was hoped that, in an applied field, these polymers would be sufficiently mobile for the dipoles to undergo alignment with the field. This would be observed as a high dielectric constant.

7.7 Dielectric analysis of polymer samples

7.7.1 Sample preparation

Density measurements were carried out on the polymers using a potassium iodide density column, range 1.00 - 1.20 gcm^{-3}. The results are shown below.

Sample	Density gcm^{-3}
t-Butyl Ester Homopolymer	1.059
n-Butyl Ester Homopolymer	1.075
Hexyl Ester Homopolymer	1.054
38% Dicyano Copolymer	1.037
65% Dicyano Copolymer	1.077

Table 7-2 Density values of polymer used in dielectric studies

Thin film samples were prepared by solvent casting onto flat glass or metal substrates from 5% solutions in chloroform. The solvent was evaporated slowly to avoid the growth of solvent vapour bubbles. The partially dried films were then dried for twelve hours at 200°C above the Tg of the sample to remove final traces of the solvent.

The *tert*-butyl ester polymer was glassy at room temperature and therefore easy to handle. Uniform free-standing films ~50 µm thick were carefully removed from the glass substrate and 30 nm thick circular aluminium electrodes 40 mm and 25 mm in diameter were evaporated onto either side of the sample. This facilitated the use of a guard ring in the dielectric measurement apparatus to minimise surface conduction.

The remaining samples (the butyl ester homopolymer, hexyl ester homopolymer and two copolymers) dried as soft adhesive rubbers and could not be handled as free films. These were therefore cast directly onto the bottom positive brass plate of the dielectric apparatus and the film thickness determined by the difference between the measured thickness of the bare electrode and total thickness of the electrode plus the rubbery film. A 25 mm top earth electrode was then evaporated onto the film as before.

The electroded samples were mounted in a light brass frame in which brass plates of the same dimensions as the deposited electrodes could be lightly spring-loaded to give good electrical contact to the deposited electrodes. Where appropriate, contacts were gold tipped.

7.7.2 Experimental

The environmental chamber temperature was controlled using heated gas from a liquid nitrogen supply, a fine thermocouple in the guard ring and a Eurotherm thermostat controlling to 0.10°C. Dielectric measurements were made at temperatures of Tg + 40°C to Tg -100°C and at frequencies from 10^7 - 10^{-2} Hz using a Solartron 1260 Impedance/Gain Phase Analyser and Novocontrol Broadband Dielectric Converter and PC.

7.7.3 Discussion and interpretation of dielectric measurements

7.7.3.1 Real permittivity

The permittivity as a function of frequency at different temperatures above the Tg is shown in the graphs in appendices 6.1-6.5. A typical graph is shown below.

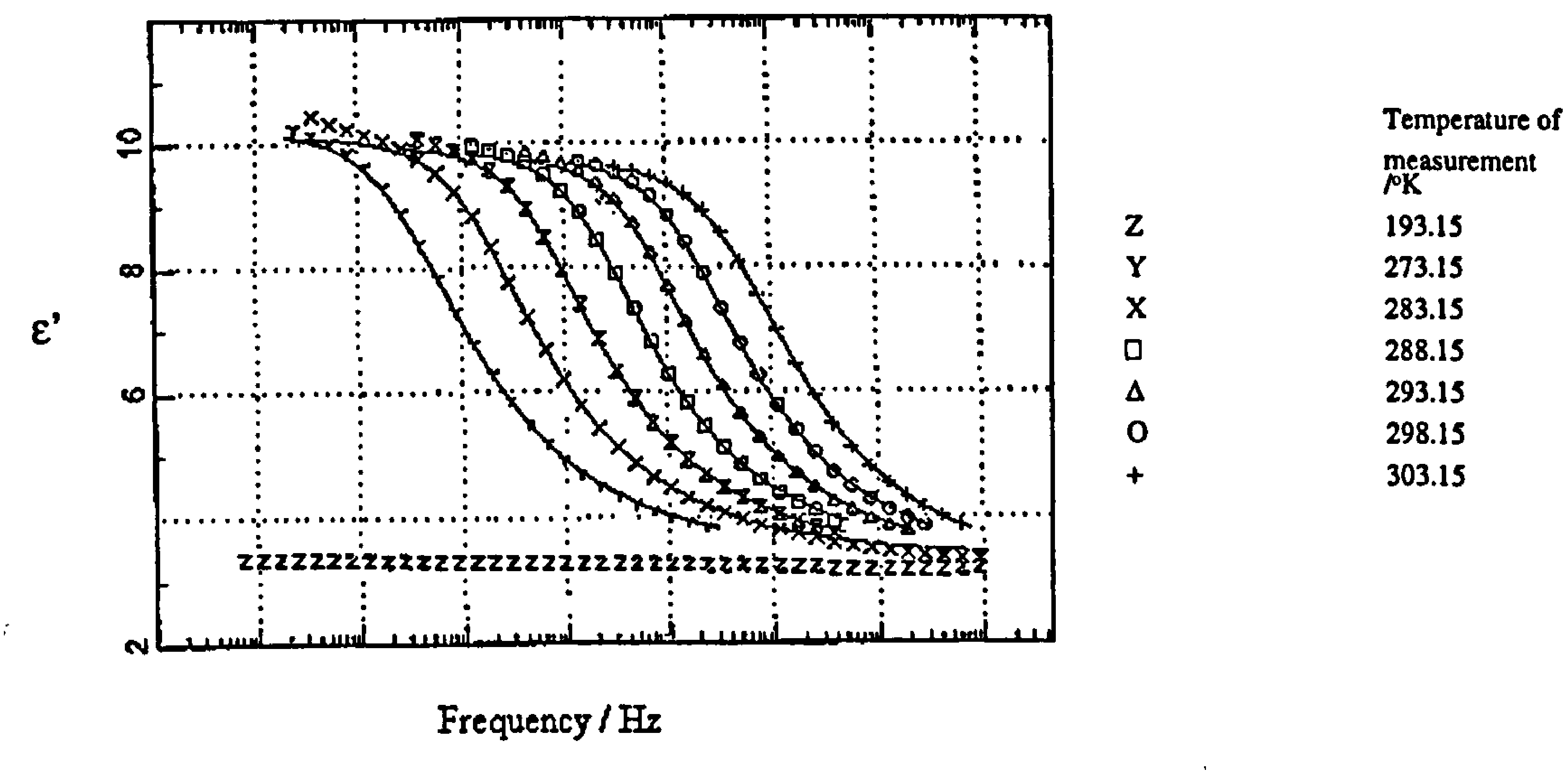


Figure 7-5 Graph showing the real permittivity at different temperatures for the 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane polymer

The relaxed permittivity values obtained from the plots in the appendices are shown below.

Sample	Relaxed permittivity ε_R
Tert-butyl ester homopolymer	14.00
Butyl ester homopolymer	9.84
Hexyl ester homopolymer	10.26
Copolymer A (24% dicyano)	12.09
Copolymer B (48% dicyano)	16.80

Table 7-3 Relaxed permittivity values obtained for polymers

These values are reasonably high for a rubber; polyurethane has a relaxed permittivity of 9. Comparing the values obtained for the butyl ester homopolymer, hexyl ester homopolymer and the two copolymers, it can be seen that the two homopolymers had similar permittivities suggesting that the length of the ester alkyl chain does not affect the permittivity. As the concentration of cyano group increased from that in the homopolymers to that in copolymer A and then in copolymer B, the permittivity also increased. This was to be expected since the relaxed permittivity involves the orientational polarisation of dipoles in the sample. As the number of dipoles in the sample increased, the orientational polarisation component will increase leading to an increase in permittivity.

The value for the *tert*-butyl ester homopolymer does not fit in with this trend as it gives as permittivity value of 14, higher than those of the other homopolymers and copolymer A. This discrepancy is due to the differences in the handling of the samples. The *tert*-butyl ester readily formed free standing films the thickness of which could be easily measured leading to good reproducibility of the permittiviity (~2% variation) whereas the other samples were rubbery and formed less uniform films with a larger error in the thickness measurements leading to a variation of ~15% in the permittivity values. This suggested that the value for the *tert*-butyl ester homopolymer is a more accurate indication of the true permittivity values.

The unrelaxed permittivity is the permittivity due to electronic and atomic polarisation contributions only. Ideally, this would be obtained at the same temperature as the relaxed permittivity by extending the measurements to high frequencies where the dipolar contributions are absent since they cannot respond sufficiently quickly. However, when the temperature is above Tg, even at the highest frequency of measurement (1MHz), there is sufficient energy for sub-Tg dipolar relaxations to persist. Low temperature measurements are therefore used to estimate the value of the unrelaxed permittivity. The data used for analysis was that taken at the temperature where the relaxation time was approximately 10^{-2}s.

The unrelaxed permittivity values, ε_U, obtained from the graphs in appendices 6.1 to 6.5 are shown below.

Sample	Temperature of measurement / °K	Unrelaxed permittivity, ε_U
Tert-butyl ester homopolymer	338	3.24
Butyl ester homopolymer	288	2.79
Hexyl ester homopolymer	273	3.26
Copolymer A (24% dicyano)	283	2.46
Copolymer B (48% dicyano)	303	4.28

Table 7-4 Unrelaxed permittivity values obtained for the polymers

The relaxed and unrelaxed permittivity values can be used to estimate the effective dipole moment of the repeat unit, μ from the Onsager equation (21).

$$\frac{(\varepsilon_R - \varepsilon_U)(2\varepsilon_R + \varepsilon_U)}{\varepsilon_R(\varepsilon_U + 2)^2} = \frac{n\mu^2}{9\varepsilon_0 kT} \qquad (21)$$

The values obtained are shown in the table below.

Sample	Dipole moment, μ / Debye
Tert-butyl ester homopolymer	2.97
Butyl ester homopolymer	2.44
Hexyl ester homopolymer	2.35
Copolymer A (24% dicyano)	3.06
Copolymer B (48% dicyano)	2.38

Table 7-5 Dipole moments of the repeat units in the polymers

The dipole moment of an aliphatic cyano group might be expected to be somewhat larger; for example acetonitrile has a dipole moment of 3.9D. It seems likely that the decrease in the dipole moment in these polymers is due to the adjacent mobile ester group in the repeat unit. The ester has a significantly lower dipole moment (e.g. methyl acetate has a dipole moment equal to 1.7D) and an unfavourable alignment of the ester will lead to a reduction in the observed dipole moment of the repeat unit.

7.7.3.2 Imaginary permittivity and conductivity

The graphs showing the imaginary permittivity can be seen in appendices 6.1-6.5. A typical example is shown below.

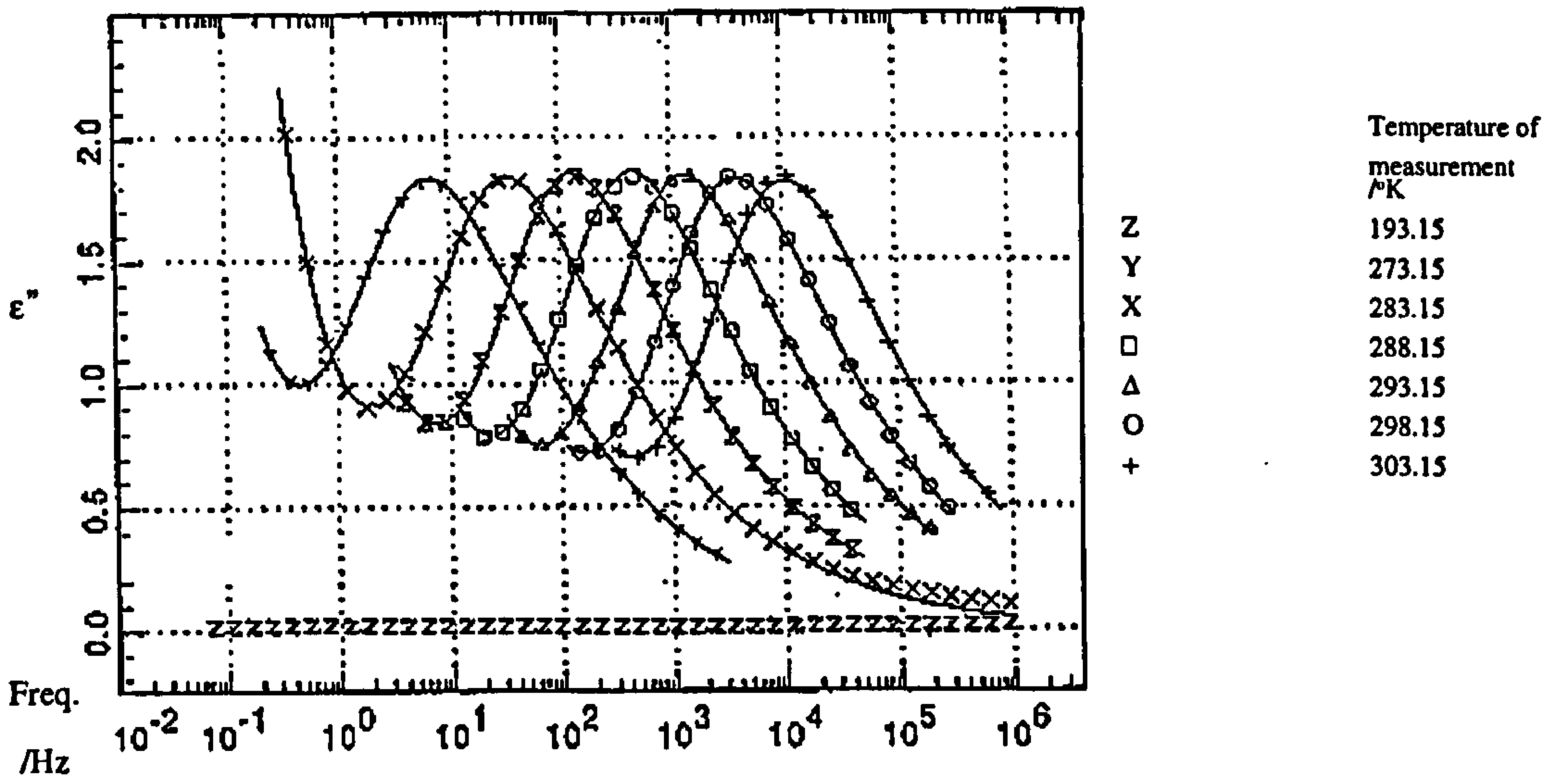


Figure 7-6 Graph showing the imaginary permittivity at different temperatures for the 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane polymer

The usual peak associated with the large drop in the real permittivity can be seen in all graphs. It can also be seen that there is an apparent upturn in the imaginary permittivity, ε''_{app}, at low frequencies and this is known to be due to a conduction process.

$$\varepsilon''_{app} = \frac{\sigma}{\omega\varepsilon_o} \qquad (23)$$

where σ is the conductivity and $\omega=2\pi f$ where f is the frequency of measurement. The frequency dependence of this effect is very strong. For every tenfold reduction in frequency, ε''_{app} increases tenfold and swamps any real dipolar effects. For this reason, lowest frequency data is not plotted to improve the clarity of the graphs.

The magnitude of the conductance varies strongly with temperature and from sample to sample. The butyl ester homopolymer shows the lowest conductance and the 48% dicyano copolymer (B) shows the highest conductance. The origin of this conductance is not clear. It may be due to residual ionic impurities although none were detected by ion chromatography. A second possibility is that small quantities of absorbed moisture may cause the conductance. This seems likely because both ester and cyano groups have a high affinity for water.

7.7.3.3 Relaxation behaviour

The temperature dependence of the relaxation time, τ, is shown in the graph below.

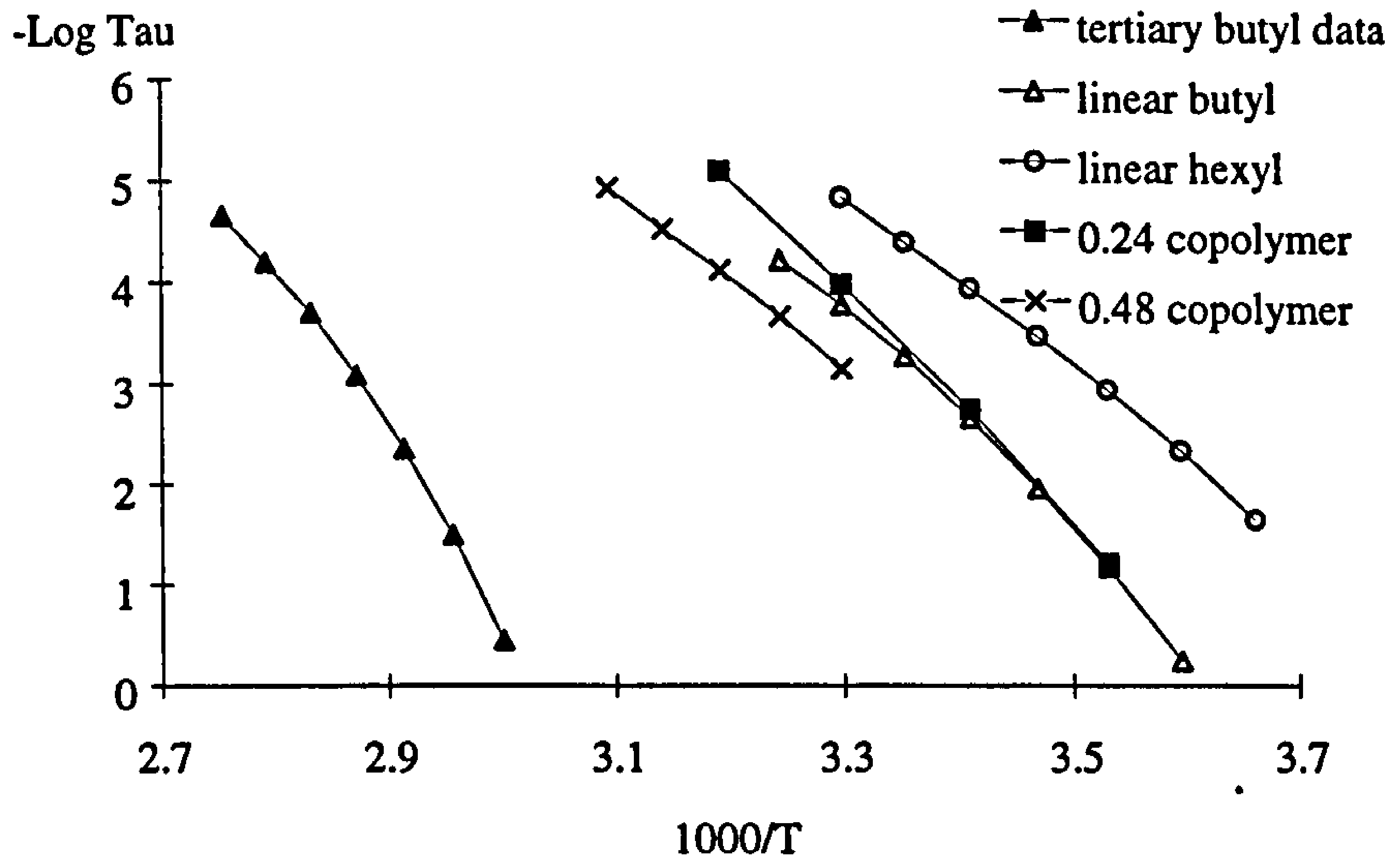


Figure 7-7 WLF plot

It should be noted that the lines linking the points on this graph are visual fits only.

This temperature dependence is characteristic of a glass transition process and this can be fitted using the WLF equation.

$$\log(\tau/\tau_0) = -\frac{C_1(T-T_0)}{C_2+(T-T_0)} \qquad (22)$$

The Tg values obtained as the midpoints in the DSC transitions were used in the WLF equation and the following fitting parameters were obtained.

Sample	DSC Tg /°K	C_1	C_2
Tert-butyl ester homopolymer	328	10.32	24.08
Butyl ester homopolymer	268.9	16.38	71.26
Hexyl ester homopolymer	250.7	22.81	134.21
Copolymer A (24% dicyano)	262.2	86.90	609.89
Copolymer B (48% dicyano)	272.1	15.67	72.59

Table 7-6 WLF parameters obtained using DSC Tg values

The so-called 'universal' values of C_1 and C_2 are 17.44 and 51.6 but fairly large deviations from these values are often seen. However, the deviations in this study are too large even considering the difficulty of accurately locating the relaxation peaks at low frequencies in the presence of high conductivity losses. The values for copolymer A (24% dicyano) are certainly too far out to represent a simple Tg process.

Alternatively, accepting that the DSC data will be subject to some error, Tg can be used as a fitting parameter and the DSC and WLF Tg values compared.

Sample	DSC Tg /°K	WLF Tg /°K	C_1	C_2
Tert-butyl ester homopolymer	328.0	324.2	13.07	35.56
Butyl ester homopolymer	268.9	268.4	13.85	46.22
Hexyl ester homopolymer	250.7	252.0	16.65	70.40
Copolymer A (24% dicyano)	262.2	265.8	21.33	91.46
Copolymer B (48% dicyano)	272.1	269.9	15.96	66.48

Table 7-7 WLF parameters obtained allowing a free fit of Tg

This yields a much more acceptable range of values for C_1 and C_2 and hence suggests that the DSC Tg values are subject to a random error of a few degrees which is a reasonable assumption. The copolymer A sample shows the largest deviation from the universal value suggesting that the dielectric relaxation time data for this sample is in error.

7.7.3.4 Electrostriction

An optical method of measuring the change in thickness of a sample in an electric field has been developed in the Leeds branch of the IRC. The sample was held with one side firmly attached to a stationary brass plate which prevented it from changing its width and breadth and hence reduces the observable electrostrictive effect considerably. The other side of the sample was provided with an evaporated gold electrode which in addition to applying an electric field, also acted to reflect the light beam which was used to sense the motion of the sample.

If an alternating field ,E, of angular frequency ω is applied across the sample of thickness d, then the displacement x, of the gold electrode is given by

$$\frac{x}{d} = \gamma E^2 = \gamma(E_0 \cos(\omega t))^2 = \frac{\gamma E_0^2}{2}(1 + \cos(2\omega t)) \qquad (24)$$

It can be seen that electrostriction generates both a static displacement and an alternating displacement with a frequency twice that of the applied field . The latter component was detected with the aid of Fourier analysis. A plot of x versus E^2 then yields γ, the electrostrictive coefficient.

Initial results for copolymer B (48% dicyano) at 10Hz and room temperature were ~5 x 10^{-20} m^2V^{-2} but results varied erratically from 3 x 10^{-20} m^2V^{-2} to 8 x 10^{-20} m^2V^{-2}. These values are the same order of magnitude as those obtained for a polyurethane sample (2-4 x 10^{-20} m^2V^{-2}).

Ideally, the unconstrained electrostrictive response would be measured and this is the ultimate goal of the polymer physics group at Leeds. There are experimental problems with handling an unconstrained film that, at present, prevent the measurement of the unconstrained electrostrictive coefficient. In practice this value would be significantly higher than that obtained for the constrained film since the sample would be free to alter all of its dimensions and not just the thickness.

7.8 Conclusions

Values for the densities, relaxed permittivities and unrelaxed permittivities have been obtained for five polymer samples and the constrained electrostrictive coefficient for the 48% dicyano copolymer has been measured.

The difficulty of handling the rubbery polymer samples has limited the accuracy of the permittivity measurements and it is necessary to improve the techniques used for handling rubbery materials.

It has been shown that the ester chain length had little effect on the relaxed permittivity and that as the concentration of polar cyano groups increased, the relaxed permittivity increased.

The dipole unit moment per repeat unit (~2.5-3D) was somewhat smaller than what might be expected for an aliphatic cyano group and this was probably due to the unfavourable alignment of the ester group.

Low frequency dielectric data above the Tg was strongly influenced by a conductivity process which was presumed to be ionic and was probably due to absorbed moisture.

Constrained electrostrictive measurements were made for the 48% dicyano copolymer and the values obtained were comparable to those observed for a polyurethane sample.

7.9 References

[1] Halliday, D. and Resnick, R., 'Physics', (3rd Edition), Wiley, New York, (1978)

[2] Harrop, P.J., '*Dielectrics*', Butterworths, London (1972)

[3] Onsager, L., *J. Am. Chem. Soc.* **58**, 1486 (1936)

[4] Williams, M.L., Landel, R.F. and Ferry, J.D., *J. Am. Chem. Soc.* **77**, 3701 (1955)

Chapter 8

Conclusions and future work

8. Conclusions and future work

8.1 Conclusions

It has been possible to synthesise novel polymers using the free-radical polymerisation of vinylcyclopropane monomers. Rubbery polymers with glass transition temperatures below room temperature have been synthesised in the cases of 1-cyano-1-butoxycarbonyl- and 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropanes. The polymers were found to be atactic and contain predominantly *trans* double bonds. The permittivities of these polymers along with the 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane homopolymer have been measured.

Copolymers of 1,1-dicyano-2-vinylcyclopropane and 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane have been synthesised using various ratios of the two monomers. It is thought that the dicyano monomer is less reactive and incorporated less readily into the polymer chain than the hexyl ester monomer. The copolymers have been shown to contain predominantly *trans* double bonds and be statistical in sequence. The glass transition temperature of the copolymers was found to increase and the solubility decrease as the percentage of dicyano monomer present increased.

The permittivities of the soluble copolymers were measured and shown to increase as the percentage of dicyano monomer incorporated increased.

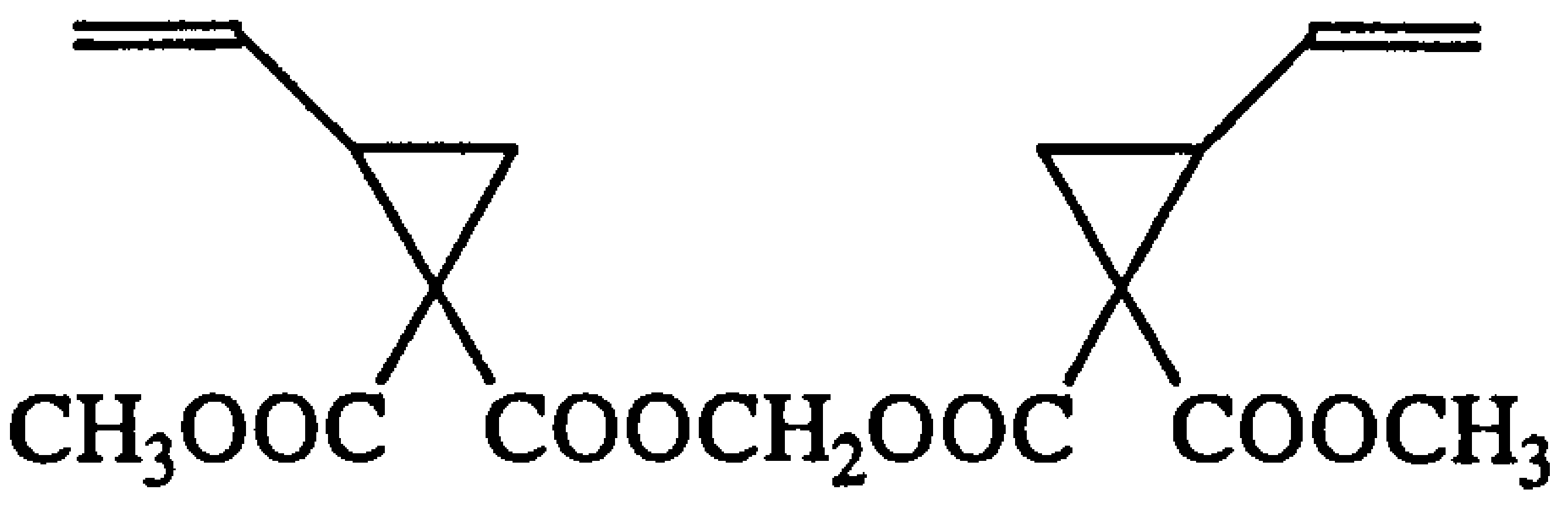
The work described in this thesis has also shown that 1,1-dicyano-2-vinylcyclopropane does not copolymerise with butyl acrylate in either solution or emulsion polymerisation processes.

The olefin metathesis of two disubstituted cyclopentenes and of malononitrile was also found to be unsuccessful for the formation of polymers.

8.2 Future work

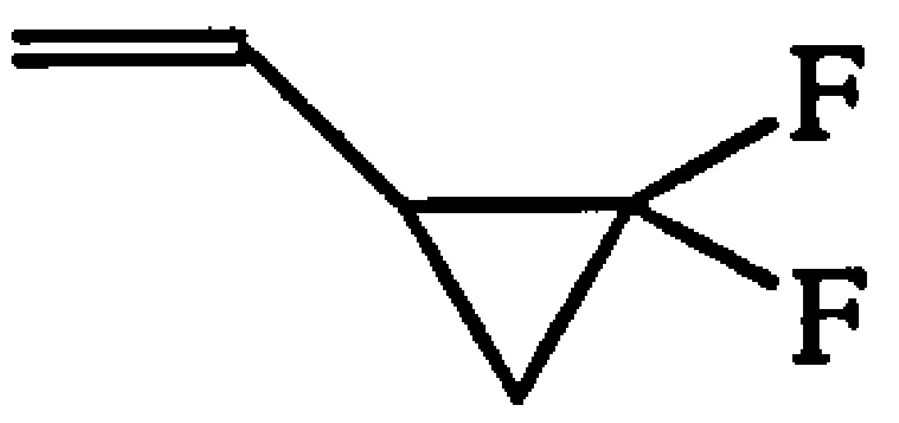
The work described in this thesis has shown that the polymerisation of vinylcyclopropane monomers is a viable route to polar, elastomeric polymers. In order to form a true rubber, it is necessary to have physical crosslinks between the polymer chains to prevent the chains from slipping past each other irreversibly, that is to prevent flow occurring.

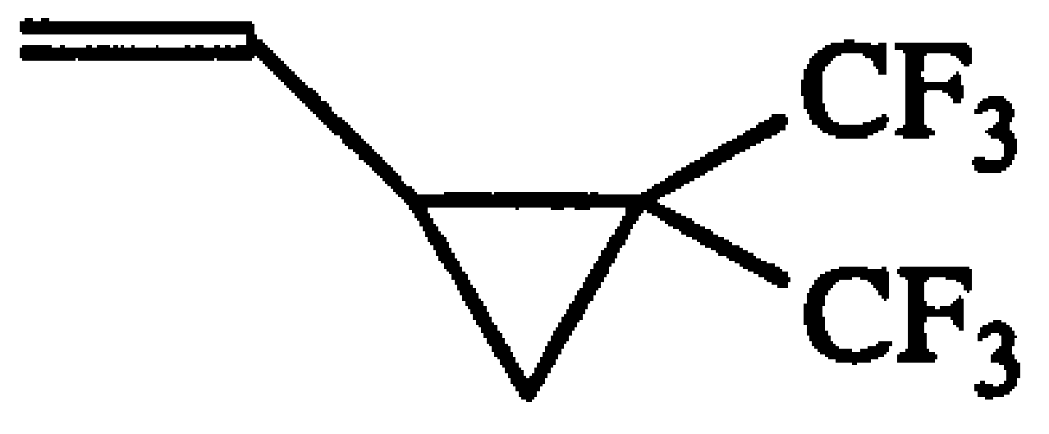
Future work on this topic should involve incorporating chemical crosslinks into the polymer. Moszner *et al.* have successfully incorporated crosslinks into polymers formed from vinylcyclopropanes by using monomers of the type shown below[1].



This monomer, along with several others investigated, formed insoluble crosslinked polymers and this approach could be used to incorporate crosslinks into the monomers of interest in this work.

Dielectric analysis showed that there was considerable ionic conduction in the polymer samples. It is thought that this is due to water present in the polymers. The substituents on the polymer have a high affinity for water and it is virtually impossible to keep the polymers completely dry. It would therefore be advantageous to synthesis polymers without such a high affinity for water. Possible monomers of interest are those containing fluorine such as those shown below.





The first monomer shown has already been studied in some detail and there are many references to its synthesis in the literature.[2] However, no descriptions of attempts to polymerise it have been reported. The second monomer does not appear in the literature.

In conclusion, it should be noted that this thesis forms the very first stage of work in this area undertaken in the IRC. The results show some promise but there is still a large amount of work that needs to be undertaken to produce polymers which fit the exact requirements of the physicists who want to study electrostriction. These suggestions may help future workers to approach this goal.

8.3 References

[1] Moszner, N. et al., *Abs. Papers Am. Chem. Soc.* **214**, 10-POLY (1997)

[2] Sargeant, P.B., *J. Org. Chem.* **35**, 678-682 (1970)

Kamel, M. *et al.*, *Chem. Ber.* **109**, 2351-2369 (1976)

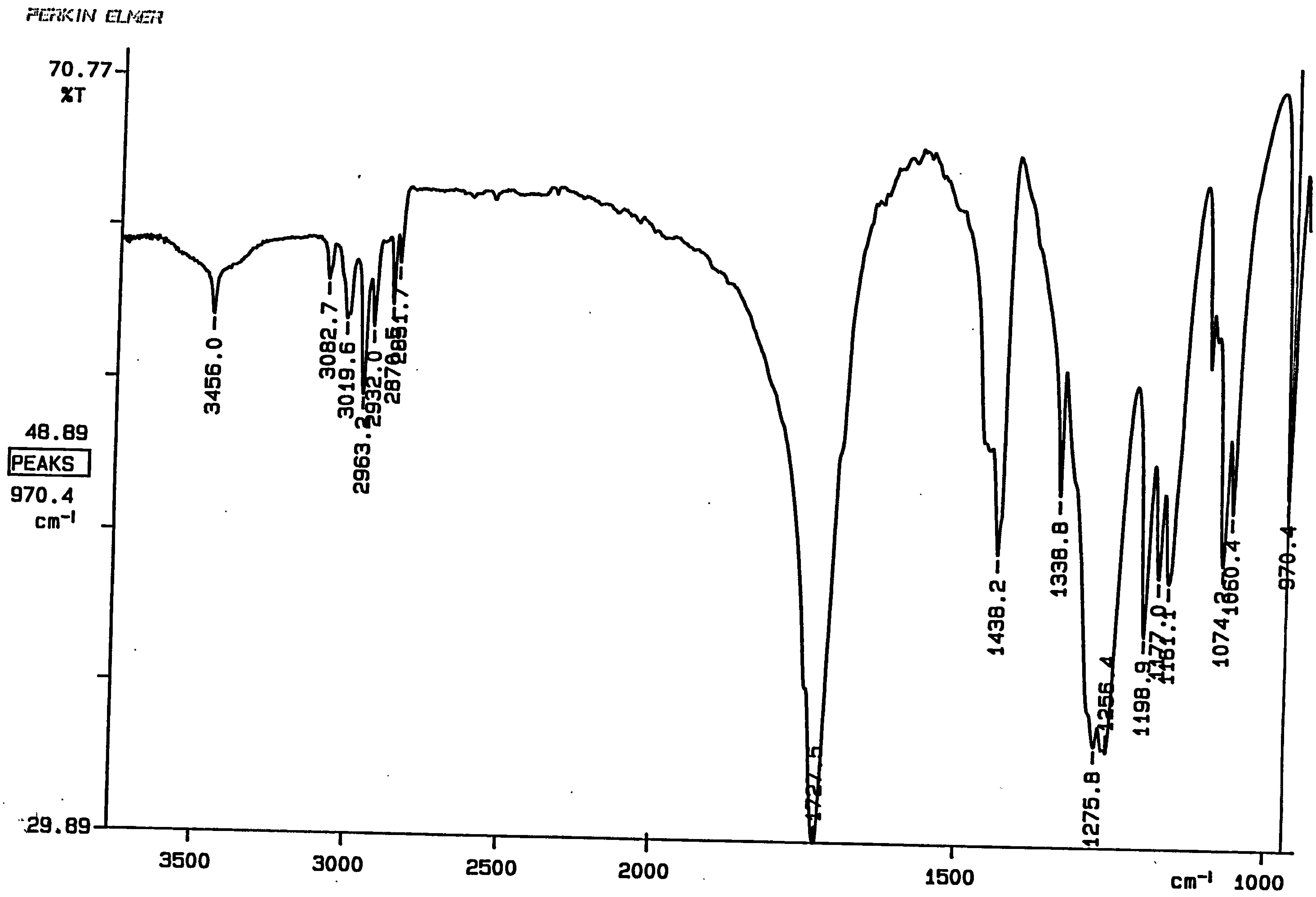
Mitsch, R.A., *J. Am. Chem. Soc.* **87**, 758-761 (1965)

Dolbier, W.R. *et al.*, *J. Org. Chem.* **55**, 5420-5422 (1990)

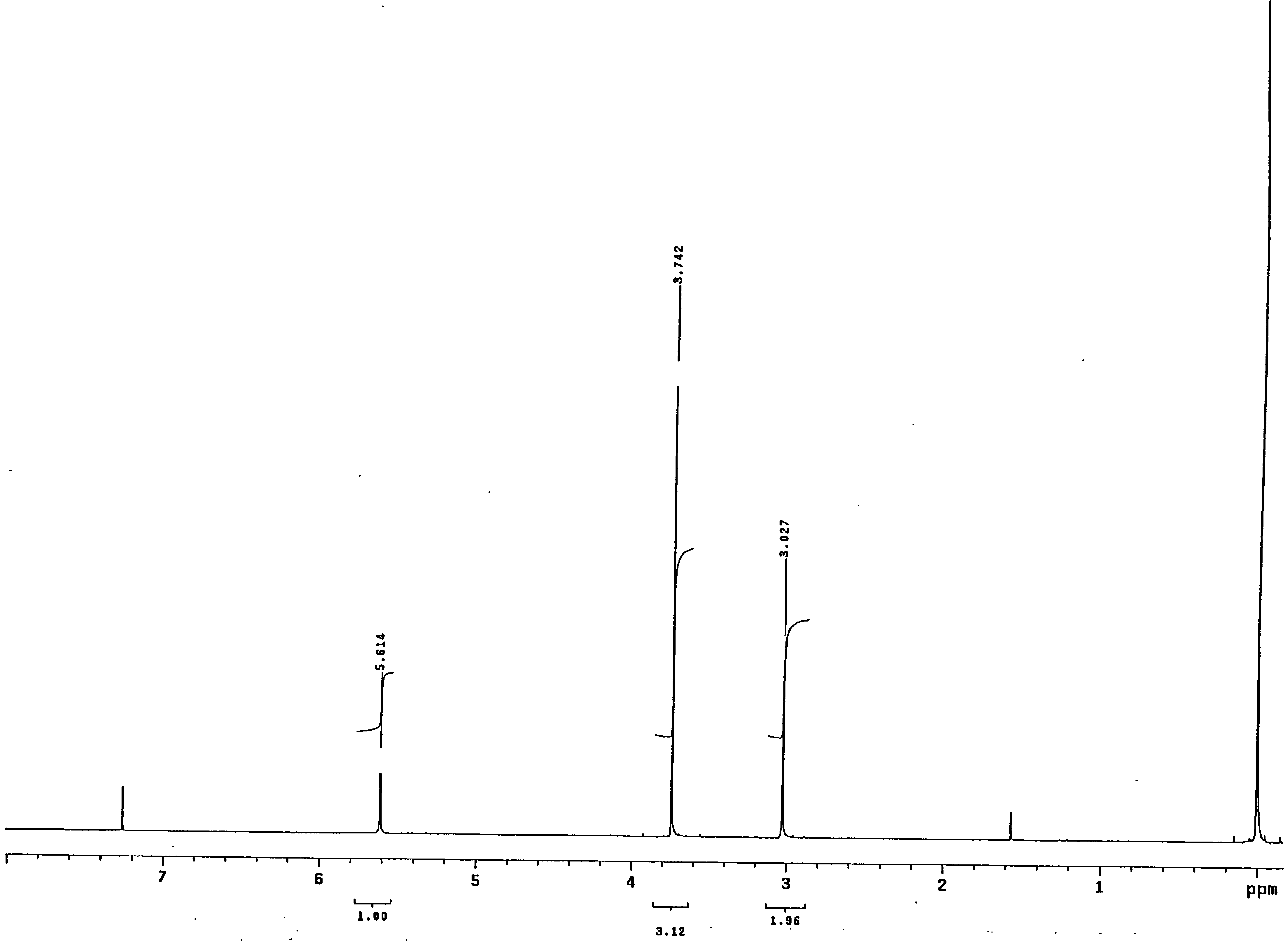
Nerdel *et al.* German Patent 1227458 (1966)

Appendix 1

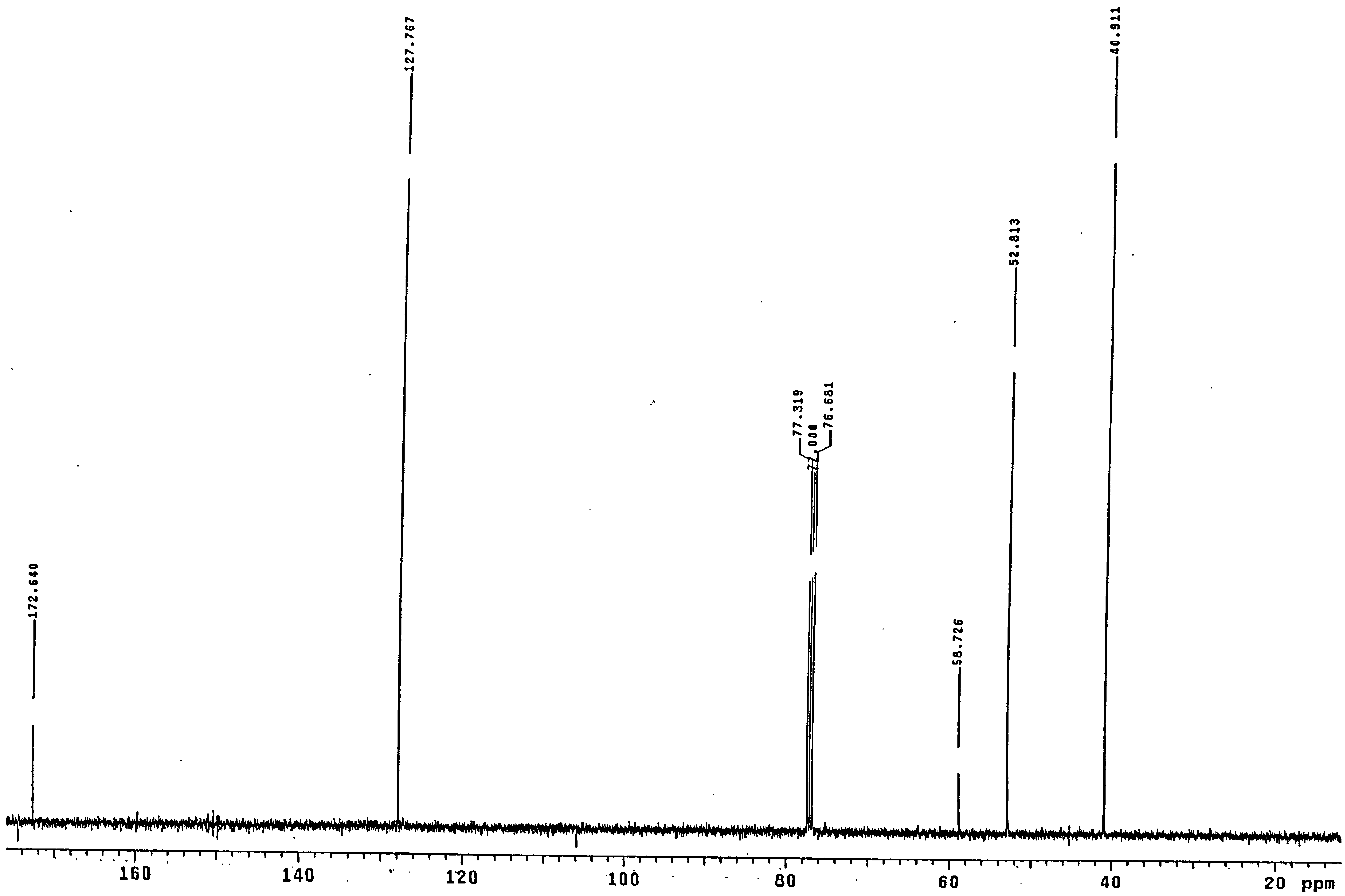
Analytical data for chapter 2



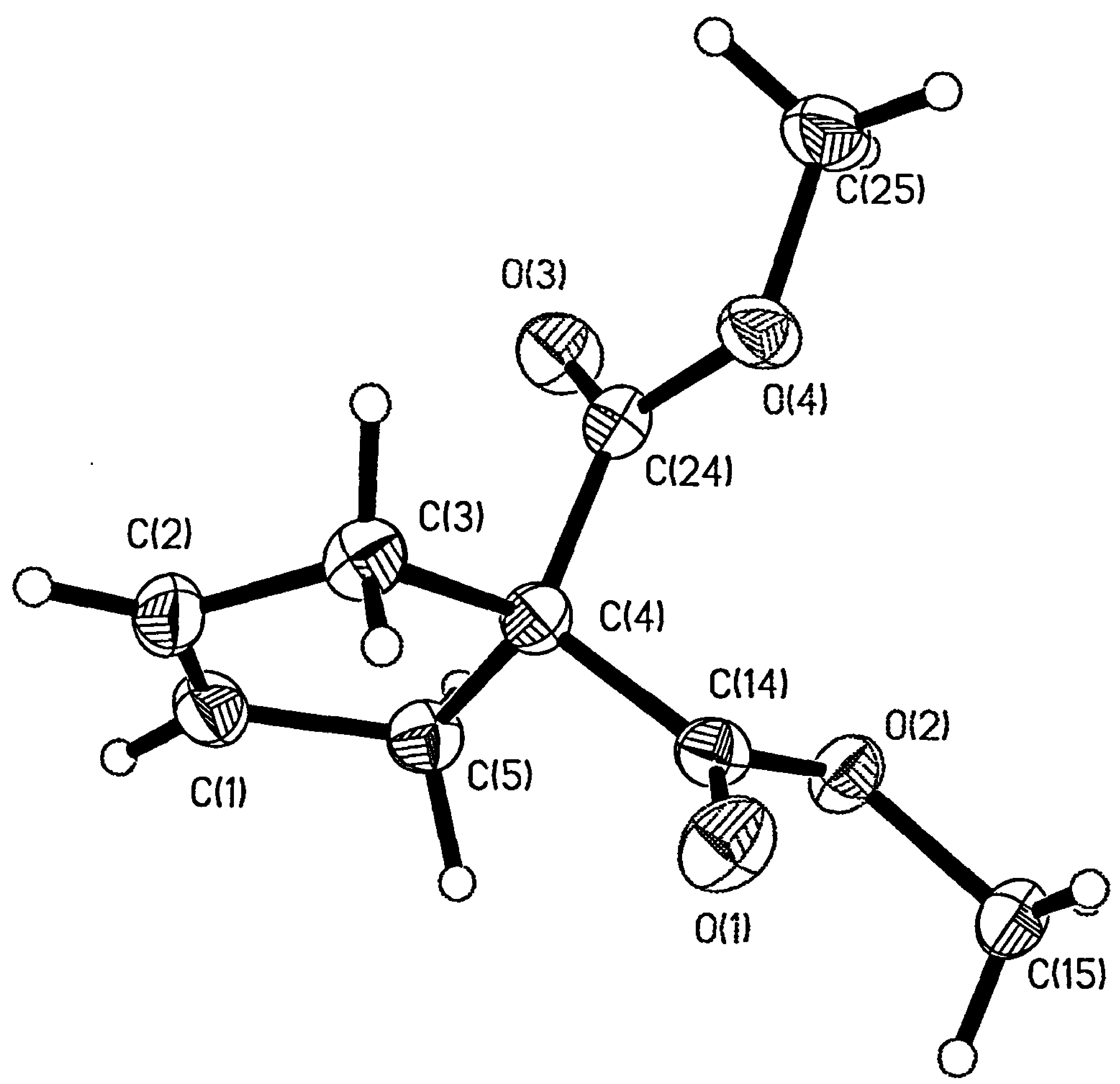
Appendix 1.1 Infra-red spectrum of dimethyl 3-cyclopentene-1,1-dicarboxylate



Appendix 1.2 ^{1}H NMR spectrum of dimethyl 3-cyclopentene-1,1-dicarboxylate



Appendix I.2 ^{13}C NMR spectrum of dimethyl 3-cyclopentene-1,1-dicarboxylate



Appendix 1.4 X-ray crystallography data for dimethyl 3-cyclopentene-1,1-dicarboxylate

Table 1. Crystal data and structure refinement for dimethyl 3-cyclopentene-1,1-dicarboxylate.

Identification code	96srv71
Empirical formula	C9 H12 O4
Formula weight	184.19
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 13.5576(6) A alpha = 90 deg.
	b = 6.0160(3) A beta = 113.278(1) deg.
	c = 12.2027(5) A gamma = 90 deg.
Volume, Z	914.26(7) A^3, 4
Density (calculated)	1.338 Mg/m^3
Absorption coefficient	0.105 mm^-1
F(000)	392
Crystal size	0.30 x 0.30 x 0.20 mm
Theta range for data collection	1.64 to 25.24 deg.
Limiting indices	-16<=h<=15, -6<=k<=6, -14<=l<=13
Reflections collected	3468
Independent reflections	1450 [R(int) = 0.0201]
Absorption correction	Not applied
Max. and min. transmission	none and none
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1442 / 0 / 166
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0944
R indices (all data)	R1 = 0.0359, wR2 = 0.1100
Extinction coefficient	not refined
Largest diff. peak and hole	0.200 and -0.194 e.A^-3

Table 2. Atomic coordinates (x 10^5) and equivalent isotropic displacement parameters (A^2 x 10^4) for dimethyl 3-cyclopentene-1,1-dicarboxylate. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(2)	38013(7)	19990(2)	37494(8)	268(3)
O(4)	15643(7)	34130(2)	21149(8)	290(3)
O(1)	41597(8)	55960(2)	35529(9)	323(3)
O(3)	10494(8)	23330(2)	35747(9)	328(3)

C(4)	26494(10)	46080(2)	40654(11)	224(3)
C(5)	29708(11)	39830(2)	54072(12)	262(3)
C(3)	23078(12)	71080(2)	39610(13)	265(4)
C(14)	36096(10)	41900(2)	37359(11)	230(3)
C(24)	16770(10)	32770(2)	32557(12)	231(3)
C(15)	47717(12)	13550(3)	35933(14)	291(4)
C(1)	25754(11)	59200(3)	58974(13)	297(4)
C(2)	22194(11)	75690(3)	51316(13)	297(4)
C(25)	5791(13)	24760(3)	12409(14)	358(4)

Table 3. Bond lengths [A] and angles [deg] for dimethyl 3-cyclopentene-1,1-dicarboxylate.

O(2)-C(14)	1.342(2)	O(2)-C(15)	1.455(2)
O(4)-C(24)	1.342(2)	O(4)-C(25)	1.454(2)
O(1)-C(14)	1.206(2)	O(3)-C(24)	1.208(2)
C(4)-C(24)	1.525(2)	C(4)-C(14)	1.527(2)
C(4)-C(3)	1.564(2)	C(4)-C(5)	1.565(2)
C(5)-C(1)	1.502(2)	C(5)-H(5B)	0.99(2)
C(5)-H(5A)	1.02(2)	C(3)-C(2)	1.506(2)
C(3)-H(3B)	0.99(2)	C(3)-H(3A)	0.96(2)
C(15)-H(15B)	0.96(2)	C(15)-H(15A)	0.97(2)
C(15)-H(15C)	0.93(2)	C(1)-C(2)	1.317(2)
C(1)-H(1)	0.95(2)	C(2)-H(2)	0.92(2)
C(25)-H(25B)	0.94(2)	C(25)-H(25A)	0.97(2)
C(25)-H(25C)	0.97(2)		
C(14)-O(2)-C(15)	116.17(11)	C(24)-O(4)-C(25)	115.62(11)
C(24)-C(4)-C(14)	110.58(11)	C(24)-C(4)-C(3)	107.44(11)
C(14)-C(4)-C(3)	113.12(11)	C(24)-C(4)-C(5)	111.33(11)
C(14)-C(4)-C(5)	108.79(10)	C(3)-C(4)-C(5)	105.50(11)
C(1)-C(5)-C(4)	103.58(11)	C(1)-C(5)-H(5B)	112.5(9)
C(4)-C(5)-H(5B)	111.4(9)	C(1)-C(5)-H(5A)	109.8(10)
C(4)-C(5)-H(5A)	111.1(9)	H(5B)-C(5)-H(5A)	108.4(14)
C(2)-C(3)-C(4)	103.40(11)	C(2)-C(3)-H(3B)	112.9(9)
C(4)-C(3)-H(3B)	112.5(10)	C(2)-C(3)-H(3A)	112.0(10)
C(4)-C(3)-H(3A)	109.4(10)	H(3B)-C(3)-H(3A)	106.8(13)
O(1)-C(14)-O(2)	124.08(12)	O(1)-C(14)-C(4)	125.95(13)
O(2)-C(14)-C(4)	109.85(11)	O(3)-C(24)-O(4)	123.85(12)
O(3)-C(24)-C(4)	125.22(12)	O(4)-C(24)-C(4)	110.79(11)
O(2)-C(15)-H(15B)	103.6(11)	O(2)-C(15)-H(15A)	108.9(11)
H(15B)-C(15)-H(15A)	111(2)	O(2)-C(15)-H(15C)	108.7(12)
H(15B)-C(15)-H(15C)	113(2)	H(15A)-C(15)-H(15C)	112(2)

C(2)-C(1)-C(5)	112.97(13)	C(2)-C(1)-H(1)	126.9(11)
C(5)-C(1)-H(1)	120.0(11)	C(1)-C(2)-C(3)	112.98(13)
C(1)-C(2)-H(2)	124.5(11)	C(3)-C(2)-H(2)	122.4(11)
O(4)-C(25)-H(25B)	105.3(12)	O(4)-C(25)-H(25A)	109.2(11)
H(25B)-C(25)-H(25A)	111(2)	O(4)-C(25)-H(25C)	109.3(11)
H(25B)-C(25)-H(25C)	112(2)	H(25A)-C(25)-H(25C)	110(2)

Table 4. Anisotropic displacement parameters (A^2 x 10^4) for dimethyl 3-cyclopentene-1,1-dicarboxylate. The anisotropic displacement factor exponent takes the form:

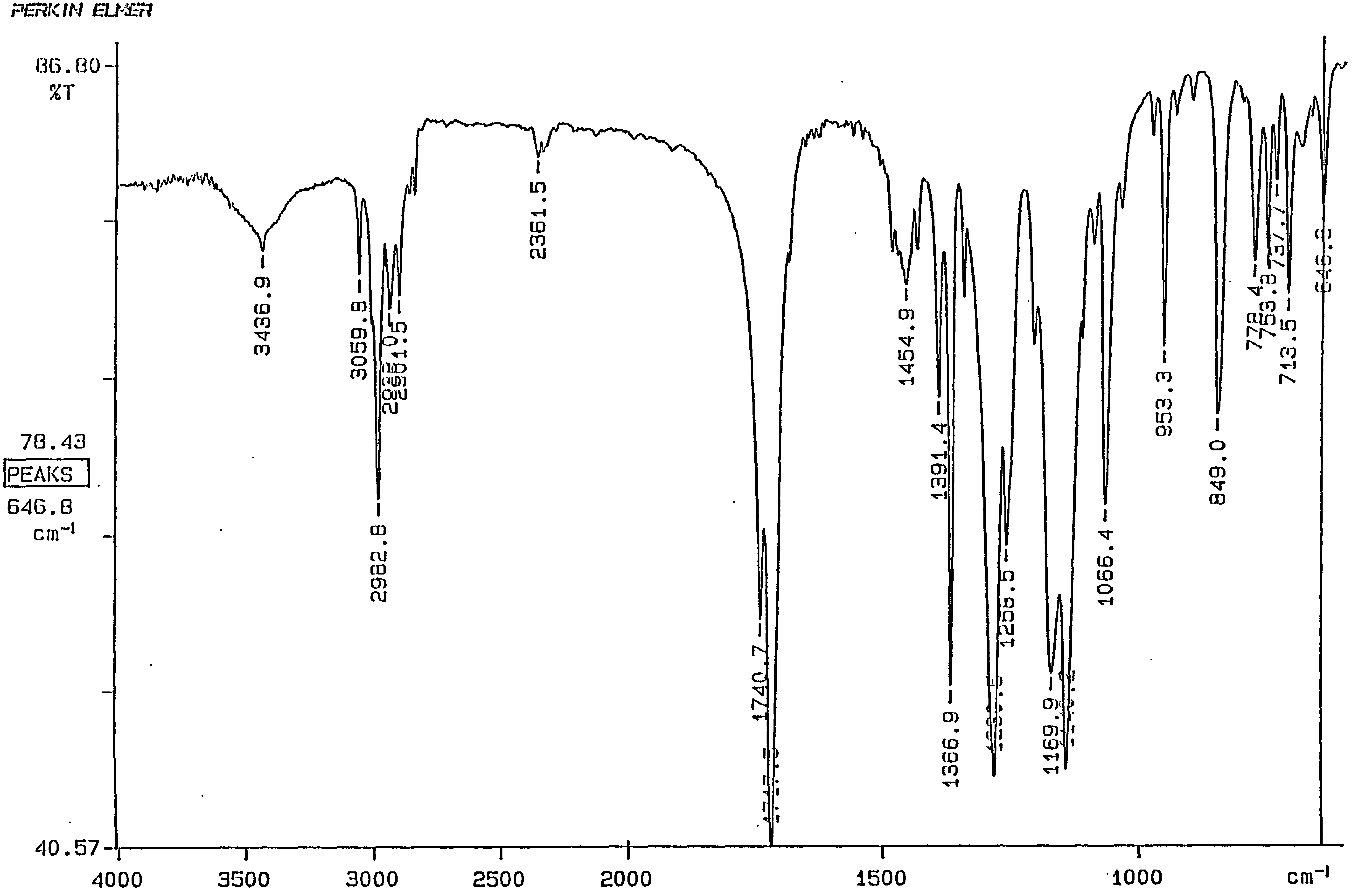
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(2)	238(5)	243(6)	358(6)	-19(4)	154(4)	-4(4)
O(4)	219(5)	425(6)	227(5)	-31(4)	90(4)	-67(4)
O(1)	295(6)	292(6)	436(6)	34(4)	201(5)	-32(4)
O(3)	304(6)	393(6)	315(6)	-8(4)	153(5)	-101(5)
C(4)	220(7)	228(7)	233(7)	9(5)	100(5)	-2(5)
C(5)	261(7)	283(8)	240(7)	25(5)	98(6)	0(6)
C(3)	253(7)	229(8)	319(8)	23(6)	119(6)	4(6)
C(14)	216(7)	253(8)	209(7)	2(5)	70(5)	-10(6)
C(24)	233(7)	227(7)	254(7)	13(5)	117(6)	25(6)
C(15)	249(7)	317(9)	337(8)	-34(7)	147(7)	20(6)
C(1)	270(7)	368(9)	264(7)	-68(6)	117(6)	-42(6)
C(2)	259(8)	271(8)	374(8)	-88(6)	140(7)	-21(6)
C(25)	244(8)	526(11)	284(8)	-72(7)	83(6)	-68(7)

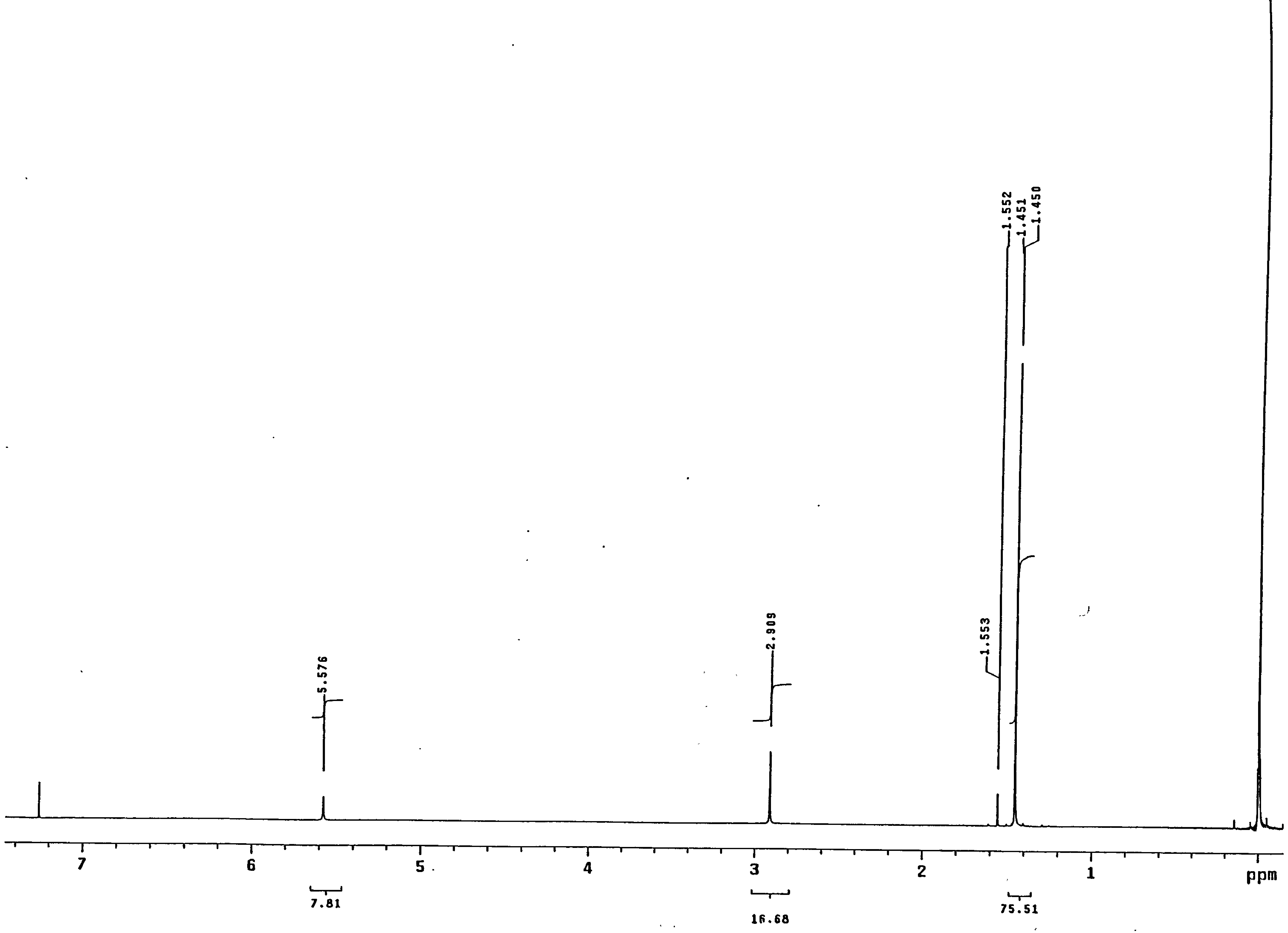
Table 5. Hydrogen coordinates (x 10^3) and isotropic displacement parameters (A^2 x 10^3) for dimethyl 3-cyclopentene-1,1-dicarboxylate.

	x	y	z	U(eq)
H(3B)	163(1)	740(3)	326(2)	31(4)
H(3A)	285(1)	801(3)	386(2)	33(4)
H(5B)	264(1)	256(3)	549(1)	31(4)
H(15B)	473(1)	-24(4)	354(2)	45(5)

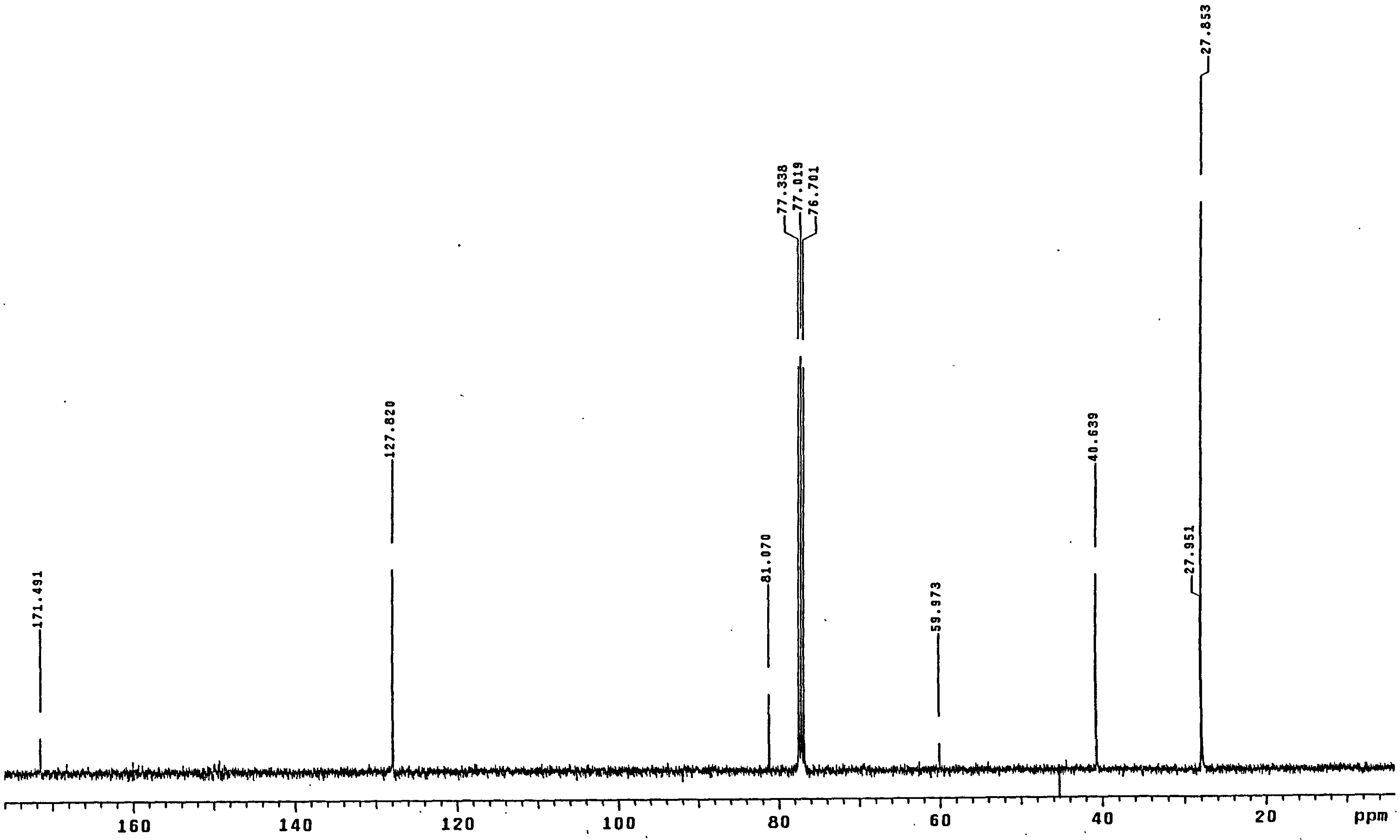
H(5A)	378(2)	385(3)	584(2)	36(4)
H(25B)	66(2)	254(3)	51(2)	48(5)
H(15A)	539(2)	180(3)	429(2)	41(5)
H(2)	198(1)	890(3)	530(2)	37(5)
H(25A)	51(2)	96(4)	146(2)	46(5)
H(25C)	-3(2)	336(3)	122(2)	43(5)
H(15C)	476(2)	201(3)	290(2)	43(5)
H(1)	263(2)	589(3)	670(2)	45(5)



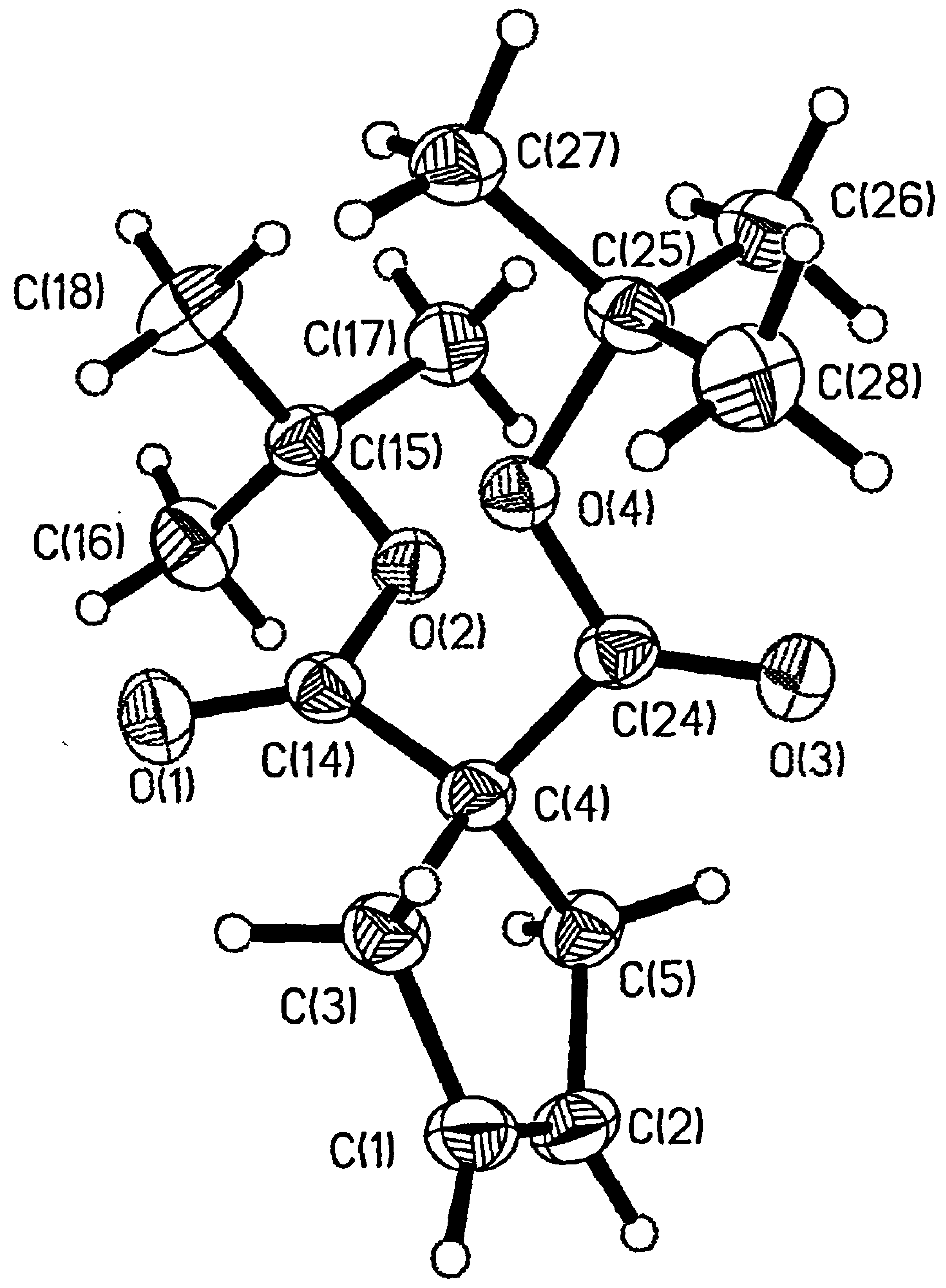
Appendix 1.5 Infra-red spectrum of ditertiary butyl 3-cyclopentene-1,1-dicarboxylate



Appendix 1.6 ^{1}H NMR spectrum of ditertiary butyl 3-cyclopentene-1,1-dicarboxylate



Appendix 1.7 ^{13}C NMR spectrum of ditertiary butyl 3-cyclopentene-1,1-dicarboxylate



Appendix 1.8 X-ray crystallography data for ditertiary butyl 3-cyclopentene-1,1-dicarboxylate

Table 1. Crystal data and structure refinement for ditertiary butyl 3-cyclopentene-1,1-dicarboxylate.

Identification code	96srv70m
Empirical formula	C15 H24 O4
Formula weight	268.34
Temperature	150(2) K
Wavelength	0.71073 A
Crystal system	Triclinic
Space group	P(-1)
Unit cell dimensions	a = 9.052(1) A alpha = 108.572(2) deg.
	b = 9.136(1) A beta = 96.583(2) deg.
	c = 11.077(1) A gamma = 115.004(1) deg.
Volume, Z	753.1(1) A^3, 2
Density (calculated)	1.183 Mg/m^3
Absorption coefficient	0.084 mm^-1
F(000)	292
Crystal size	0.25 x 0.25 x 0.25 mm
Theta range for data collection	2.03 to 25.46 deg.
Limiting indices	-10<=h<=8, -9<=k<=10, -7<=l<=13
Reflections collected	3302
Independent reflections	2446 [R(int) = 0.0284]
Absorption correction	Not applied
Max. and min. transmission	none and none
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2415 / 0 / 268
Goodness-of-fit on F^2	1.118
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.0960
R indices (all data)	R1 = 0.0477, wR2 = 0.1179
Extinction coefficient	Not refined
Largest diff. peak and hole	0.163 and -0.181 e.A^-3

Table 2. Atomic coordinates (x 10^5) and equivalent isotropic displacement parameters (A^2 x 10^4) for ditertiary butyl 3-cyclopentene-1,1-dicarboxylate. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(4)	19318(14)	27370(15)	79908(11)	284(3)
O(2)	33506(14)	4381(15)	70334(11)	299(3)
O(3)	20610(2)	33110(2)	61479(12)	379(3)
O(1)	55570(2)	23890(2)	88943(12)	400(3)

C(14)	45450(2)	20580(2)	79050(2)	284(4)
C(24)	26840(2)	31310(2)	70750(2)	281(4)
C(25)	1400(2)	23460(2)	78720(2)	304(4)
C(4)	44960(2)	34280(2)	74220(2)	283(4)
C(15)	30040(2)	-11520(2)	73010(2)	309(4)
C(26)	-10200(3)	7400(3)	65880(2)	416(5)
C(5)	51930(2)	33220(2)	61930(2)	335(4)
C(3)	56660(2)	53590(2)	84850(2)	330(4)
C(27)	-1760(2)	19360(3)	90710(2)	371(4)
C(17)	15870(3)	-26290(3)	60740(2)	421(5)
C(1)	65210(2)	51920(3)	65400(2)	372(4)
C(2)	67640(2)	62660(2)	77560(2)	371(4)
C(28)	-40(3)	39740(3)	79790(2)	436(5)
C(18)	24290(3)	-9760(3)	85440(2)	475(5)
C(16)	45530(3)	-14060(3)	73980(2)	441(5)

Table 3. Bond lengths [A] and angles [deg] for ditertiary butyl 3-cyclopentene-1,1-dicarboxylate.

O(4)-C(24)	1.343(2)	O(4)-C(25)	1.485(2)
O(2)-C(14)	1.338(2)	O(2)-C(15)	1.486(2)
O(3)-C(24)	1.206(2)	O(1)-C(14)	1.206(2)
C(14)-C(4)	1.524(2)	C(24)-C(4)	1.525(2)
C(25)-C(28)	1.516(3)	C(25)-C(27)	1.516(2)
C(25)-C(26)	1.518(3)	C(4)-C(5)	1.557(2)
C(4)-C(3)	1.559(2)	C(15)-C(17)	1.511(3)
C(15)-C(18)	1.512(3)	C(15)-C(16)	1.513(3)
C(26)-H(26C)	0.98(3)	C(26)-H(26A)	0.97(2)
C(26)-H(26B)	0.97(2)	C(5)-C(1)	1.500(3)
C(5)-H(5B)	0.99(2)	C(5)-H(5A)	0.97(2)
C(3)-C(2)	1.497(3)	C(3)-H(3B)	0.99(2)
C(3)-H(3A)	1.00(2)	C(27)-H(27B)	0.99(2)
C(27)-H(27C)	0.98(2)	C(27)-H(27A)	1.00(2)
C(17)-H(17B)	1.00(2)	C(17)-H(17C)	0.96(3)
C(17)-H(17A)	1.01(2)	C(1)-C(2)	1.316(3)
C(1)-H(1)	0.98(2)	C(2)-H(2)	0.98(2)
C(28)-H(28C)	0.99(2)	C(28)-H(28B)	0.97(2)
C(28)-H(28A)	0.98(3)	C(18)-H(18A)	0.98(3)
C(18)-H(18B)	0.99(3)	C(18)-H(18C)	0.98(3)
C(16)-H(16C)	0.97(2)	C(16)-H(16B)	1.00(3)
C(16)-H(16A)	0.99(2)		
C(24)-O(4)-C(25)	121.01(13)	C(14)-O(2)-C(15)	121.47(13)

O(1)-C(14)-O(2)	125.5(2)	O(1)-C(14)-C(4)	124.9(2)
O(2)-C(14)-C(4)	109.55(14)	O(3)-C(24)-O(4)	125.5(2)
O(3)-C(24)-C(4)	124.4(2)	O(4)-C(24)-C(4)	110.03(13)
O(4)-C(25)-C(28)	109.75(14)	O(4)-C(25)-C(27)	102.83(13)
C(28)-C(25)-C(27)	110.2(2)	O(4)-C(25)-C(26)	109.33(14)
C(28)-C(25)-C(26)	113.4(2)	C(27)-C(25)-C(26)	110.8(2)
C(14)-C(4)-C(24)	110.28(13)	C(14)-C(4)-C(5)	109.77(14)
C(24)-C(4)-C(5)	110.65(14)	C(14)-C(4)-C(3)	112.40(14)
C(24)-C(4)-C(3)	108.07(14)	C(5)-C(4)-C(3)	105.57(13)
O(2)-C(15)-C(17)	102.50(13)	O(2)-C(15)-C(18)	109.0(2)
C(17)-C(15)-C(18)	111.8(2)	O(2)-C(15)-C(16)	110.5(2)
C(17)-C(15)-C(16)	109.9(2)	C(18)-C(15)-C(16)	112.7(2)
C(25)-C(26)-H(26C)	107.8(14)	C(25)-C(26)-H(26A)	111.0(13)
H(26C)-C(26)-H(26A)	109(2)	C(25)-C(26)-H(26B)	109.5(13)
H(26C)-C(26)-H(26B)	108(2)	H(26A)-C(26)-H(26B)	111(2)
C(1)-C(5)-C(4)	104.26(14)	C(1)-C(5)-H(5B)	111.7(11)
C(4)-C(5)-H(5B)	110.4(11)	C(1)-C(5)-H(5A)	111.8(13)
C(4)-C(5)-H(5A)	110.6(13)	H(5B)-C(5)-H(5A)	108(2)
C(2)-C(3)-C(4)	103.83(14)	C(2)-C(3)-H(3B)	112.4(12)
C(4)-C(3)-H(3B)	110.7(12)	C(2)-C(3)-H(3A)	112.3(11)
C(4)-C(3)-H(3A)	110.5(11)	H(3B)-C(3)-H(3A)	107(2)
C(25)-C(27)-H(27B)	108.5(11)	C(25)-C(27)-H(27C)	111.5(11)
H(27B)-C(27)-H(27C)	111(2)	C(25)-C(27)-H(27A)	109.8(13)
H(27B)-C(27)-H(27A)	109(2)	H(27C)-C(27)-H(27A)	107(2)
C(15)-C(17)-H(17B)	109.0(12)	C(15)-C(17)-H(17C)	109.8(14)
H(17B)-C(17)-H(17C)	108(2)	C(15)-C(17)-H(17A)	110.8(13)
H(17B)-C(17)-H(17A)	109(2)	H(17C)-C(17)-H(17A)	110(2)
C(2)-C(1)-C(5)	112.4(2)	C(2)-C(1)-H(1)	126.6(13)
C(5)-C(1)-H(1)	120.9(12)	C(1)-C(2)-C(3)	113.3(2)
C(1)-C(2)-H(2)	124.8(12)	C(3)-C(2)-H(2)	121.8(12)
C(25)-C(28)-H(28C)	112.3(13)	C(25)-C(28)-H(28B)	109.0(13)
H(28C)-C(28)-H(28B)	110(2)	C(25)-C(28)-H(28A)	108(2)
H(28C)-C(28)-H(28A)	110(2)	H(28B)-C(28)-H(28A)	108(2)
C(15)-C(18)-H(18A)	110.3(14)	C(15)-C(18)-H(18B)	109(2)
H(18A)-C(18)-H(18B)	110(2)	C(15)-C(18)-H(18C)	107.2(14)
H(18A)-C(18)-H(18C)	111(2)	H(18B)-C(18)-H(18C)	109(2)
C(15)-C(16)-H(16C)	105.8(14)	C(15)-C(16)-H(16B)	109.5(14)
H(16C)-C(16)-H(16B)	111(2)	C(15)-C(16)-H(16A)	112.6(13)
H(16C)-C(16)-H(16A)	111(2)	H(16B)-C(16)-H(16A)	107(2)

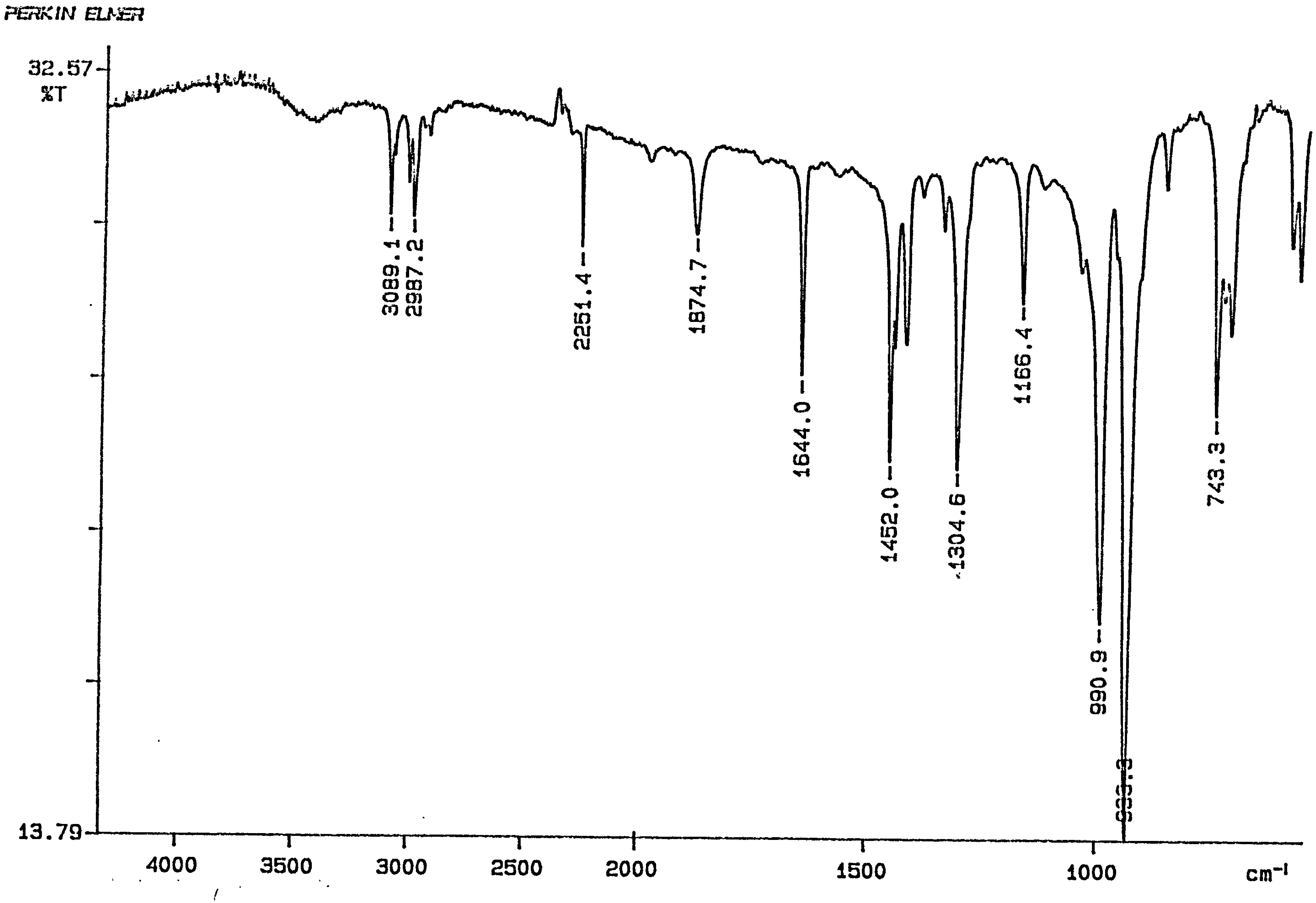
Table 4. Anisotropic displacement parameters (A^2 x 10^4) for ditertiary butyl 3-cyclopentene-1,1-dicarboxylate. The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(4)	249(6)	328(6)	274(6)	129(5)	98(5)	131(5)
O(2)	314(6)	261(6)	282(6)	114(5)	56(5)	111(5)
O(3)	342(7)	496(8)	350(7)	249(6)	99(6)	193(6)
O(1)	400(7)	377(7)	341(7)	122(6)	-4(6)	163(6)
C(14)	255(8)	318(9)	271(9)	108(7)	113(7)	133(7)
C(24)	294(9)	234(8)	268(8)	91(7)	91(7)	93(7)
C(25)	238(8)	328(9)	325(9)	120(8)	99(7)	125(7)
C(4)	277(9)	280(9)	53(8)	104(7)	87(7)	102(7)
C(15)	330(9)	289(9)	346(9)	167(8)	116(8)	152(7)
C(26)	319(10)	420(11)	366(11)	111(9)	96(9)	94(9)
C(5)	351(10)	379(10)	305(10)	153(8)	154(8)	180(9)
C(3)	295(9)	291(9)	313(9)	94(8)	62(8)	92(8)
C(27)	306(10)	451(11)	354(10)	173(9)	151(8)	163(9)
C(17)	416(11)	308(10)	458(12)	164(9)	48(10)	120(9)
C(1)	339(10)	430(11)	471(11)	291(10)	208(9)	191(9)
C(2)	307(9)	313(10)	487(12)	211(9)	110(9)	113(8)
C(28)	461(12)	432(12)	498(13)	200(11)	183(11)	270(10)
C(18)	640(15)	429(12)	457(12)	244(11)	305(12)	266(11)
C(16)	428(12)	413(12)	495(13)	153(10)	98(10)	247(10)

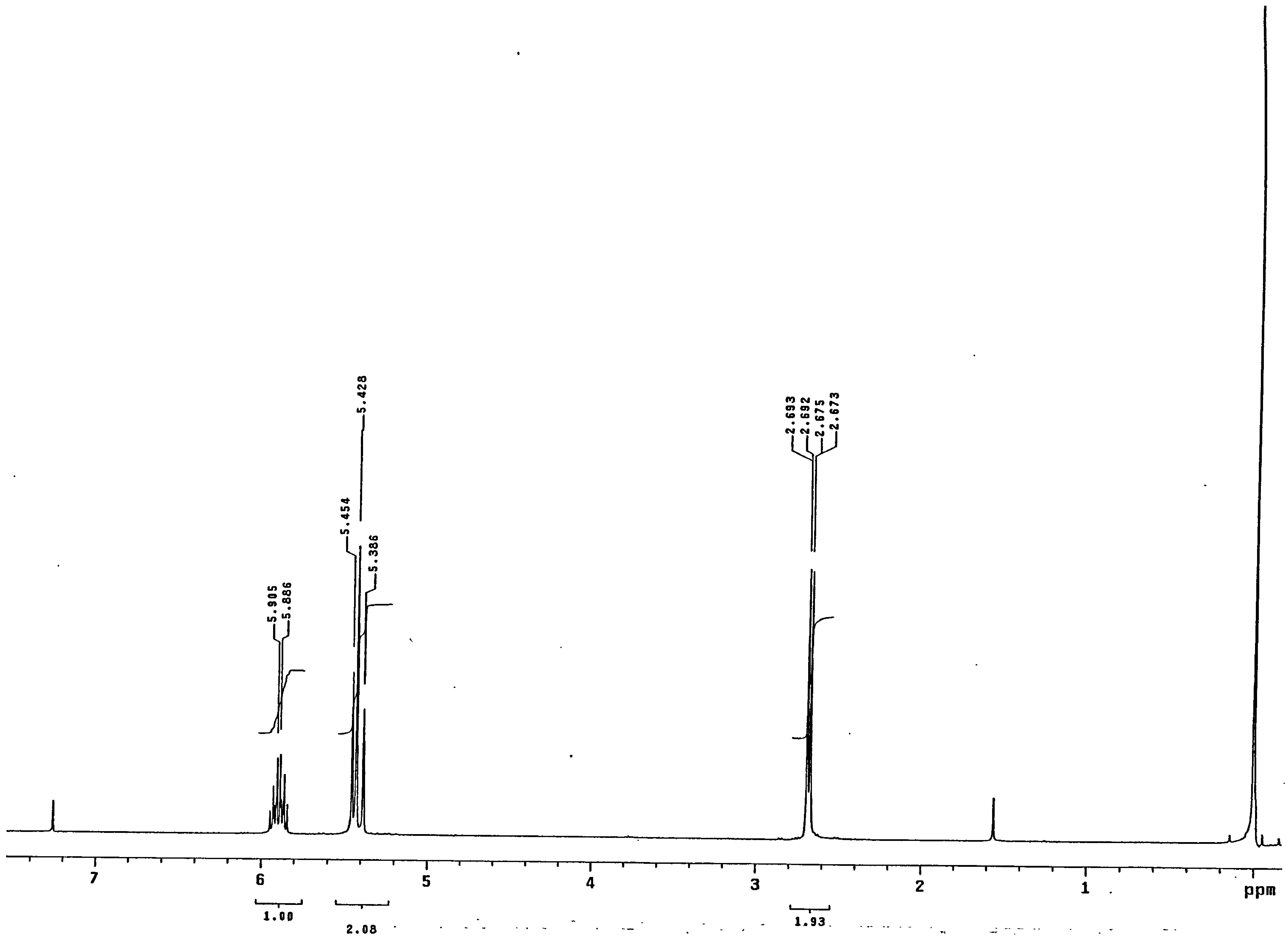
Table 5. Hydrogen coordinates (x 10^3) and isotropic displacement parameters (A^2 x 10^3) for ditertiary butyl 3-cyclopentene-1,1-dicarboxylate.

	x	y	z	U(eq)
H(27B)	-137(3)	160(3)	905(2)	36(5)
H(27C)	61(3)	295(3)	991(2)	40(5)
H(28C)	13(3)	424(3)	719(2)	50(6)
H(17B)	127(3)	-378(3)	615(2)	47(6)
H(3B)	498(3)	591(3)	882(2)	42(5)
H(28B)	85(3)	497(3)	877(2)	49(6)

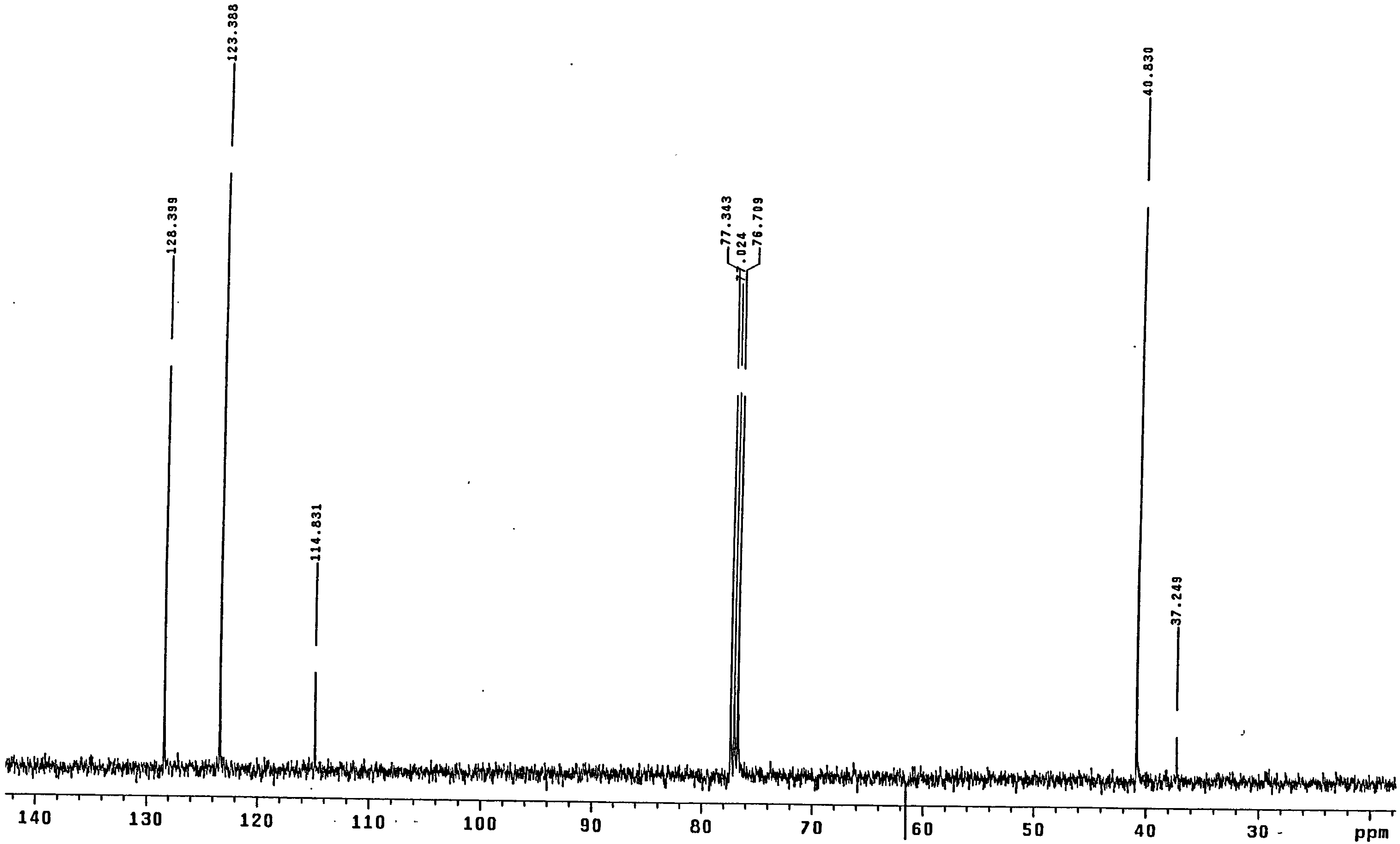
H(5B)	427(3)	287(3)	538(2)	40(5)
H(17C)	60(3)	-248(3)	602(2)	61(7)
H(16C)	417(3)	-257(3)	740(2)	60(7)
H(2)	755(3)	754(3)	816(2)	48(6)
H(27A)	2(3)	92(3)	903(2)	54(6)
H(3A)	635(3)	537(3)	927(2)	39(5)
H(26C)	-220(3)	44(3)	657(2)	58(7)
H(5A)	567(3)	253(3)	605(2)	49(6)
H(18A)	334(3)	4(3)	932(2)	57(7)
H(16B)	499(3)	-133(3)	662(3)	66(7)
H(16A)	550(3)	-49(3)	821(2)	51(6)
H(26A)	-80(3)	99(3)	582(2)	50(6)
H(28A)	-112(4)	376(3)	808(3)	75(8)
H(1)	711(3)	551(3)	589(2)	47(6)
H(17A)	196(3)	-267(3)	524(2)	54(6)
H(18B)	142(4)	-82(3)	842(3)	71(8)
H(18C)	211(3)	-208(4)	865(2)	65(7)
H(26B)	-87(3)	-25(3)	658(2)	50(6)



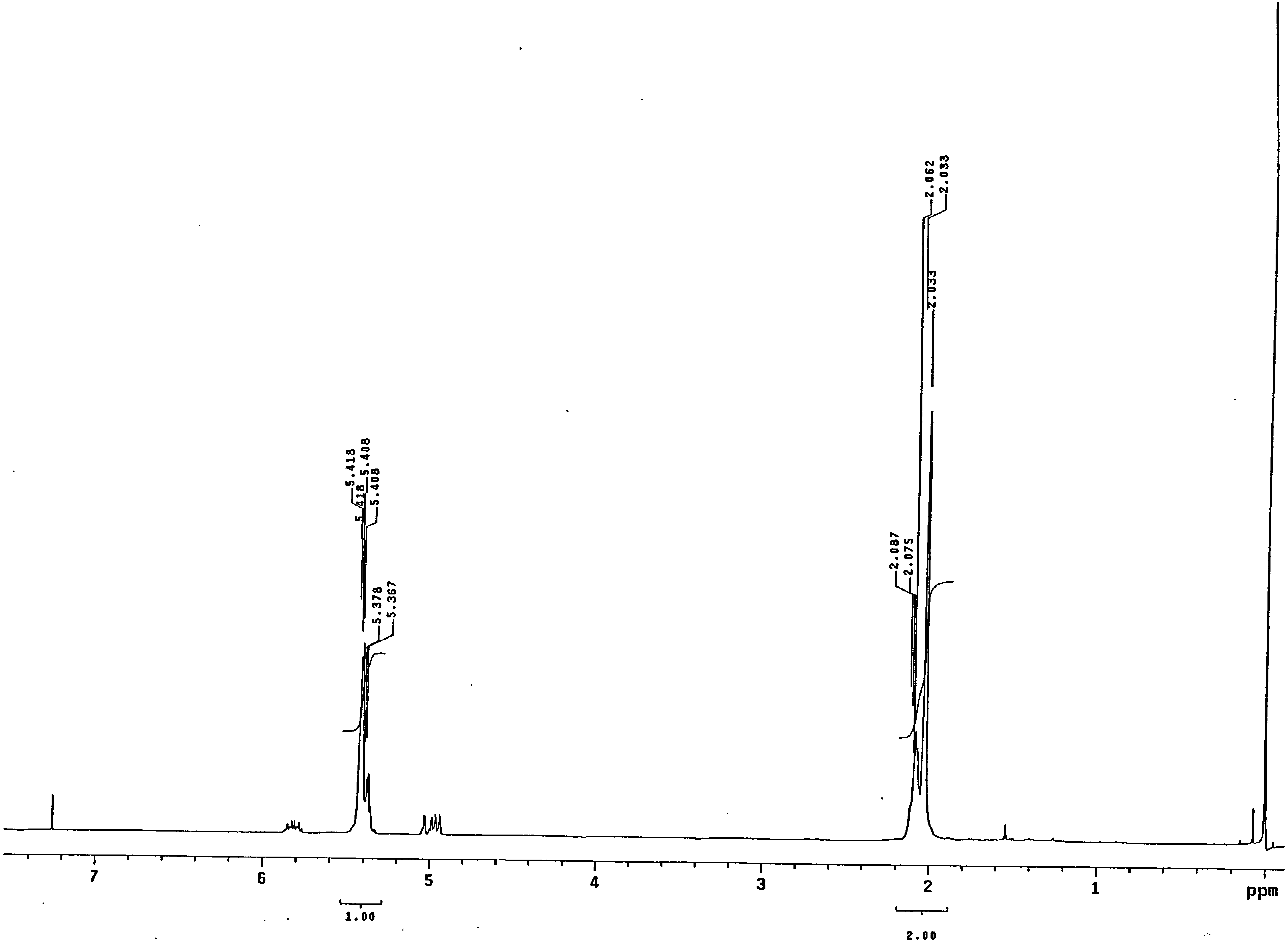
Appendix 1.9 Infra-red spectrum of diallyl malononitrile



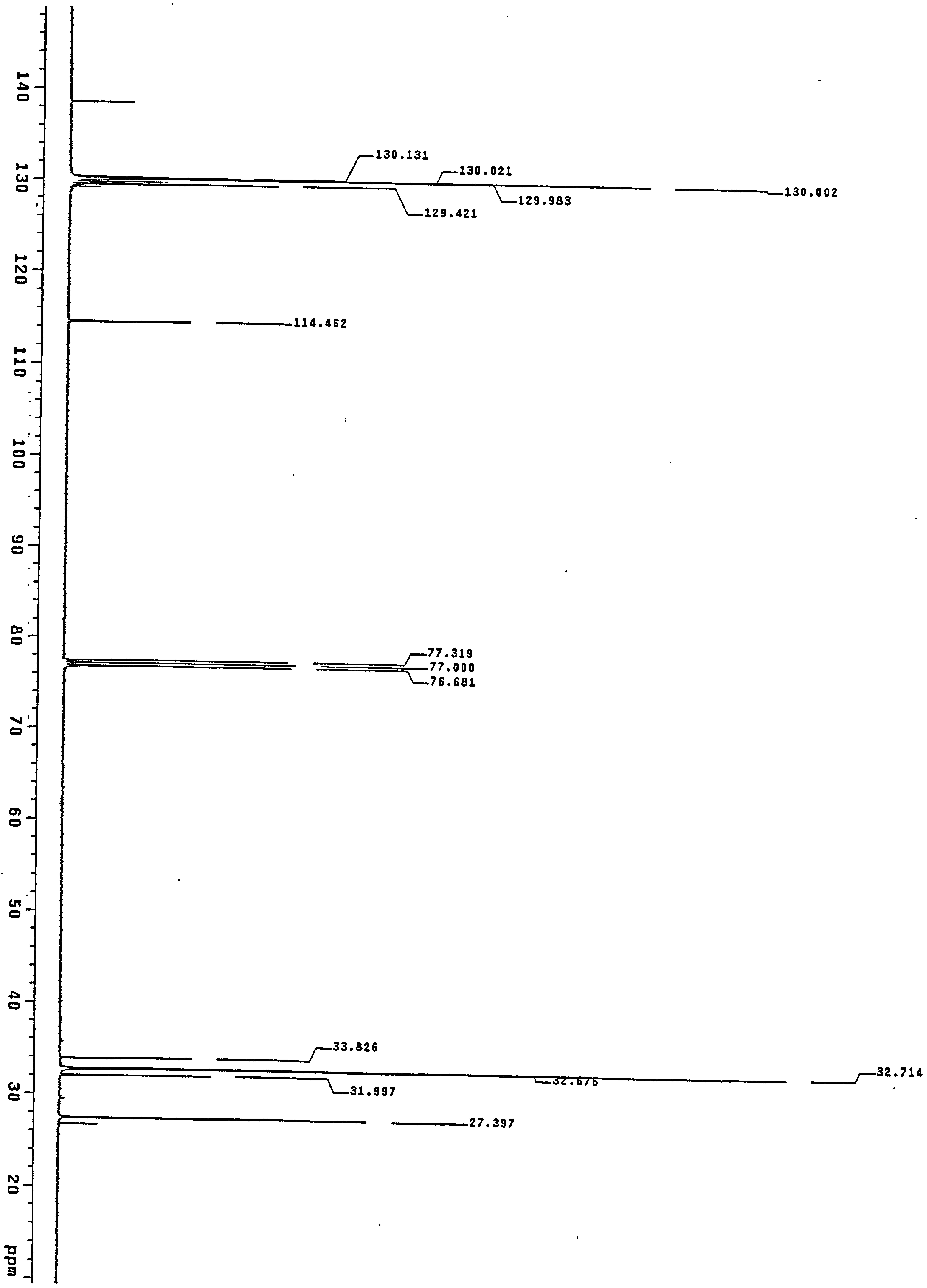
Appendix 1.10 ^{1}H NMR spectrum of diallyl malononitrile

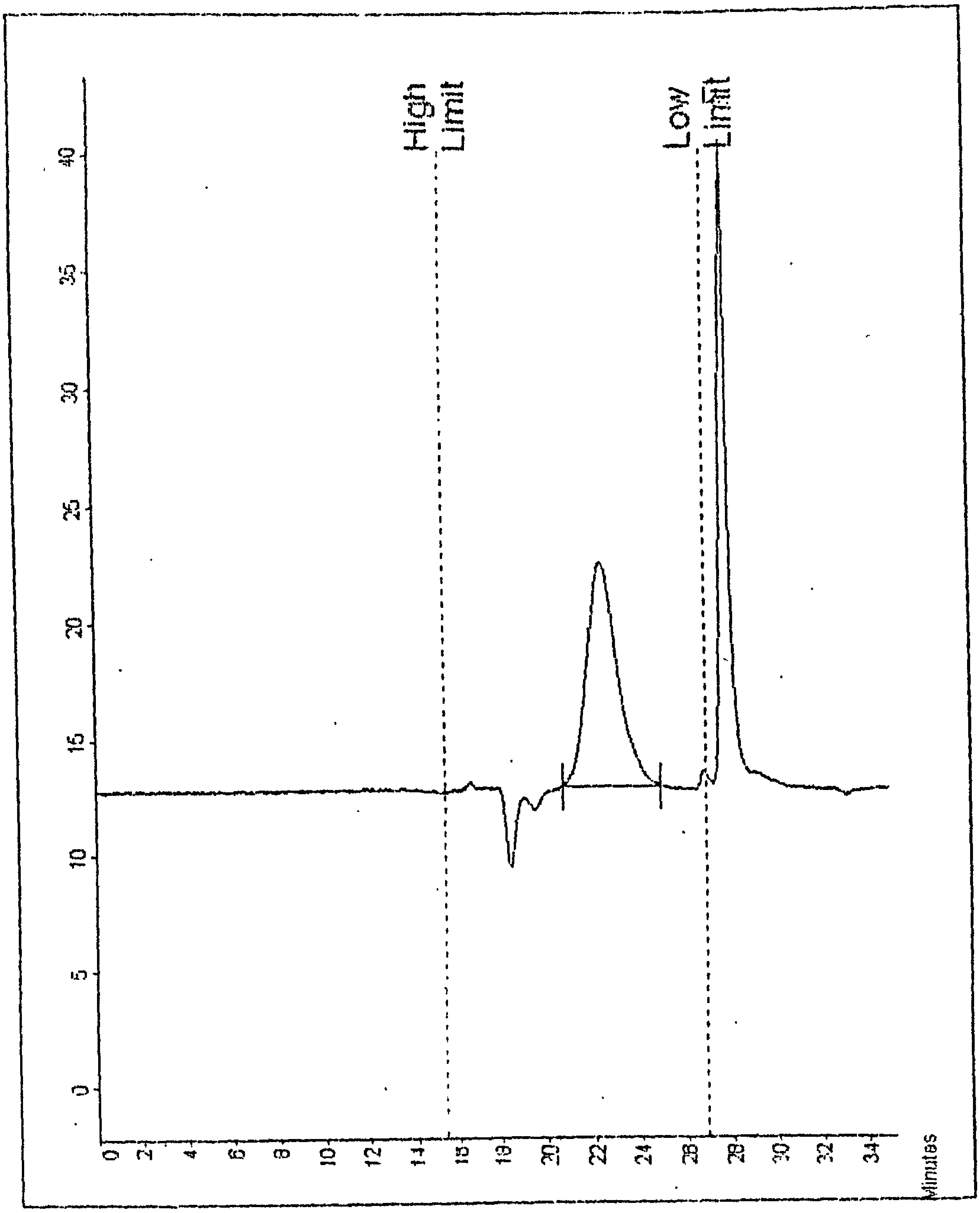


Appendix 1.11 ^{13}C NMR spectrum of diallyl malononitrile



Appendix 1.12 ^{1}H NMR spectrum of 1,4-polybutadiene prepared using classical initiator

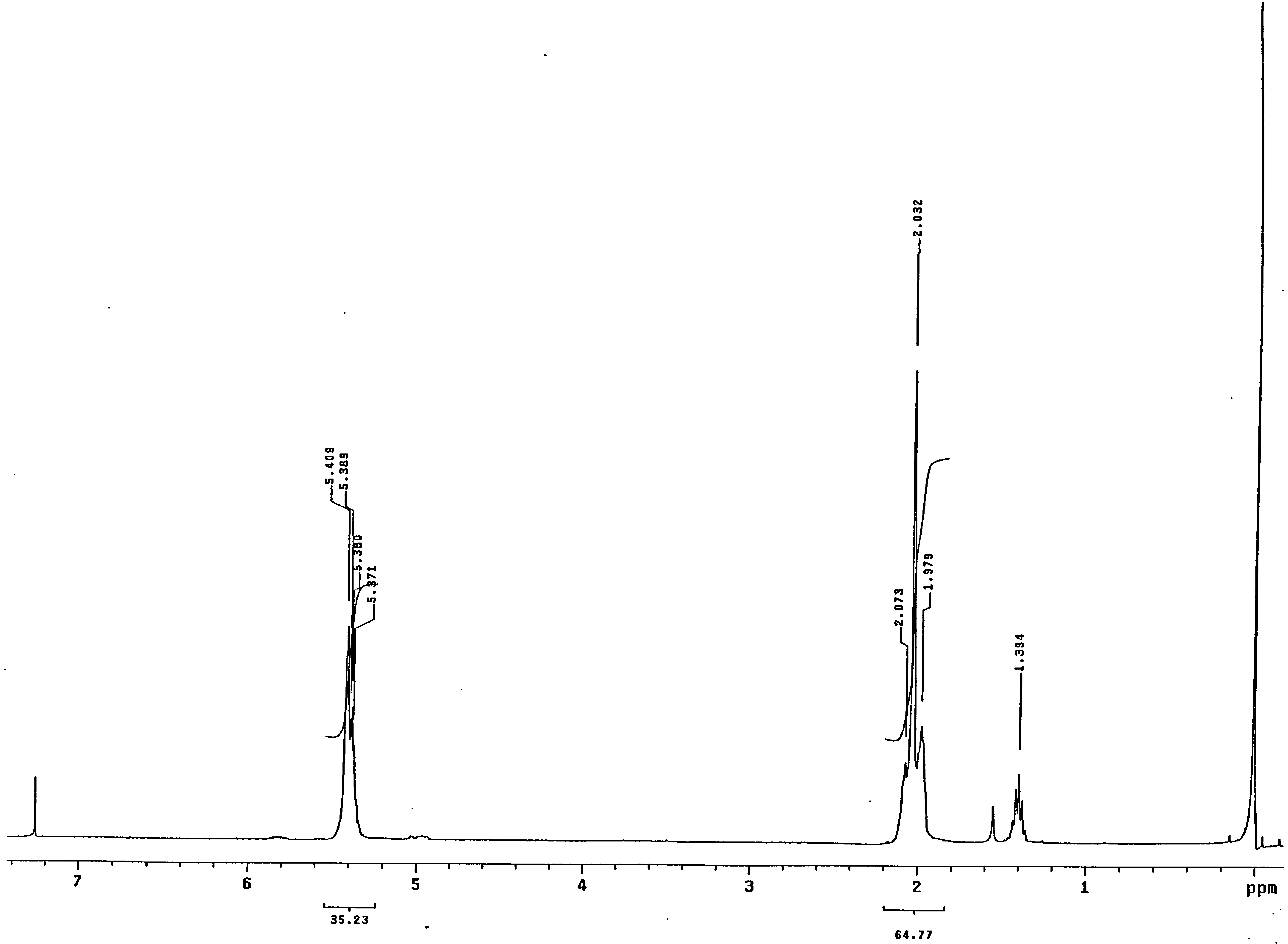

140
130
120
110
100
90
80
70
60
50
40
30
20
ppm
130.131
130.021
130.002
129.983
129.421
114.462
77.319
77.000
76.681
33.826
32.714
32.676
31.997
27.397



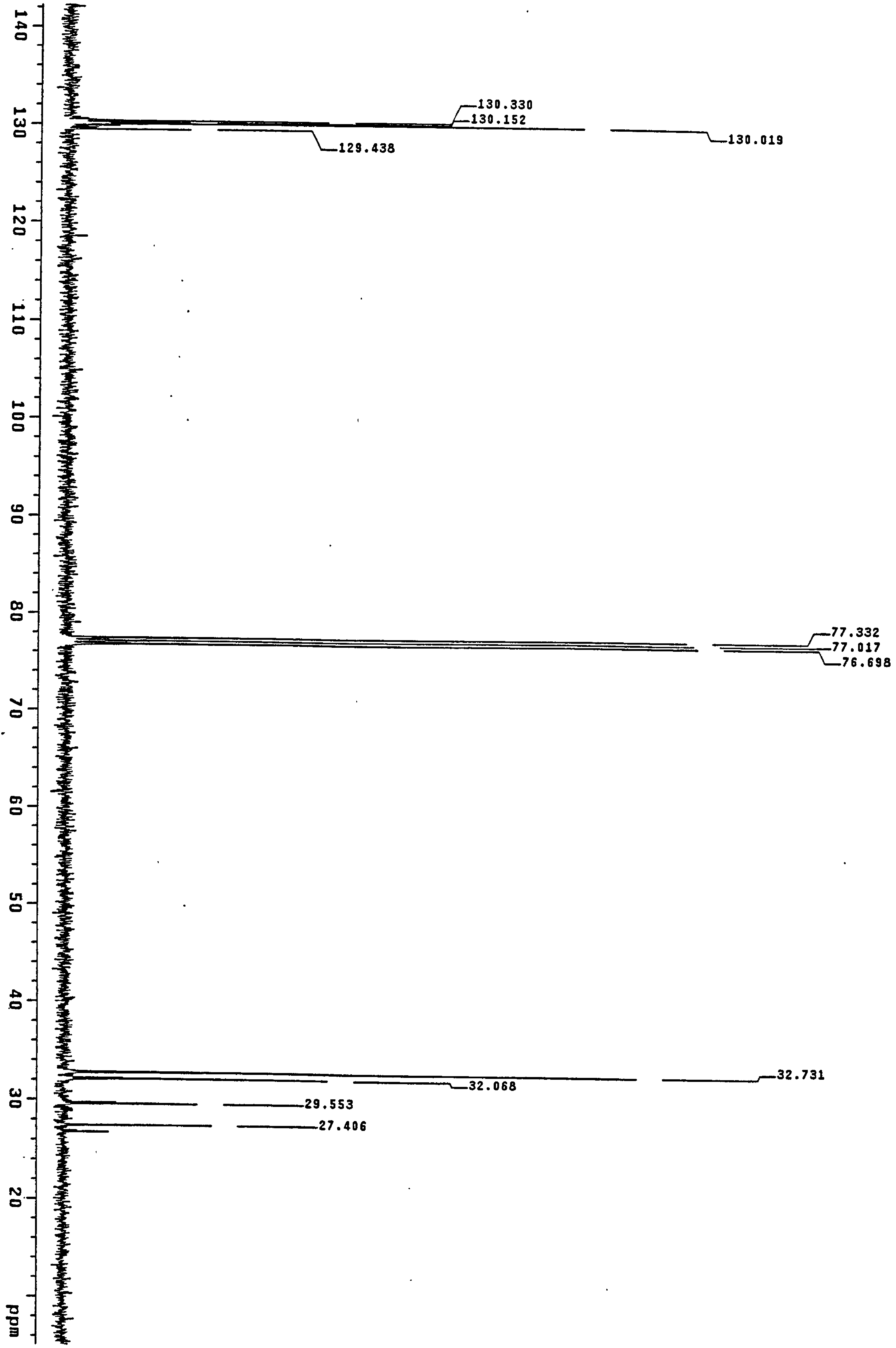
Molecular Weight Averages

Mp =	1216	Mz =	1421
Mn =	1002	Mz+1 =	1671
Mw =	1198	Mv =	1167
Polydispersity =	1.195	Peak Area =	182045

Appendix 1.14 GPC trace for 1,4-polybutadiene prepared using classical initiator



Appendix 1.15 ^{1}H NMR spectrum of 1,4-polybutadiene prepared using well-defined initiator


140
130
120
110
100
90
80
70
60
50
40
30
20
ppm
130.330
130.152
130.019
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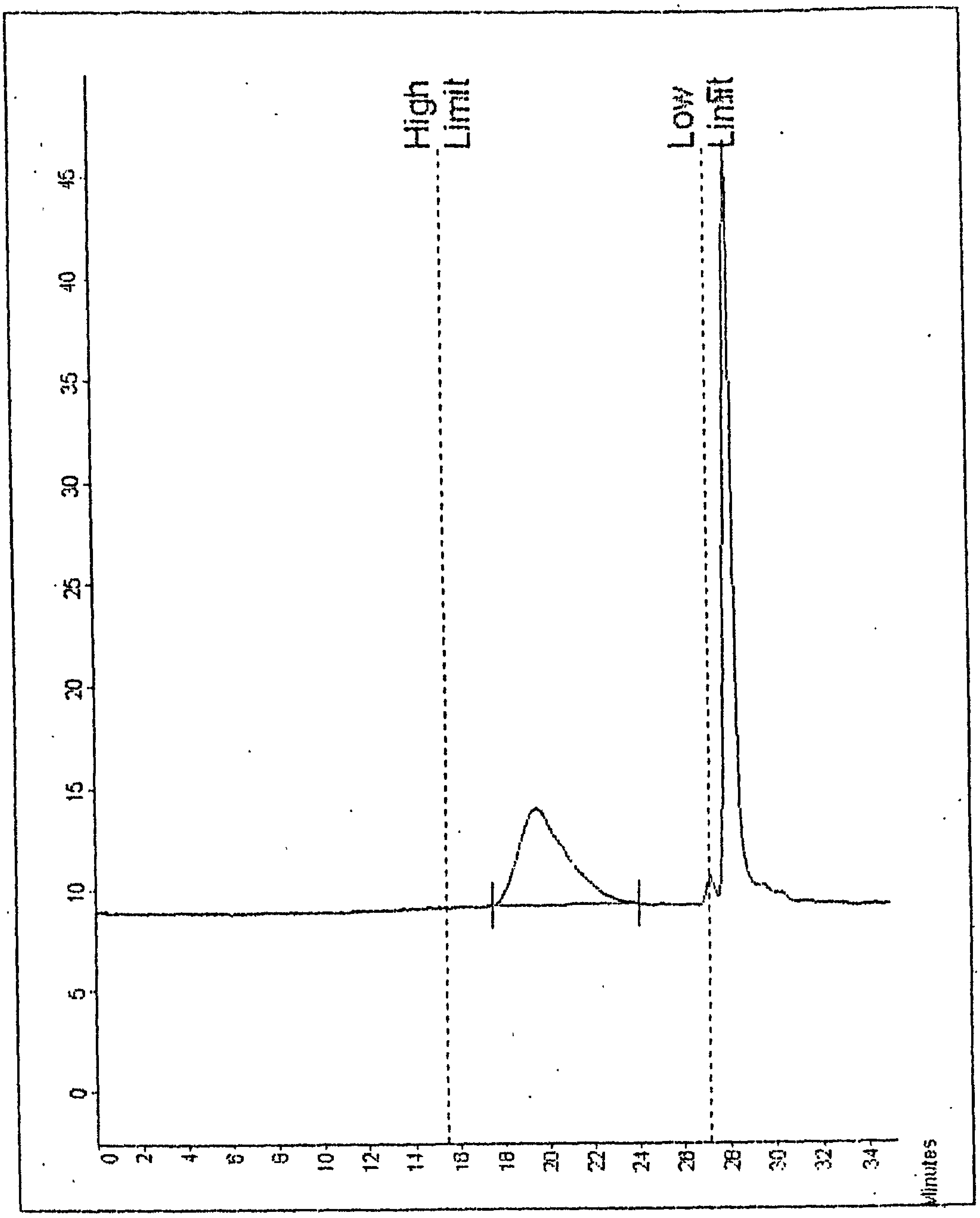
32.068
29.553
27.406



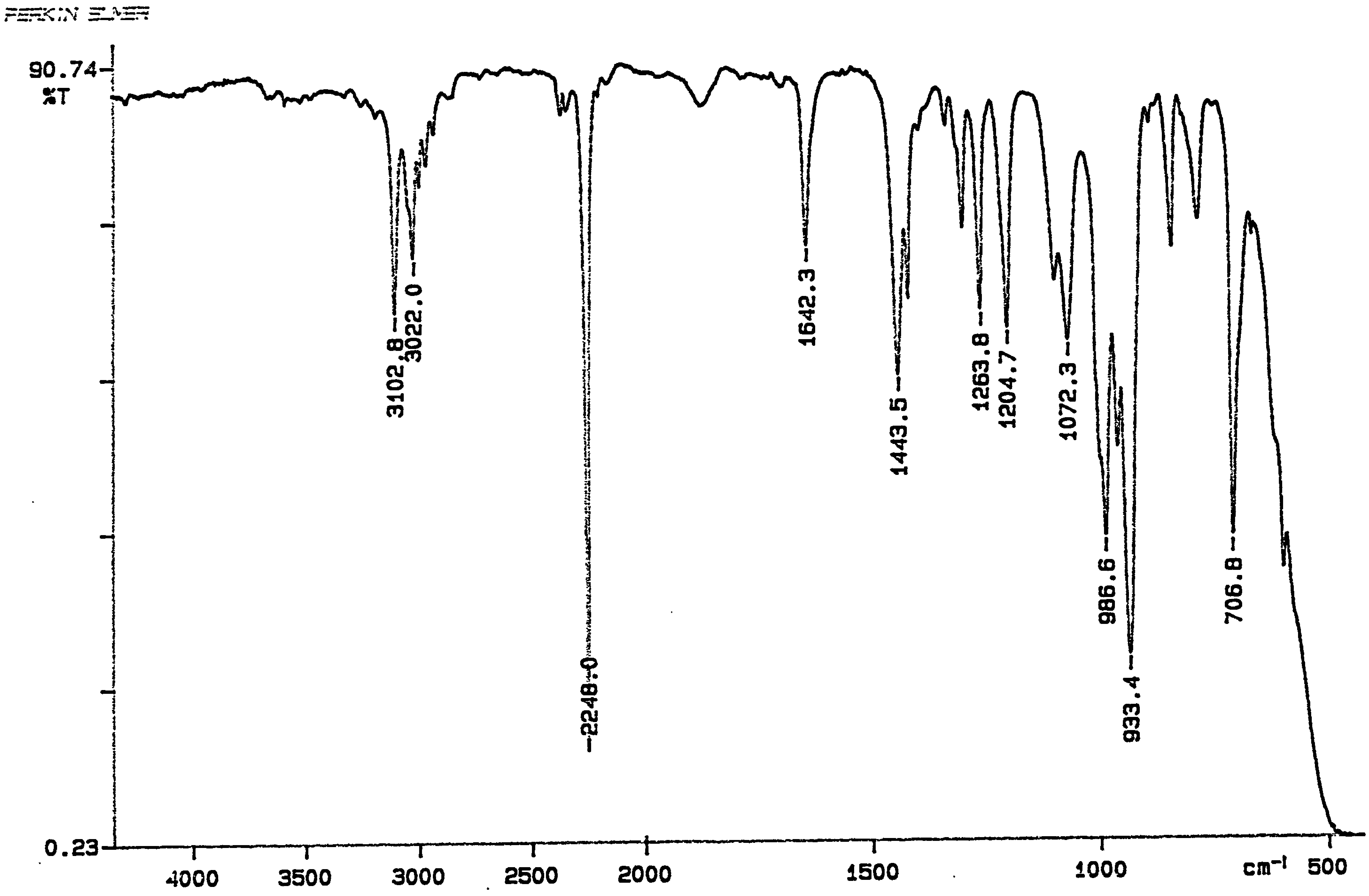
Molecular Weight Averages

Mp = 15122
Mn = 5295
Mw = 13849
Polydispersity = 2.616
Mz = 26601
Mz+1 = 39842
Mv = 12268
Peak Area = 146485

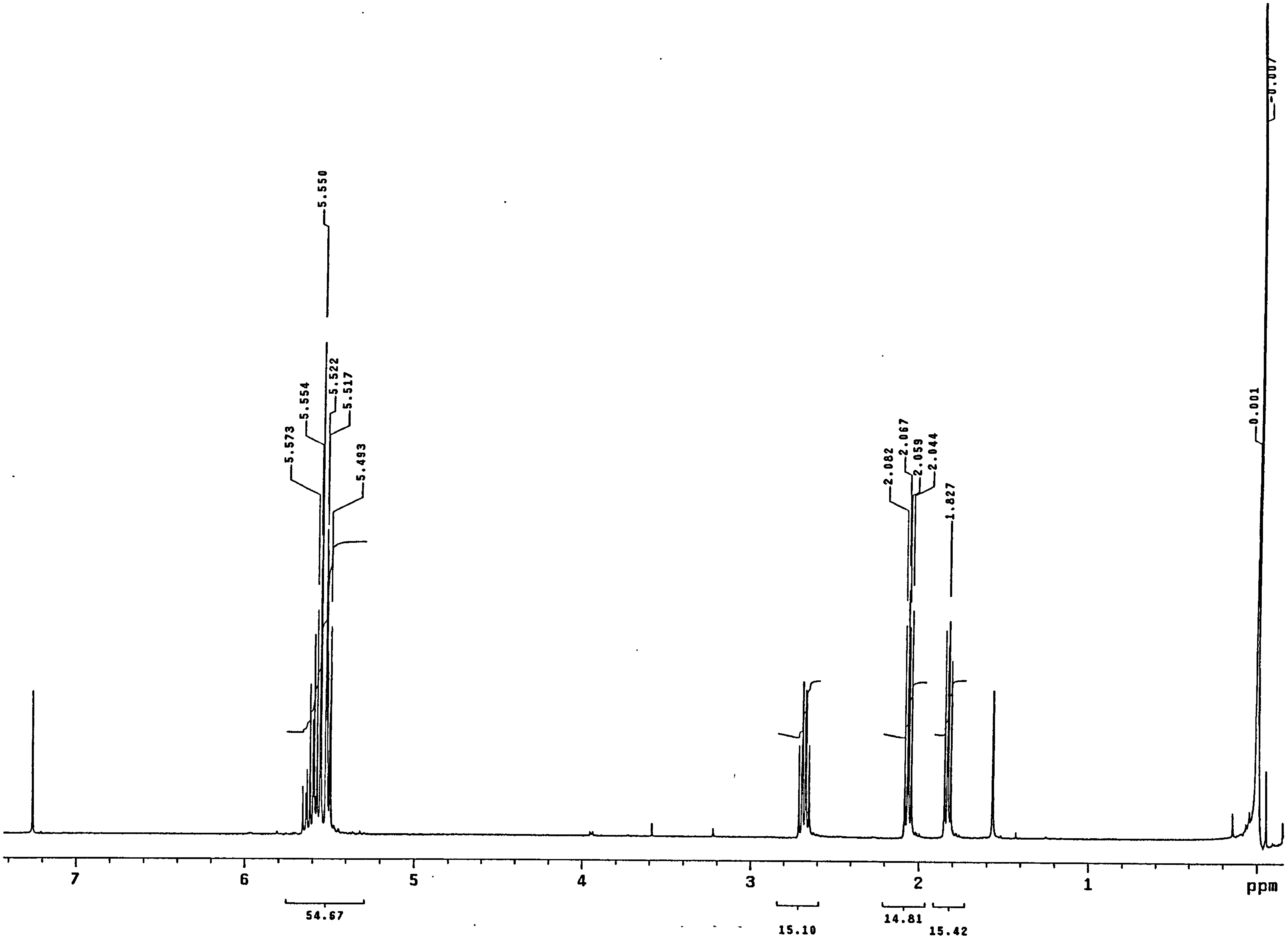
Appendix 1.17 GPC trace of 1,4-polybutadiene prepared using well-defined initiator

Appendix 2

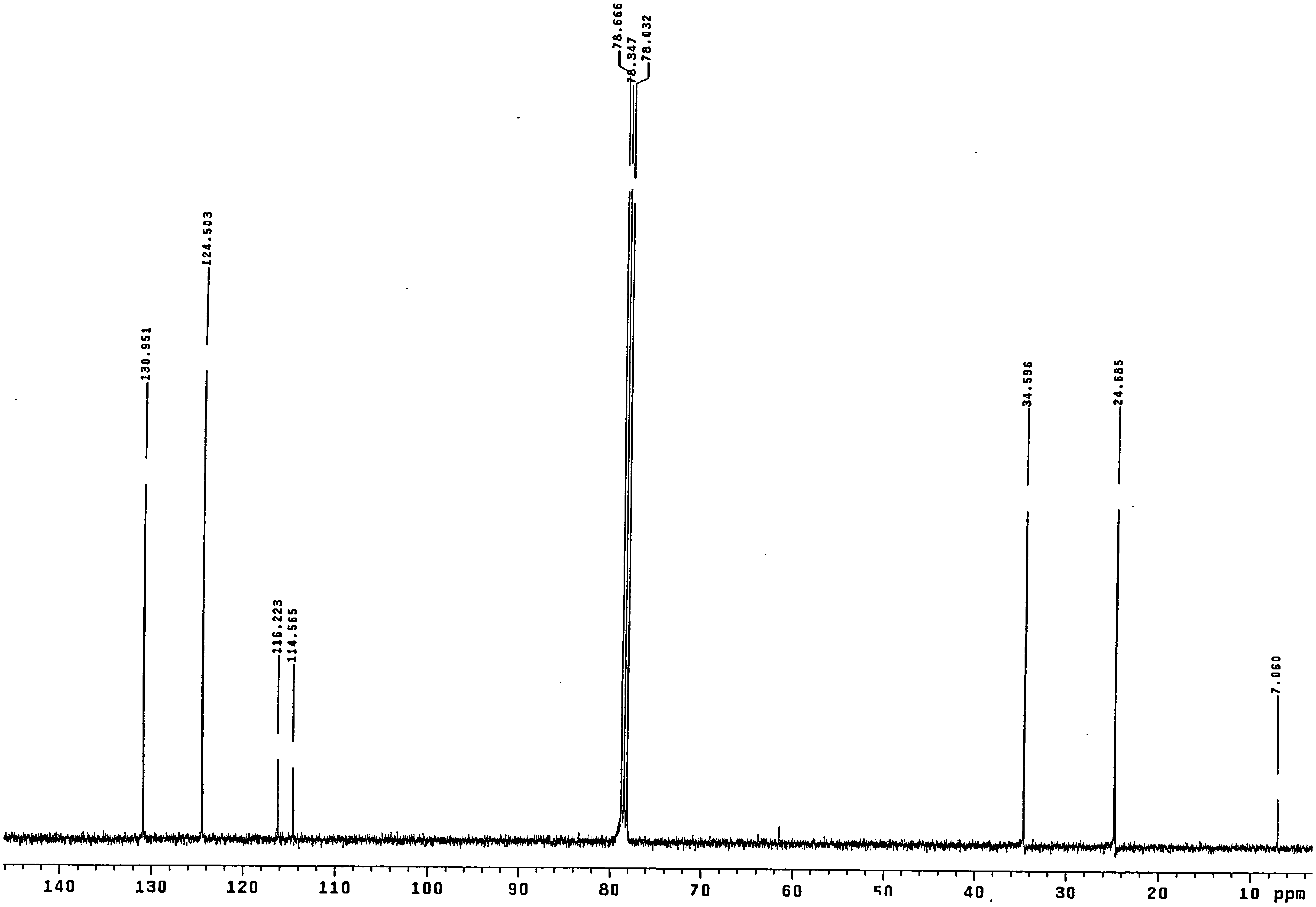
Analytical data for chapter 3



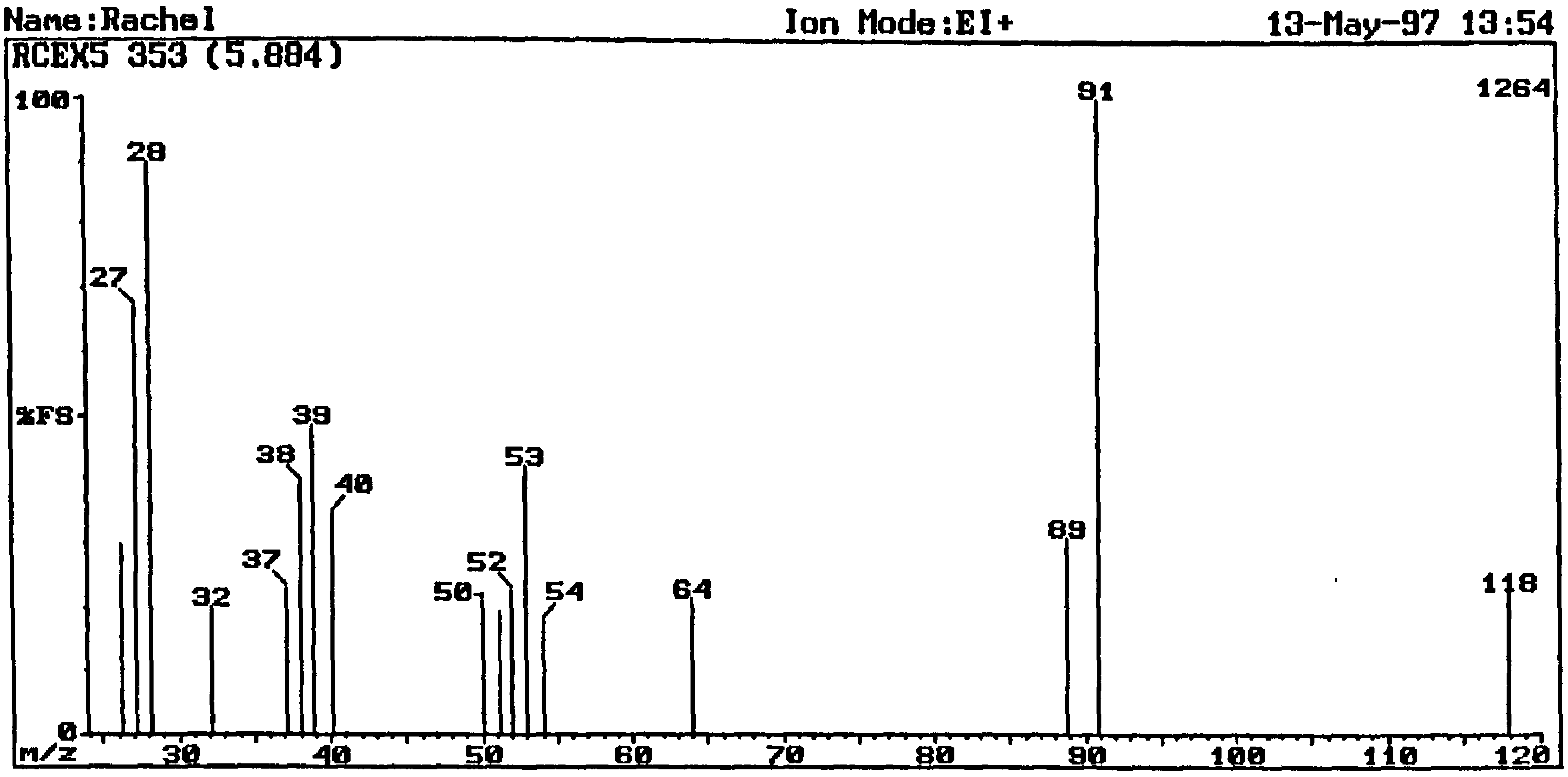
Appendix 2.1 Infra-red spectrum of 1,1-dicyano-2-vinylcyclopropane



Appendix 2.2 ^{1}H NMR spectrum of 1,1-dicyano-2-vinylcyclopropane

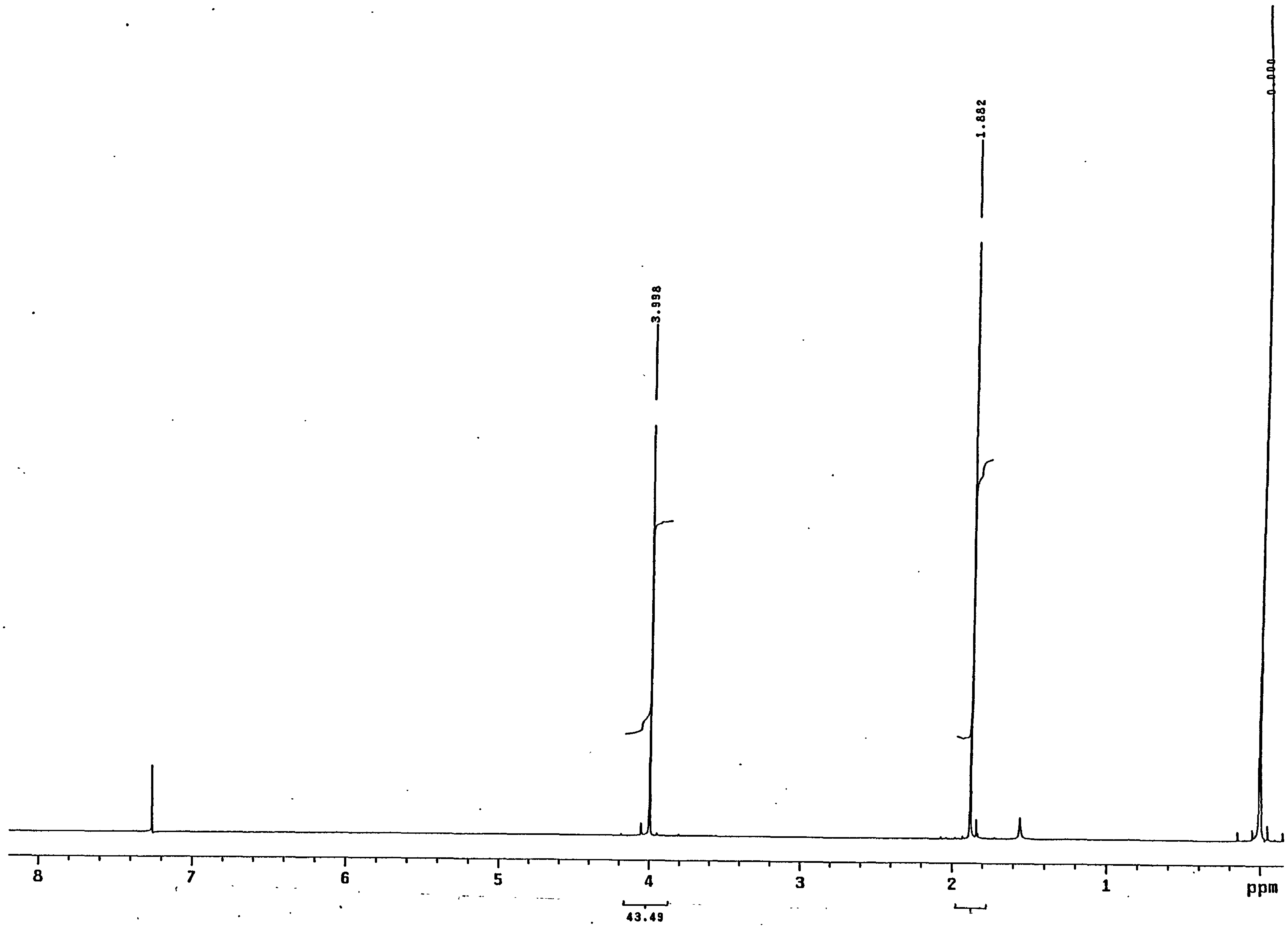


Appendix 2.3 ^{13}C NMR spectrum of 1,1-dicyano-2-vinylcyclopropane

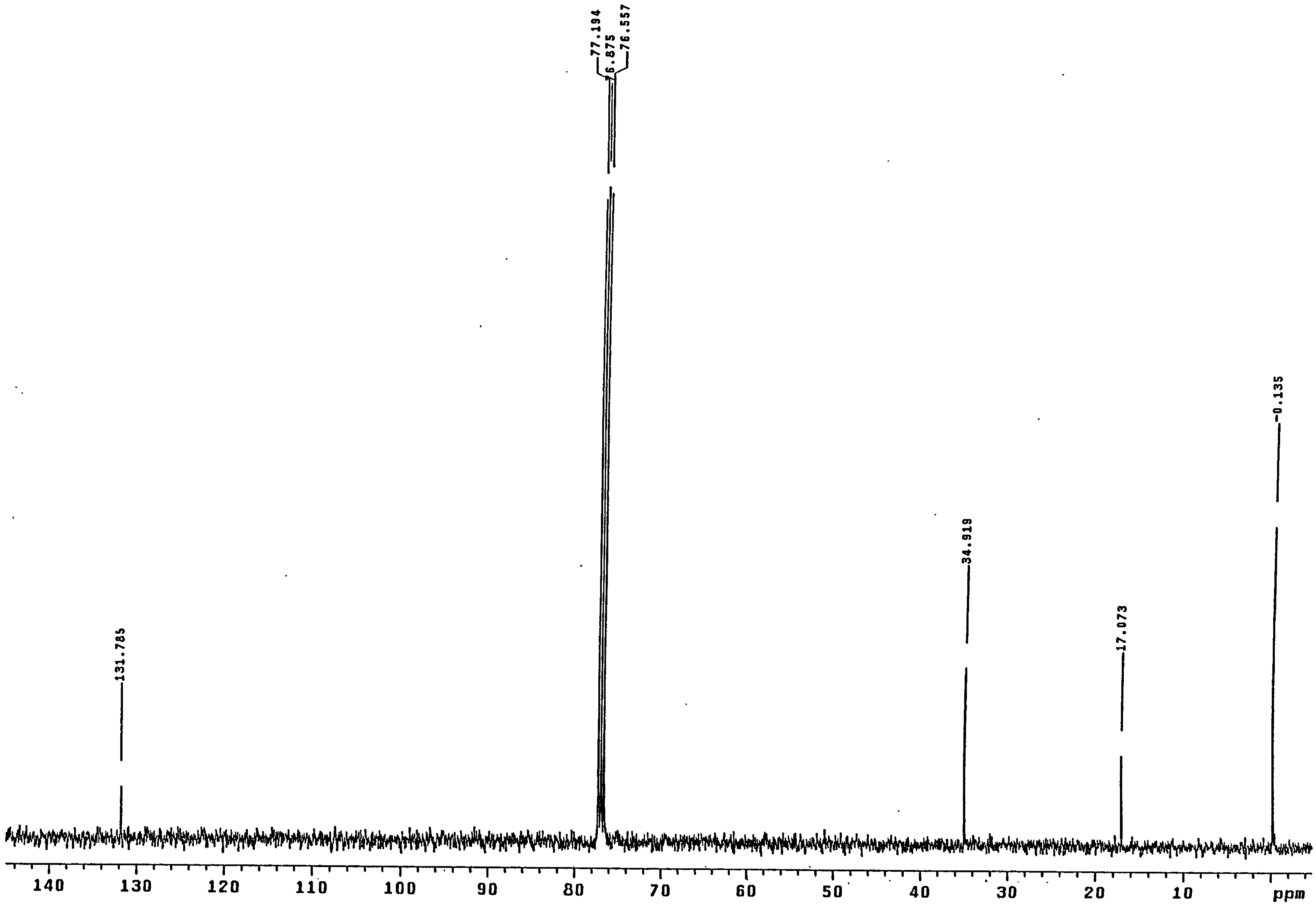


```
 -------------------------------------------------------------------
RCEX5 353 (5.884)
----------------+-----------------+-----------------+--------------
Mass   Rel Int  | Mass   Rel Int  | Mass   Rel Int  | Mass   Rel I
----------------+-----------------+-----------------+--------------
 26     29.43   |  38     38.92   |  52     22.15   |  91     100.
 27     67.09   |  39     48.10   |  53     41.46   | 118      22.
 28     89.87   |  40     34.18   |  54     17.41   |
 32     19.78   |  50     20.57   |  64     21.20   |
 37     22.47   |  51     18.99   |  89     30.70   |
----------------+-----------------+-----------------+--------------
```

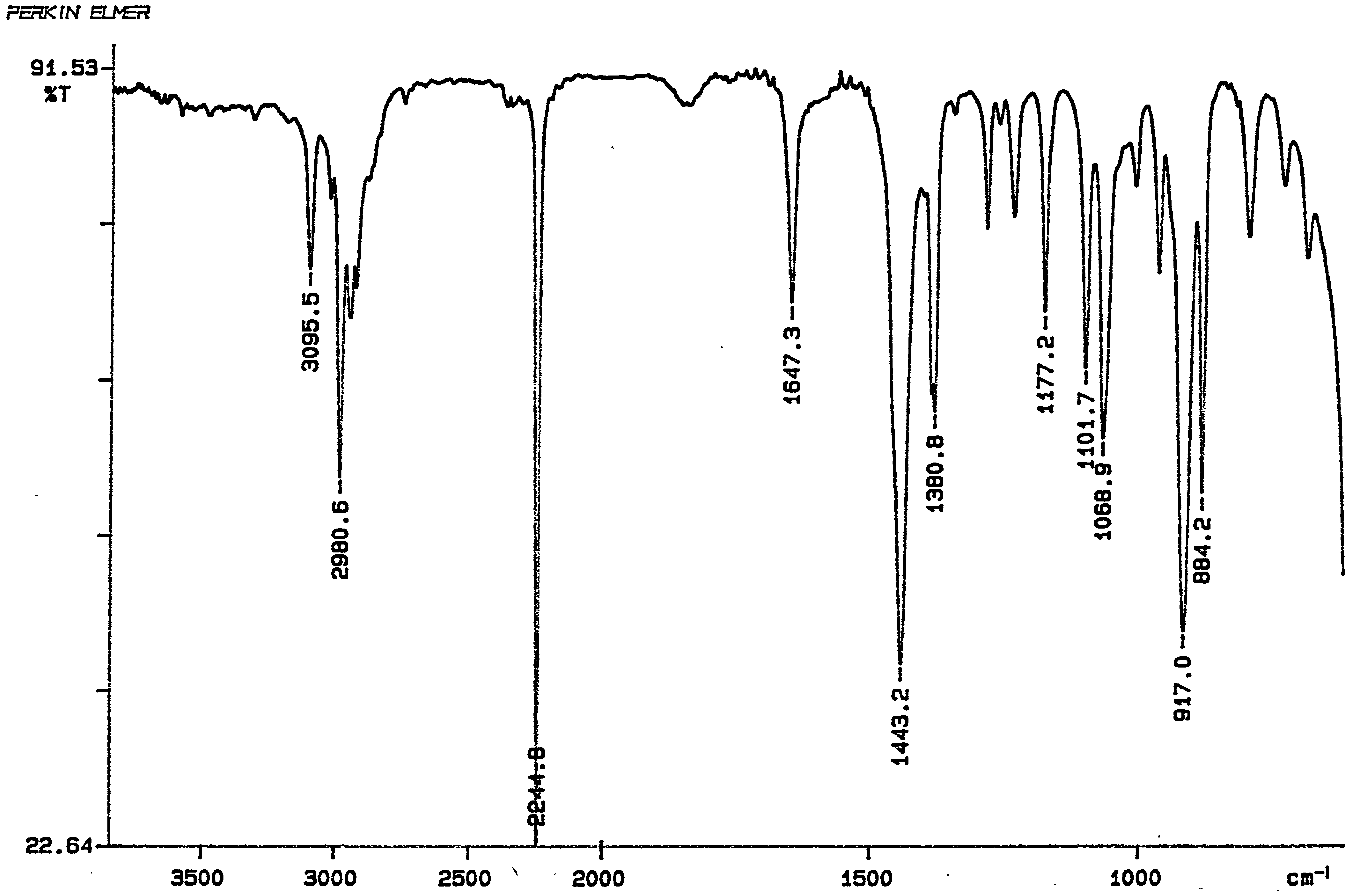
Appendix 2.4 Mass spectrum of 1,1-dicyano-2-vinylcyclopropane



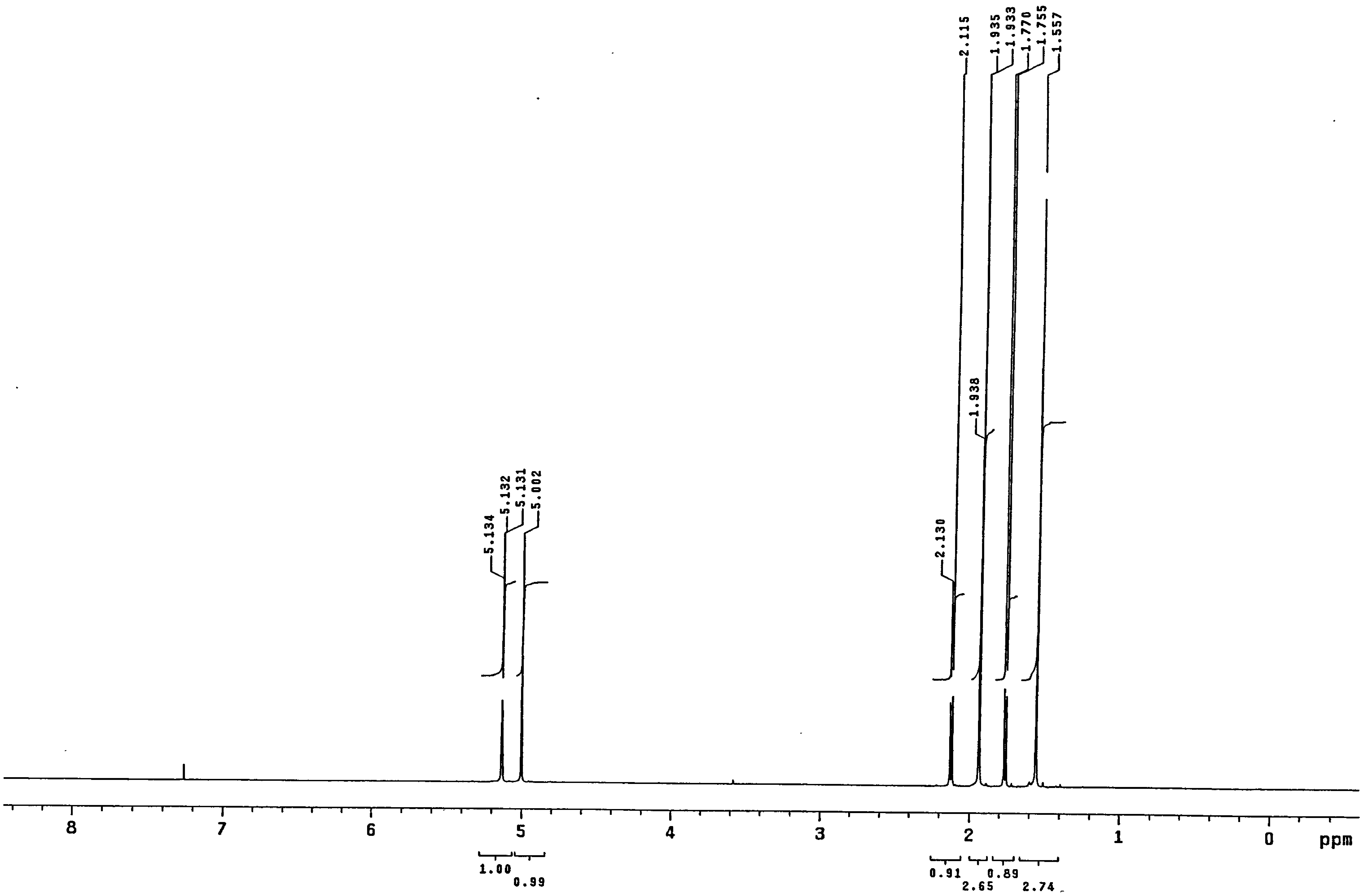
Appendix 2.5 ^1H NMR spectrum of *trans*1,4-dibromo-2,3-dimethyl-2-butene



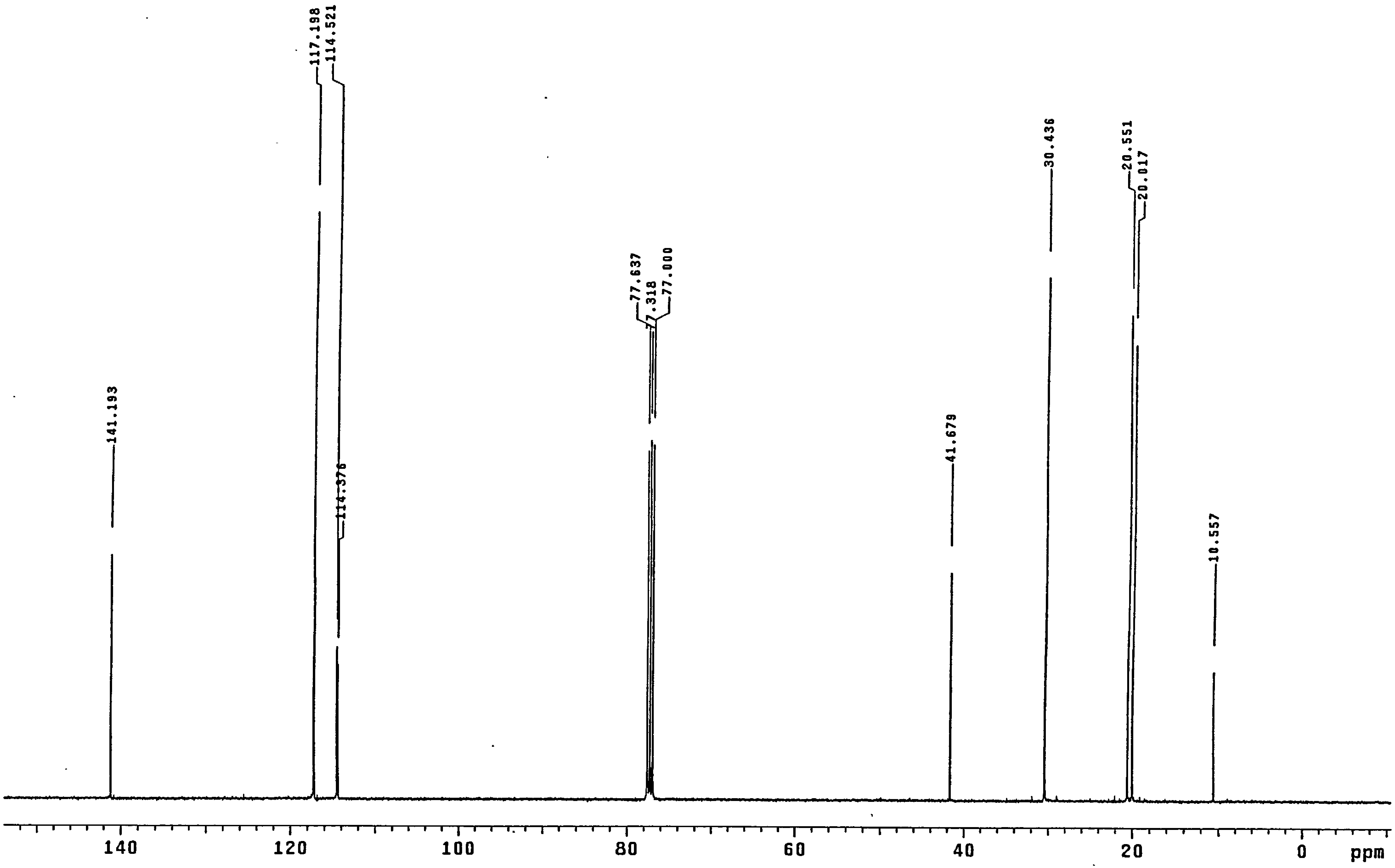
Appendix 2.6 ^{13}C NMR spectrum of *trans*1,4-dibromo-2,3-dimethyl-2-butene



Appendix 2.7 Infra-red spectrum of 1,1-dicyano-2-methyl-2-isopropenylcyclopropane

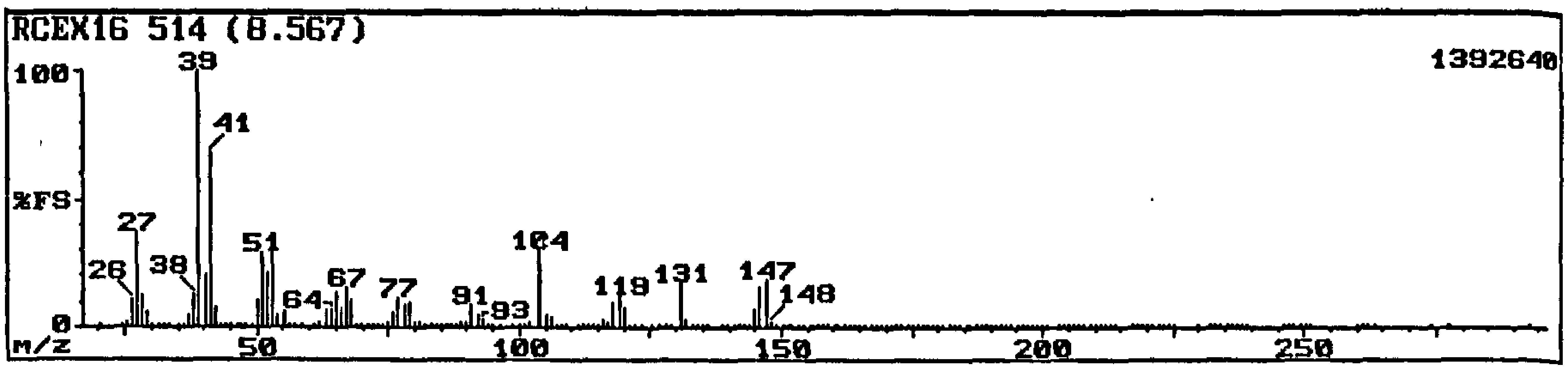


Appendix 2.8 ^{1}H NMR spectrum of 1,1-dicyano-2-methyl-2-isopropenylcyclopropane

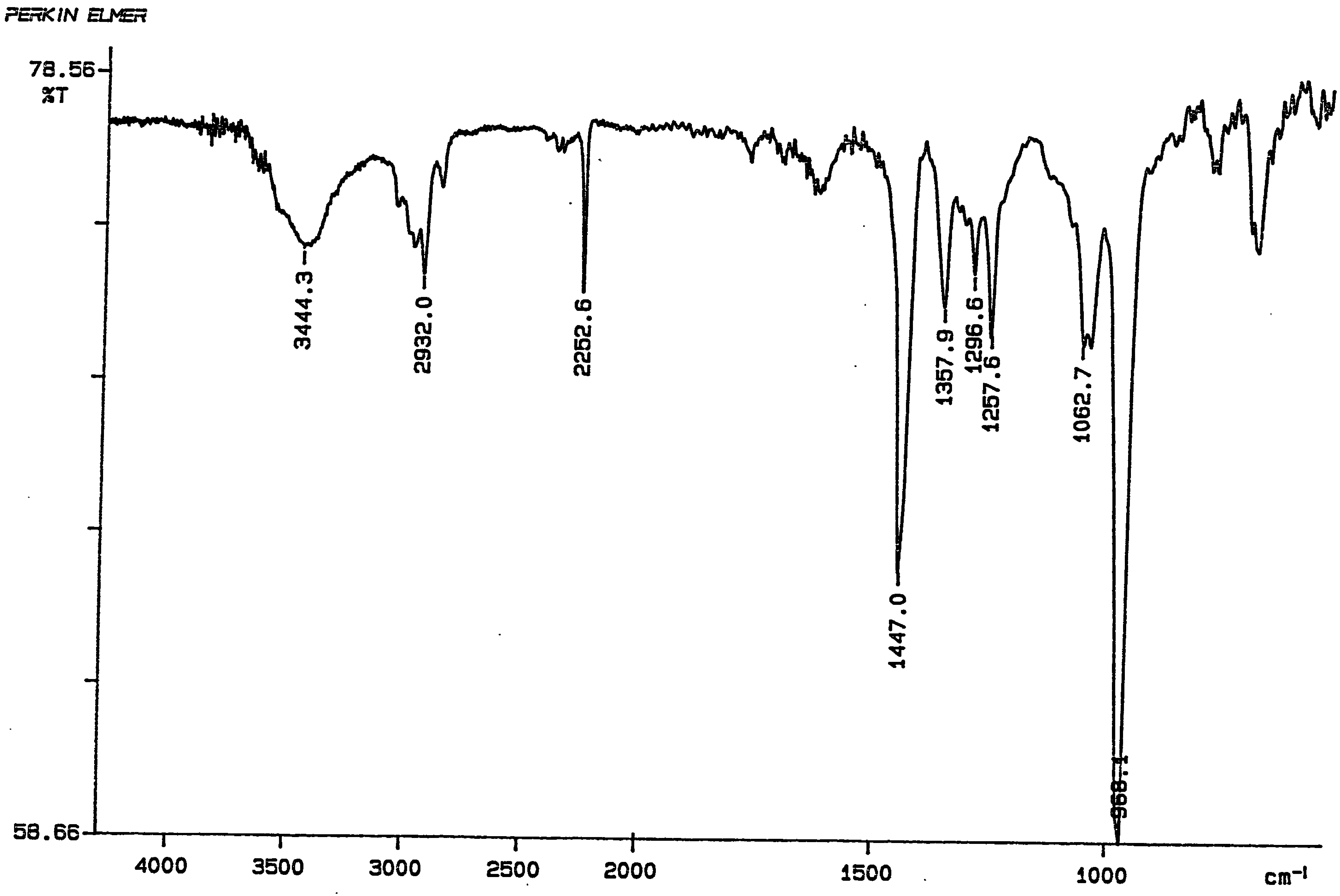


Appendix 2.9 ^{13}C NMR spectrum of 1,1-dicyano-2-methyl-2-isopropenylcyclopropane

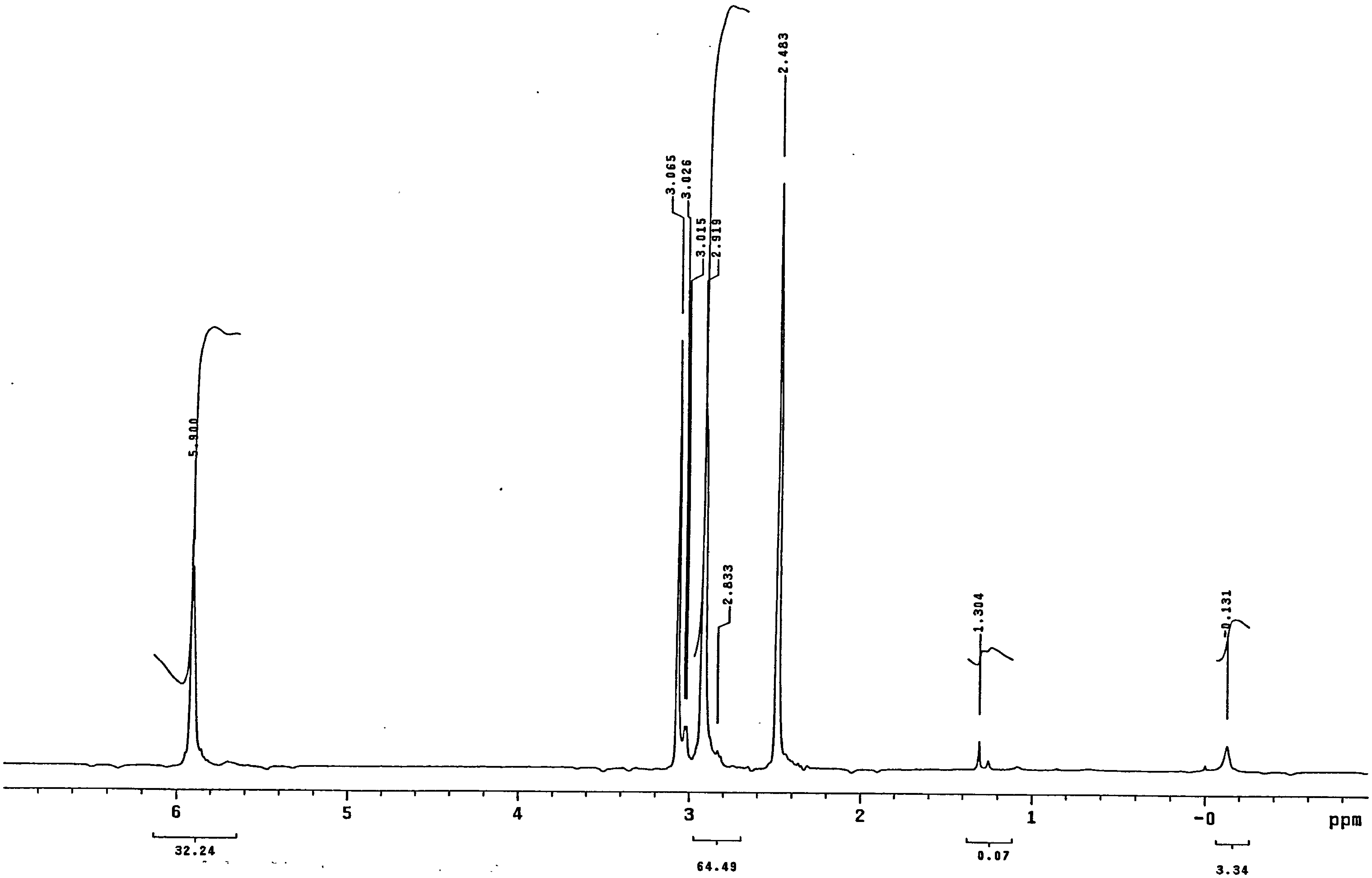
```
-----------------------------------------------------------------
RCEX16 514 (8.567)                                        1392640
-----------------+-----------------+-----------------+-----------------
Mass   Rel Int   | Mass   Rel Int  | Mass   Rel Int  | Mass   Rel Int
-----------------+-----------------+-----------------+-----------------
 20     0.08     |  79    10.00    | 141     0.13    | 194     0.18
 24     1.06     |  80     1.95    | 142     0.26    | 195     0.21
 25     2.41     |  81     1.88    | 143     1.13    | 196     0.19
 26    10.81     |  82     0.74    | 144     0.51    | 197     0.19
 27    37.06     |  83     0.15    | 145     7.13    | 198     0.07
 28    12.72     |  84     0.05    | 146    15.37    | 199     0.18
 29     5.66     |  85     0.04    | 147    18.82    | 200     0.05
 30     0.67     |  86     0.13    | 148     2.30    | 201     0.06
 31     0.04     |  87     0.34    | 149     0.44    | 203     0.02
 32     0.15     |  88     1.18    | 150     0.05    | 204     0.02
 33     0.02     |  89     2.24    | 151     0.01    | 205     0.05
 35     0.04     |  90     1.99    | 152     0.06    | 206     0.12
 36     0.50     |  91     8.97    | 153     0.14    | 207     0.23
 37     5.29     |  92     4.78    | 154     0.17    | 208     0.28
 38    12.94     |  93     3.20    | 155     0.45    | 209     0.16
 39   100.00     |  94     1.01    | 156     0.22    | 210     0.09
 40    20.29     |  95     0.25    | 157     0.58    | 211     0.10
 41    68.24     |  96     0.05    | 158     0.57    | 212     0.05
 42     7.57     |  99     0.12    | 159     0.29    | 213     0.08
 43     1.27     | 100     0.21    | 160     0.10    | 214     0.03
 44     0.34     | 101     0.36    | 161     0.05    | 217     0.01
 45     0.11     | 102     1.73    | 162     0.02    | 218     0.04
 46     0.05     | 104    29.71    | 163     0.04    | 219     0.04
 47     0.09     | 105     5.22    | 164     0.04    | 220     0.07
 48     0.42     | 106     3.66    | 165     0.08    | 221     0.10
 49     1.29     | 107     0.59    | 166     0.09    | 222     0.08
 50    10.51     | 108     0.15    | 167     0.22    | 223     0.13
 51    28.82     | 109     0.02    | 168     0.31    | 224     0.09
 52    21.47     | 111     0.01    | 169     0.78    | 225     0.01
 53    28.24     | 112     0.01    | 170     0.83    | 230     0.01
 54     5.15     | 113     0.04    | 171     0.37    | 232     0.02
 55     5.88     | 114     0.20    | 172     0.23    | 233     0.05
 56     0.63     | 115     0.50    | 173     0.10    | 234     0.04
 57     0.09     | 116     2.67    | 174     0.04    | 235     0.04
 59     0.08     | 117     1.88    | 175     0.04    | 236     0.03
 61     0.75     | 118     9.63    | 176     0.01    | 237     0.04
 62     2.11     | 119    12.79    | 177     0.03    | 238     0.03
 63     6.47     | 120     8.16    | 178     0.05    | 239     0.02
 64     6.84     | 121     0.58    | 179     0.09    | 246     0.02
 65    13.90     | 122     0.12    | 180     0.15    | 247     0.02
 66     7.87     | 123     0.01    | 181     0.15    | 248     0.02
 67    15.51     | 125     0.02    | 182     0.27    | 249     0.02
 68    10.66     | 127     0.15    | 183     0.35    | 250     0.04
 69     0.74     | 128     0.74    | 184     0.22    | 251     0.01
 70     0.05     | 129     1.08    | 185     0.39    | 260     0.02
 71     0.04     | 131    17.13    | 186     0.09    | 261     0.02
 72     0.02     | 132     2.65    | 187     0.62    | 262     0.06
 73     0.08     | 133     0.76    | 188     0.09    | 263     0.02
 74     0.63     | 134     0.11    | 189     0.02    | 274     0.02
 75     2.32     | 135     0.03    | 190     0.03    | 277     0.04
 76     6.18     | 136     0.06    | 191     0.05    | 293     0.02
 77    12.13     | 139     0.05    | 192     0.05    |
 78     8.31     | 140     0.13    | 193     0.18    |
-----------------+-----------------+-----------------+-----------------
```



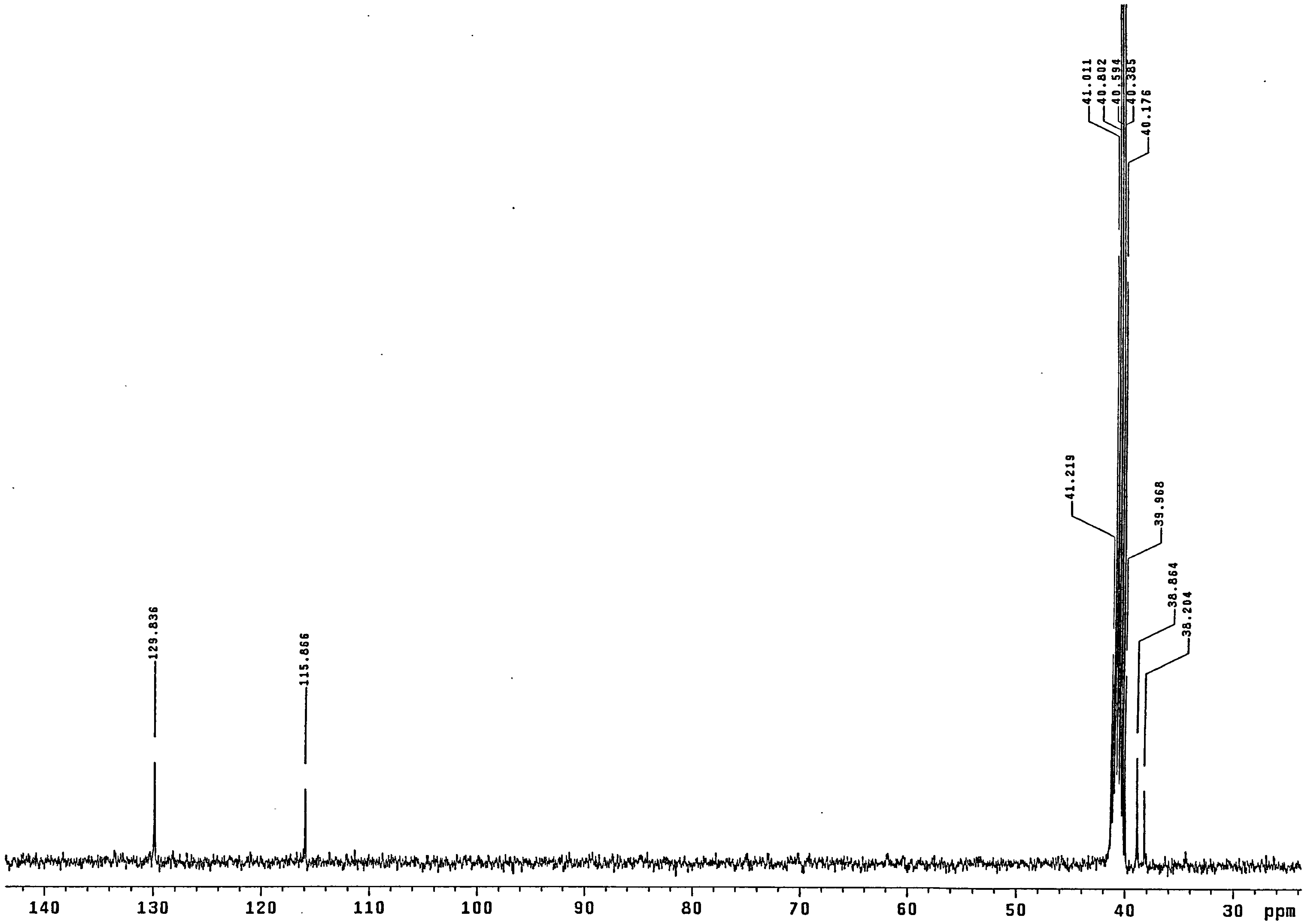
Appendix 2.10 Mass spectrum of 1,1-dicyano-2-methyl-2-isopropenylcyclopropane



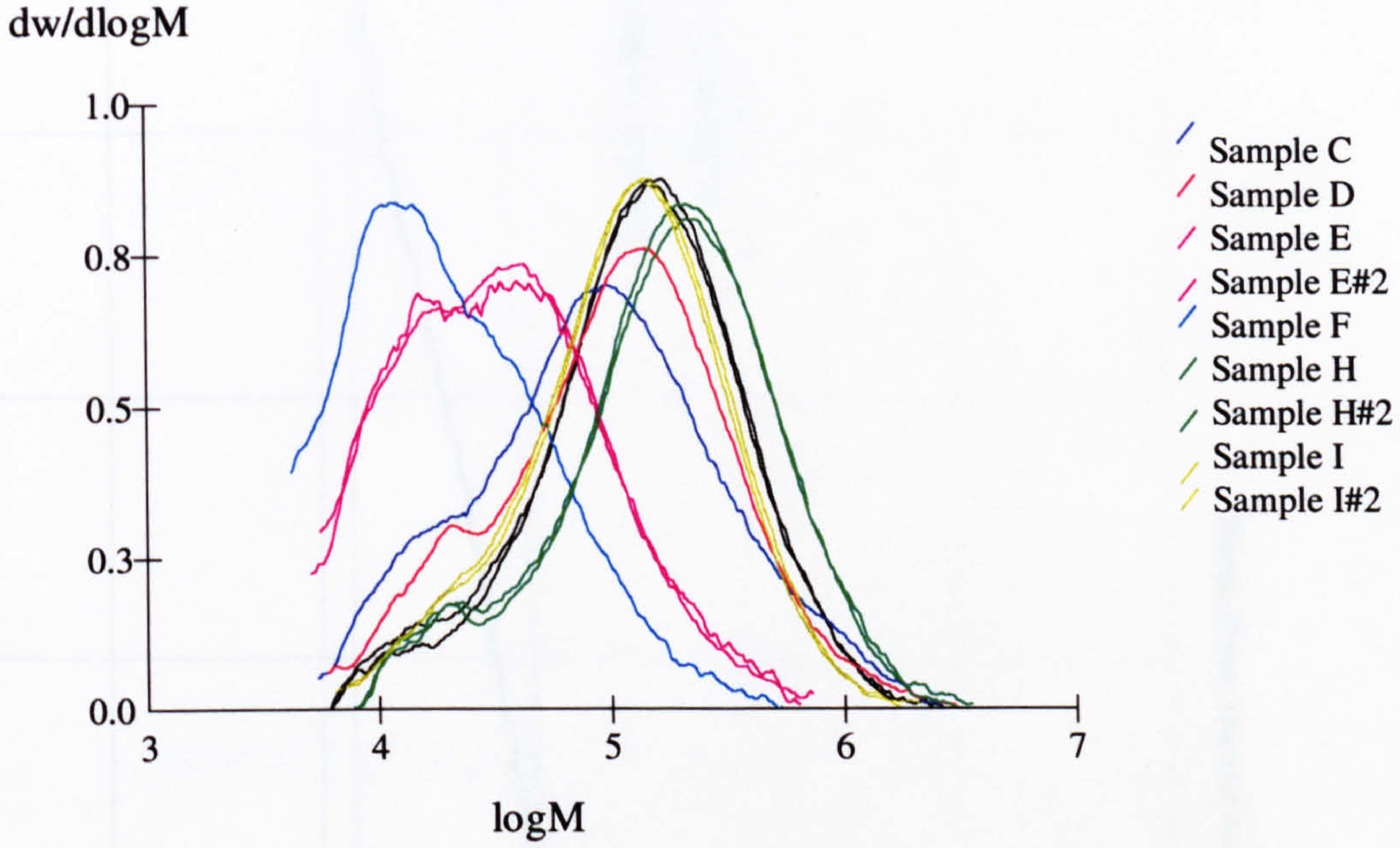
Appendix 2.11 Infra-red spectrum of poly(1,1-dicyano-2-vinylcyclopropane)



Appendix 2.12 ^{1}H NMR spectrum of poly(1,1-dicyano-2-vinylcyclopropane).



Appendix 2.13 ^{13}C NMR spectrum of poly(1,1-dicyano-2-vinylcyclopropane)



Appendix 2.14 GPC Traces for poly(1,1-dicyano-2-vinylcyclopropane)

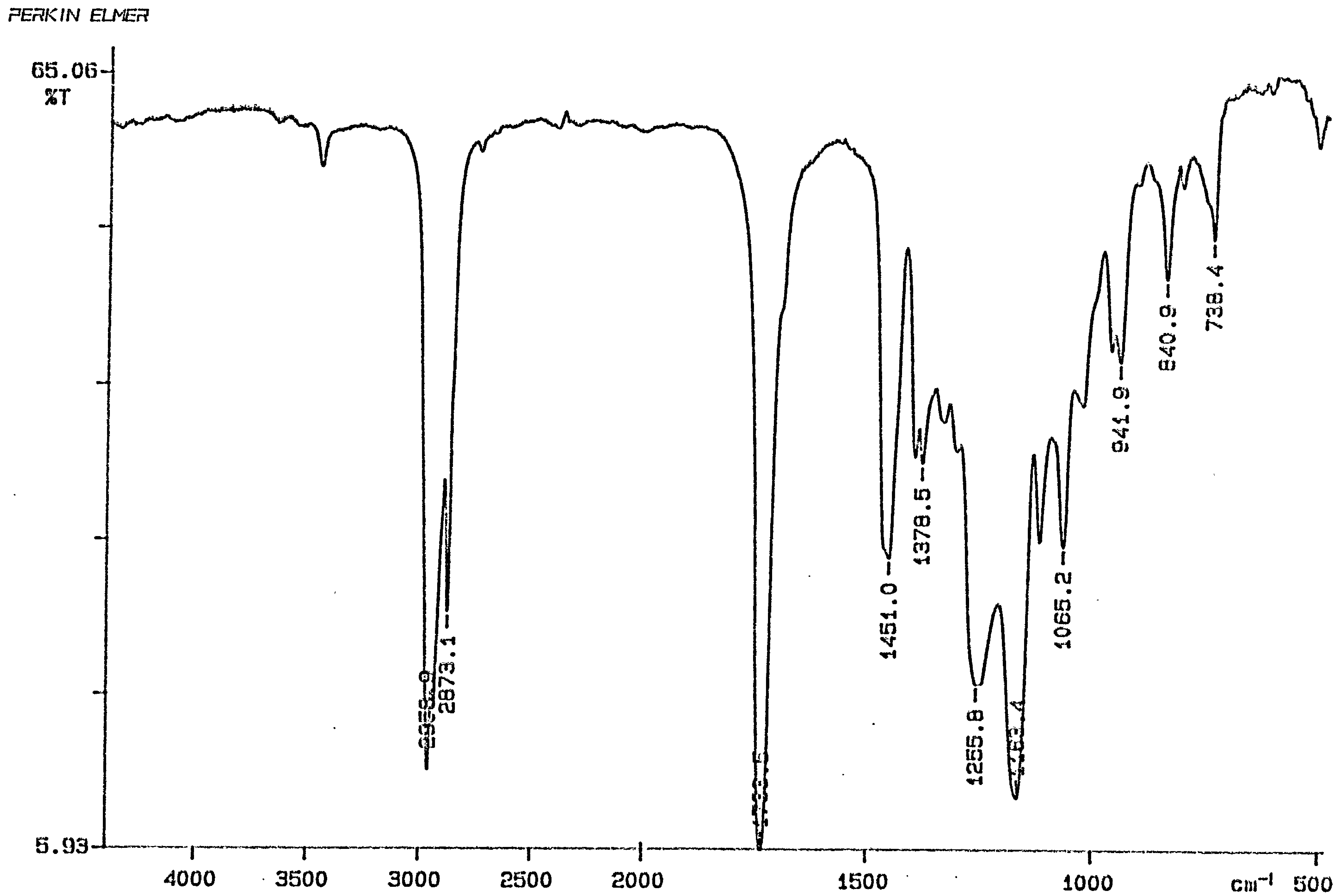
1) Heat from 25.00°C to 300.00°C at 10.00°C/min

Appendix 2.15 DSC trace of poly(1,1-dicyano-2-vinylcyclopropane)

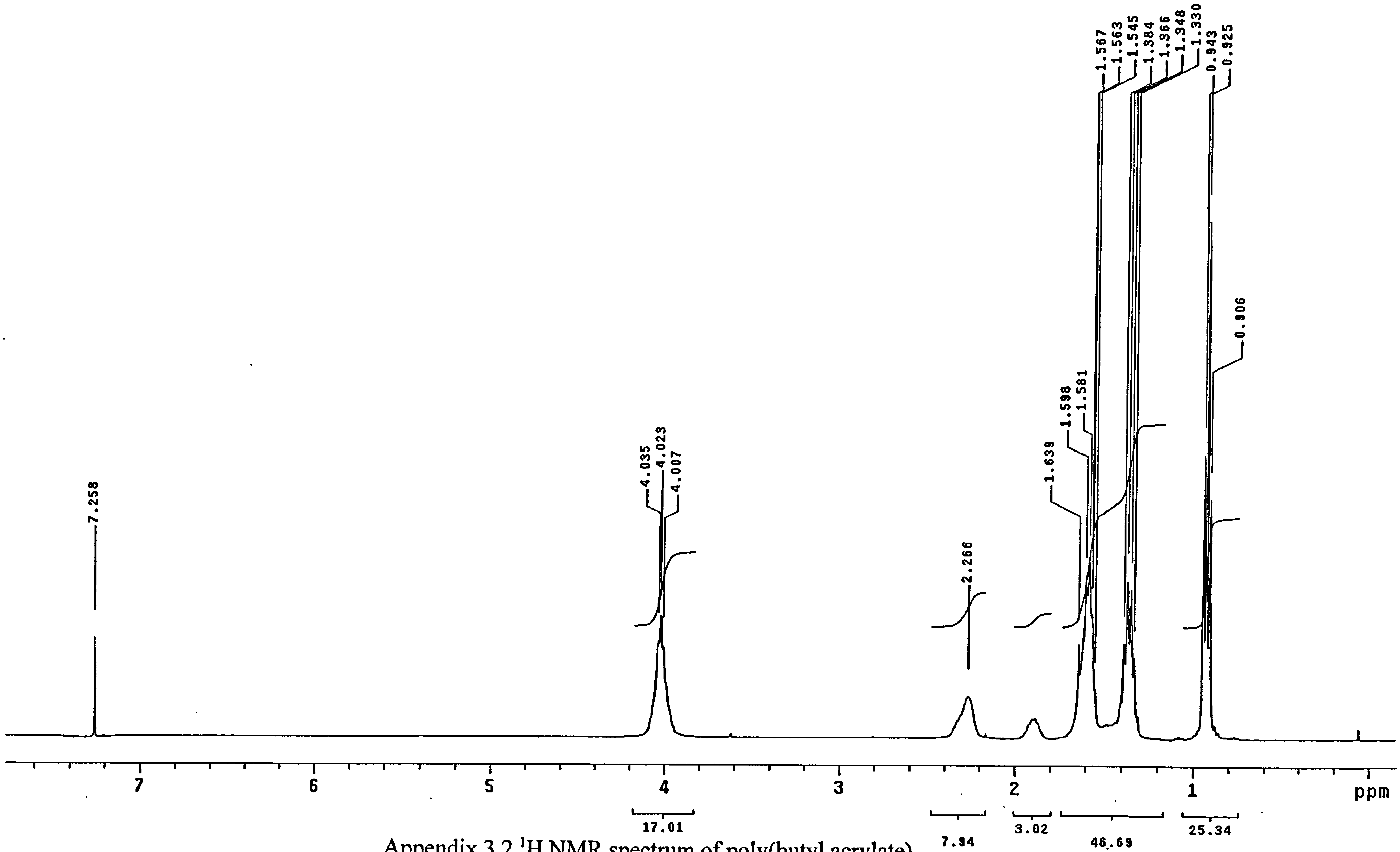
8/3/98 11:04:09 AM

Appendix 3

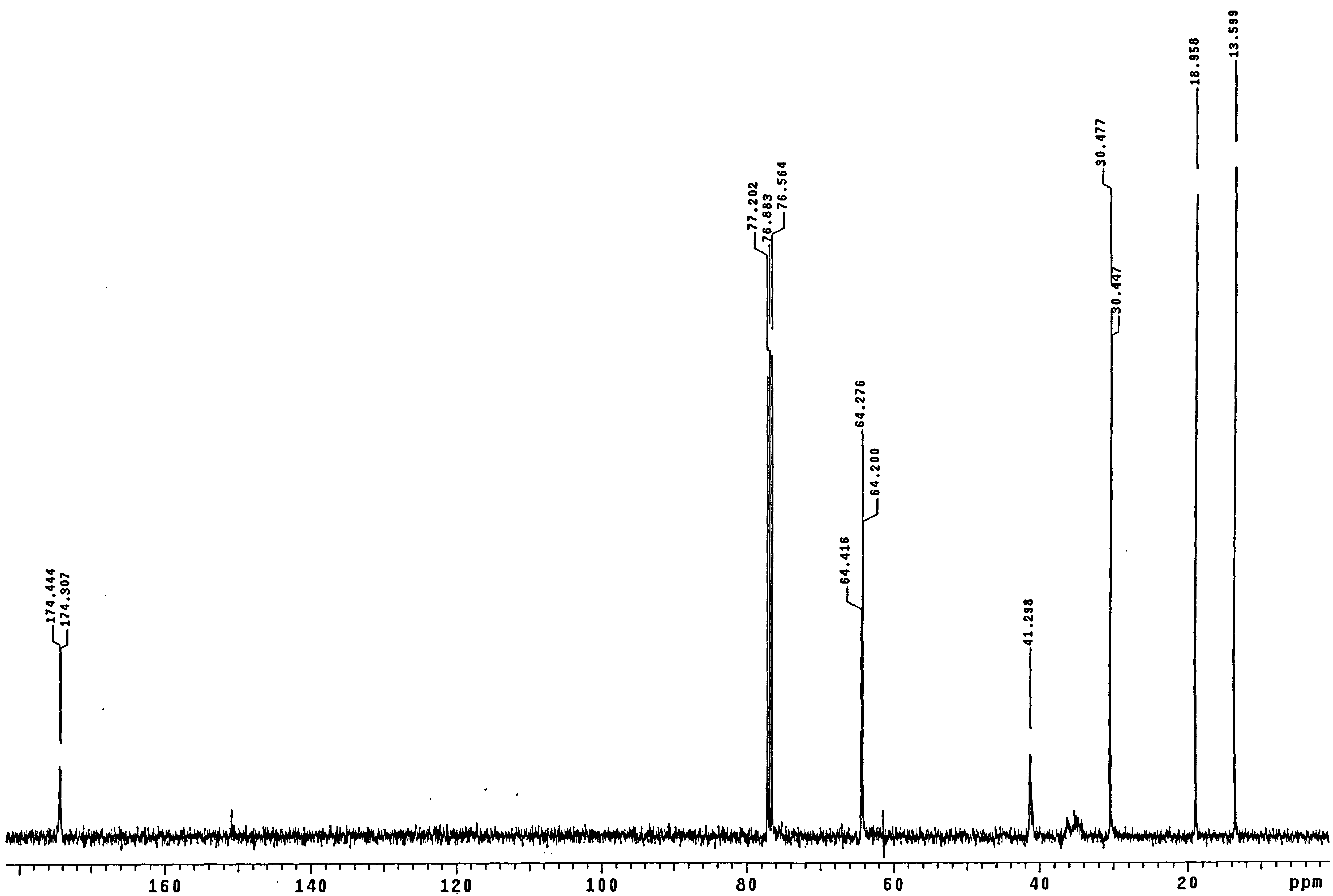
Analytical data for chapter 4



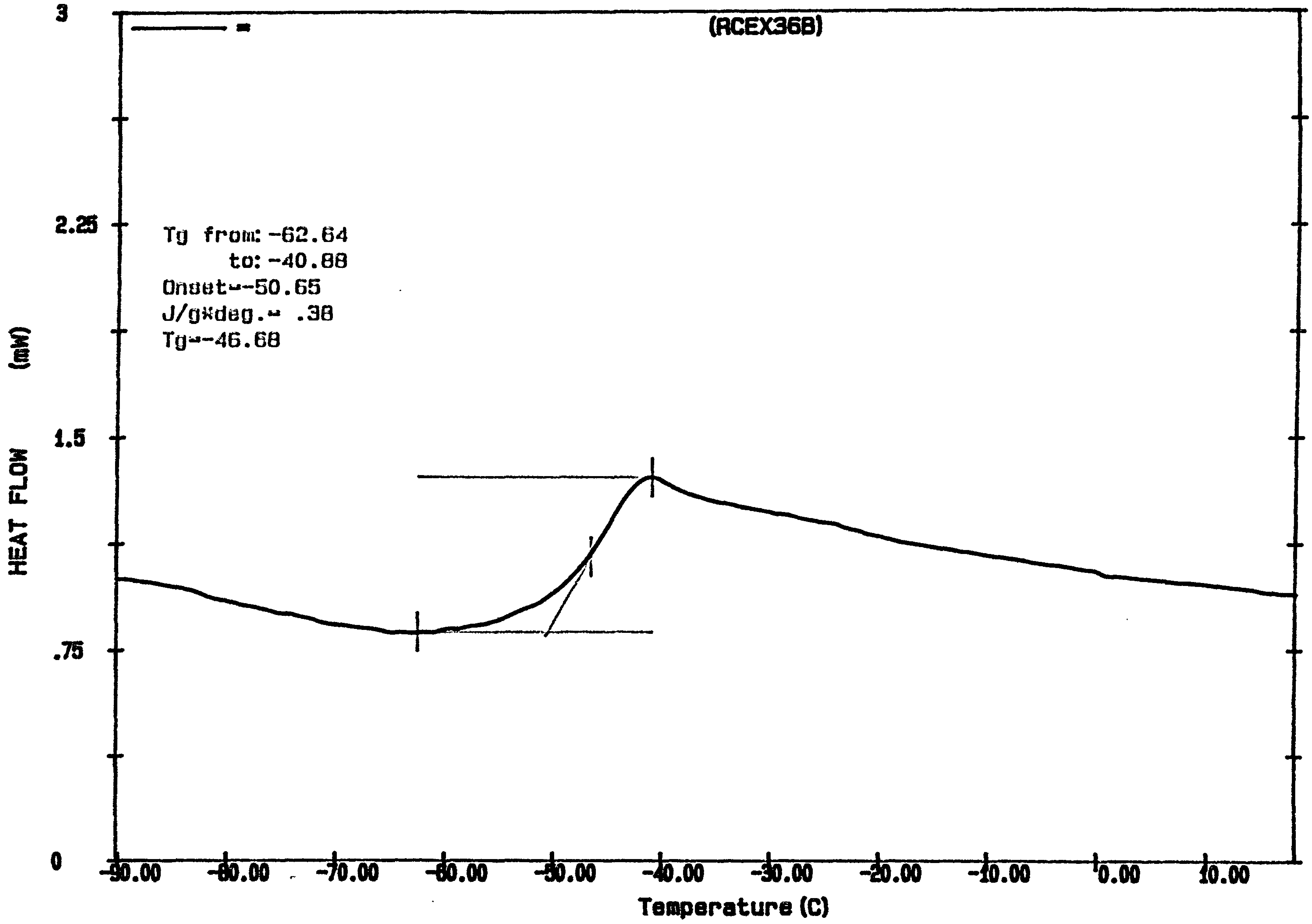
Appendix 3.1 Infra-red spectrum of poly(butyl acrylate)



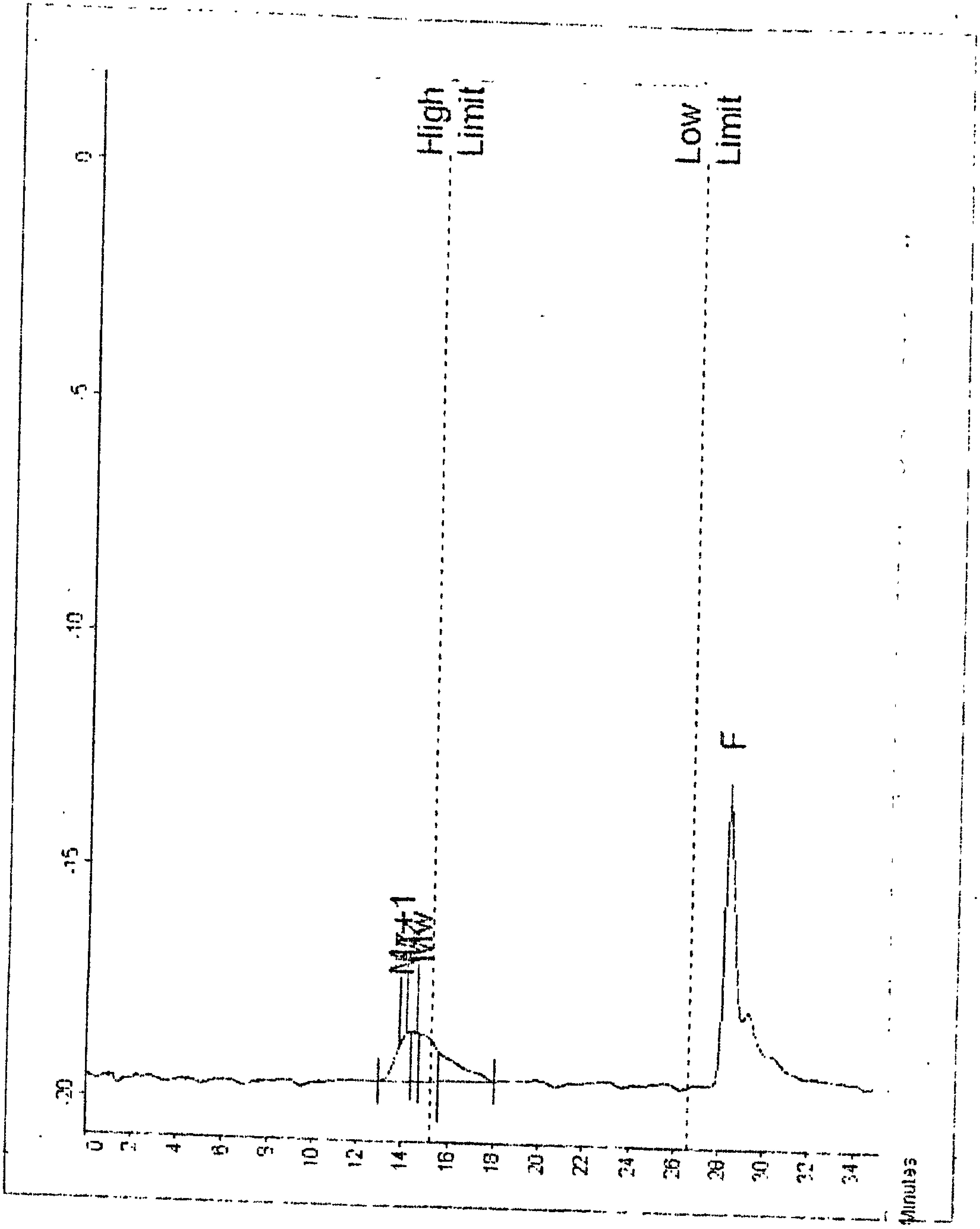
Appendix 3.2 ^1H NMR spectrum of poly(butyl acrylate)



Appendix 3.3 ^{13}C NMR spectrum of poly(butyl acrylate)



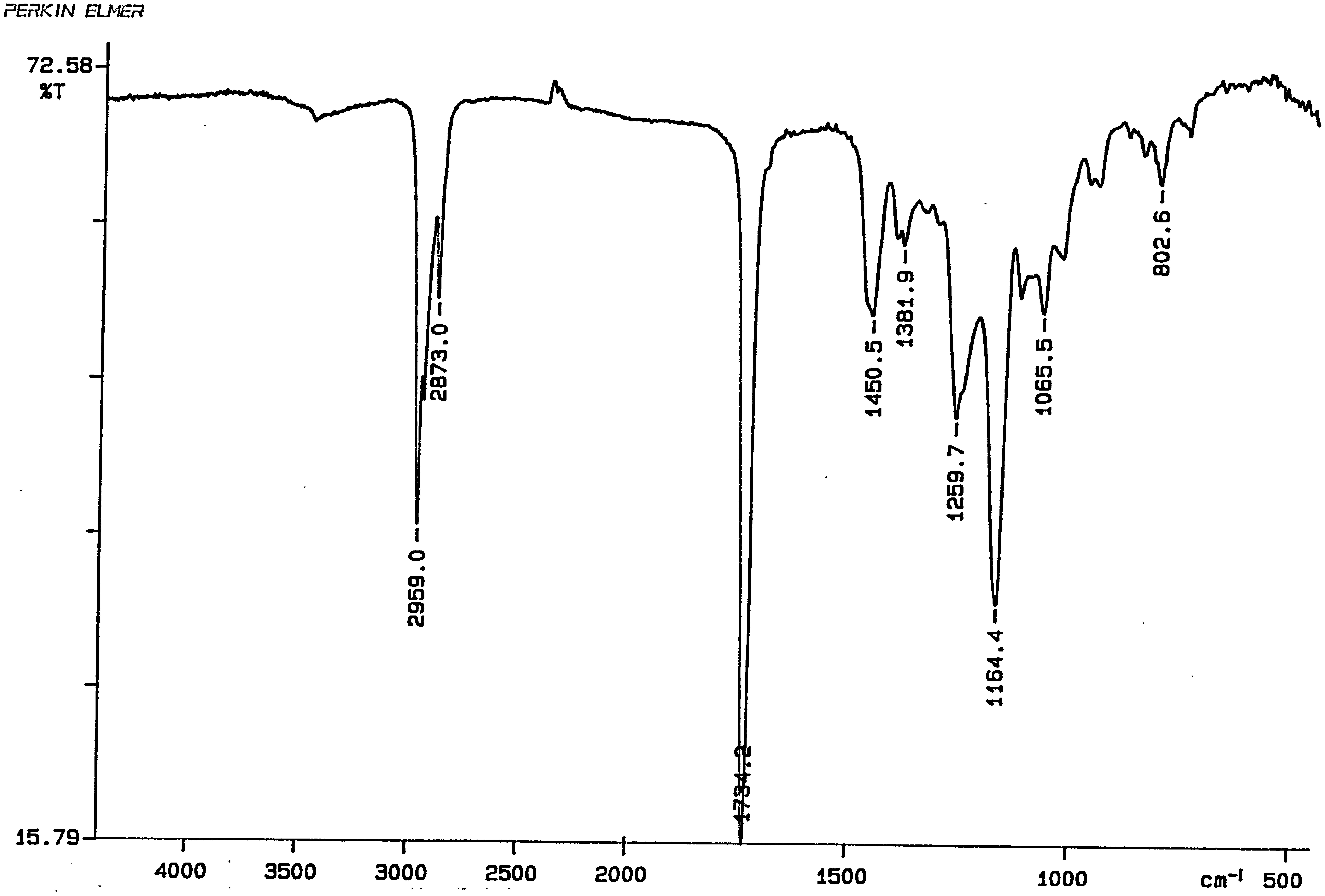
Appendix 3.4 DSC trace of poly(butyl acrylate)



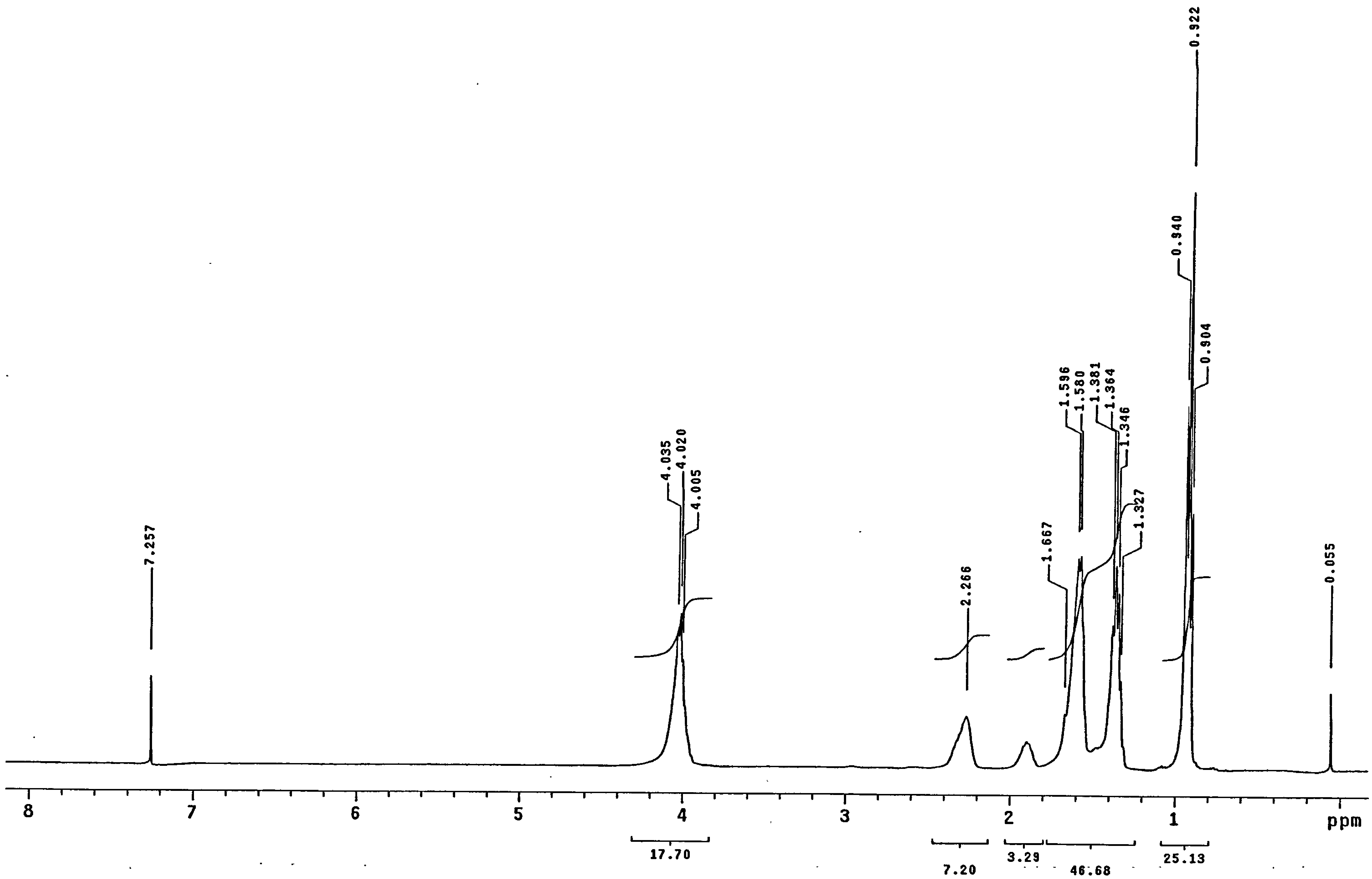
Molecular Weight Averages

Mp =	2378008	Mz =	3108132
Mn =	684027	Mz+1 =	4157968
Mw =	1813919	Mv =	1831543
Polydispersity =	2.652	Peak Area =	31050

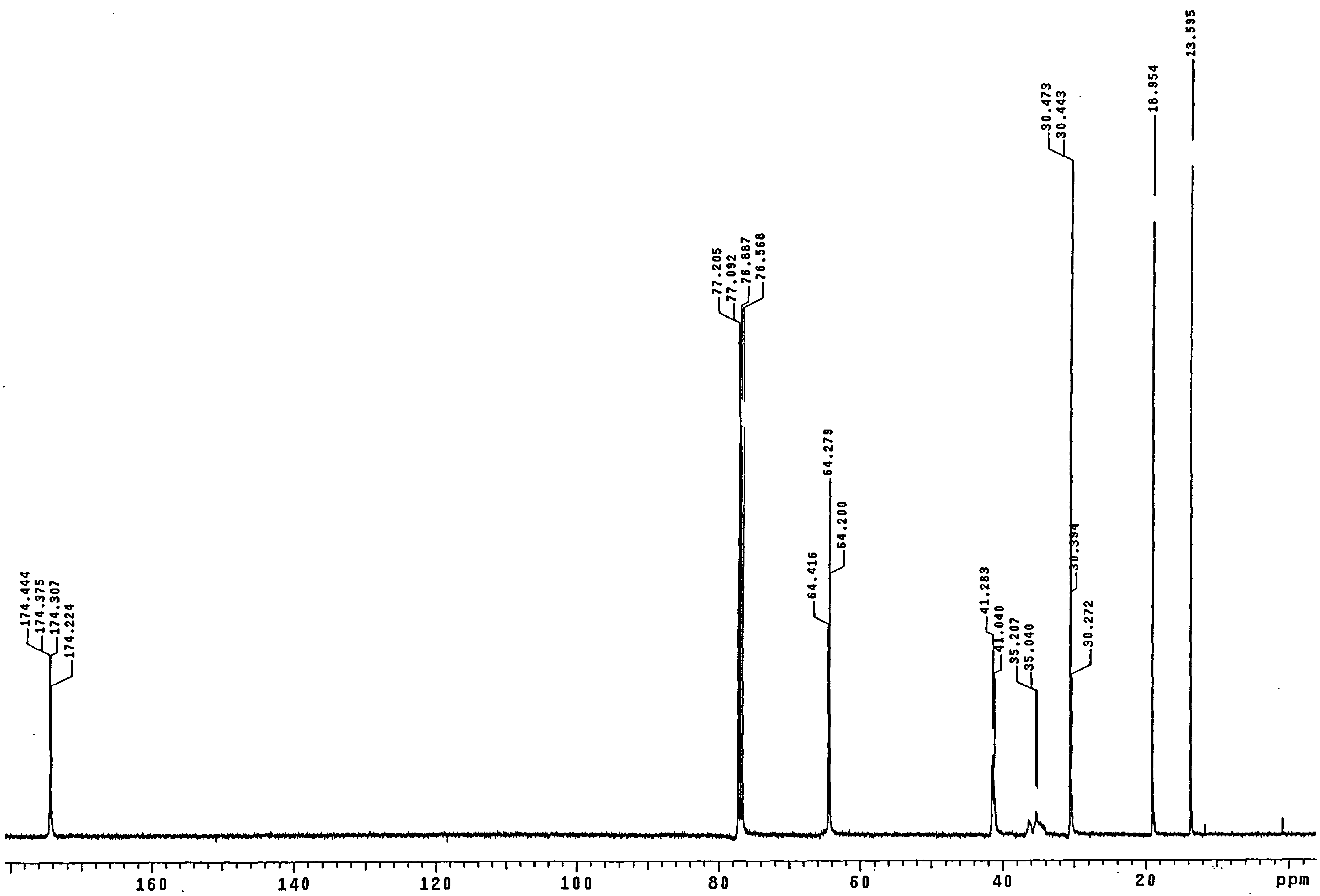
Appendix 3.5 GPC trace of poly(butyl acrylate)



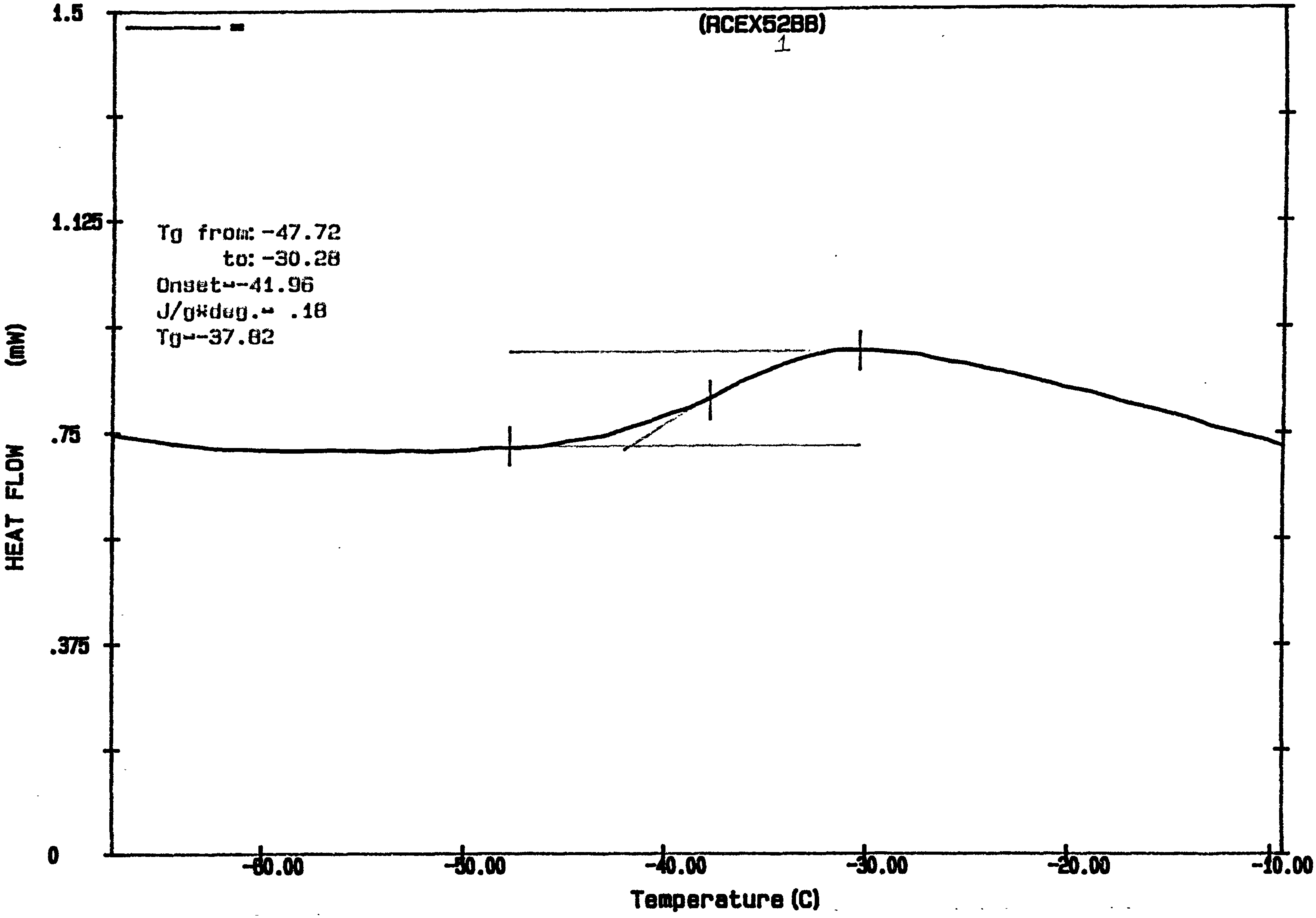
Appendix 3.6 Infra-red spectrum of polymer formed in the attempted copolymerisation of butyl



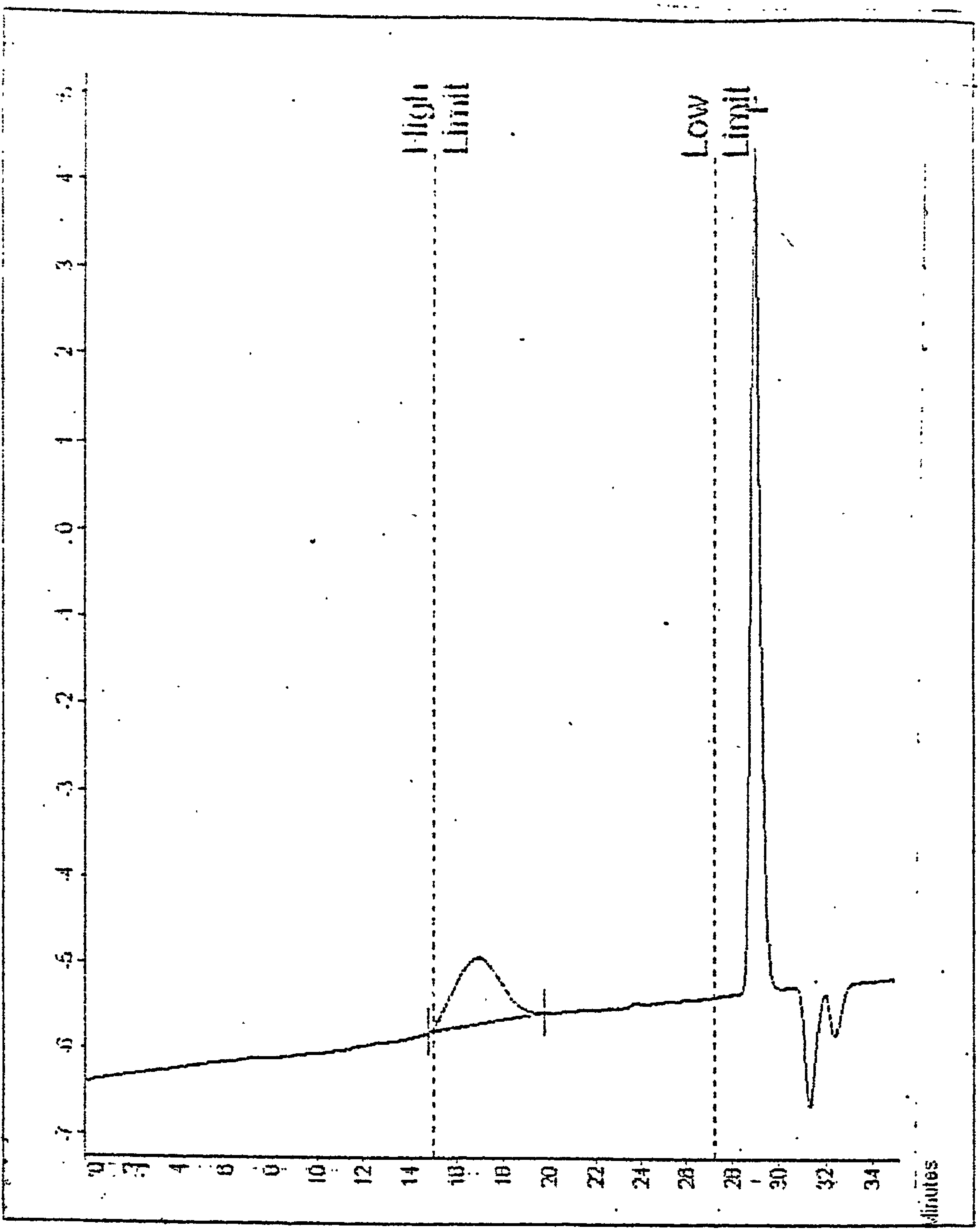
Appendix 3.7 ^{1}H NMR spectrum of polymer formed in the attempted copolymerisation of butyl *acrylate (4.5 g) and 1,1-dicyano-2-vinylcyclopropane (0.5 g)*



Appendix 3.8 ^{13}C NMR spectrum of polymer formed in the attempted copolymerisation of butyl



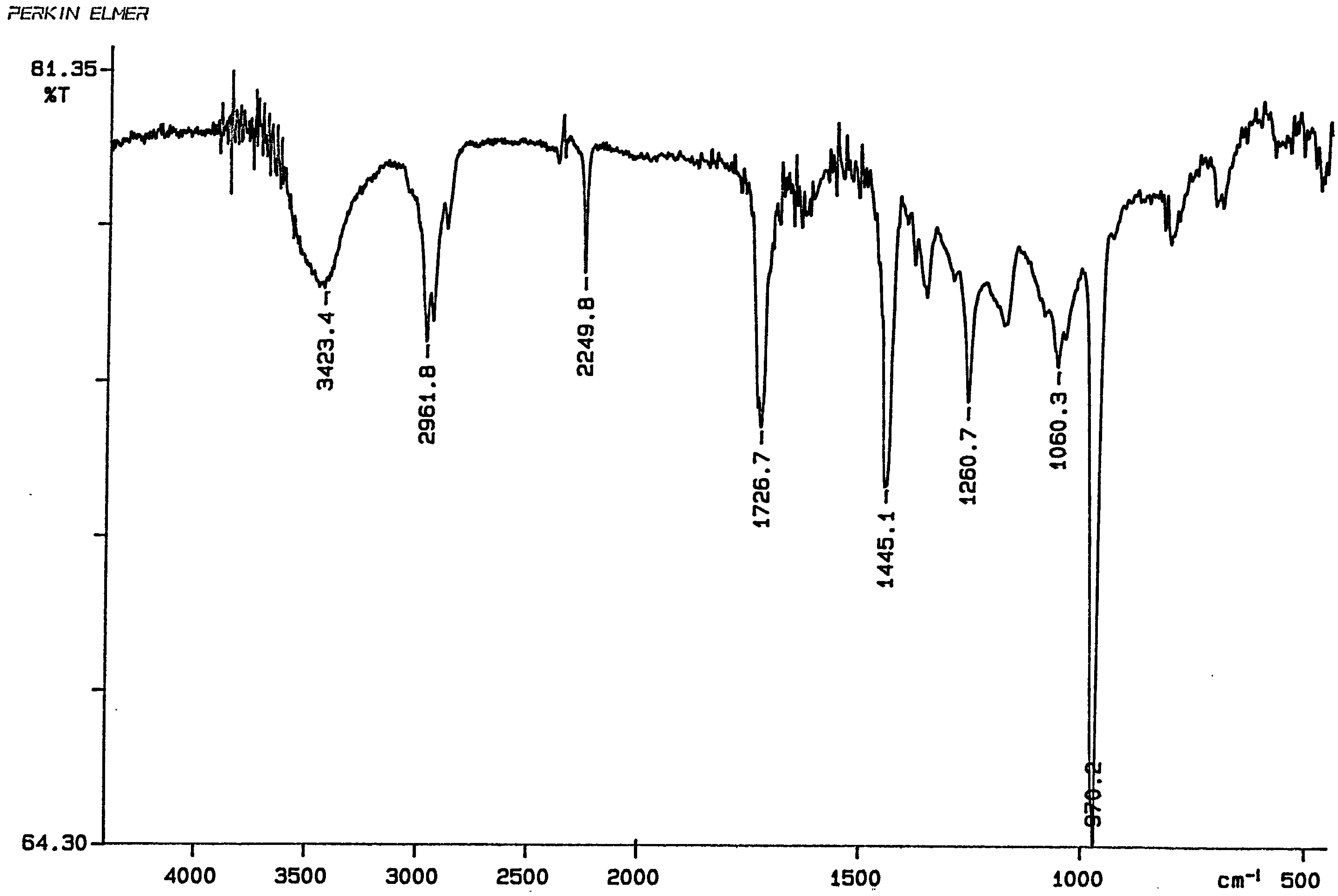
Appendix 3.9 DSC trace of polymer formed in the attempted copolymerisation of butyl acrylate *(4.5 g) and 1,1-dicyano-2-vinylcyclopropane (0.5 g)*



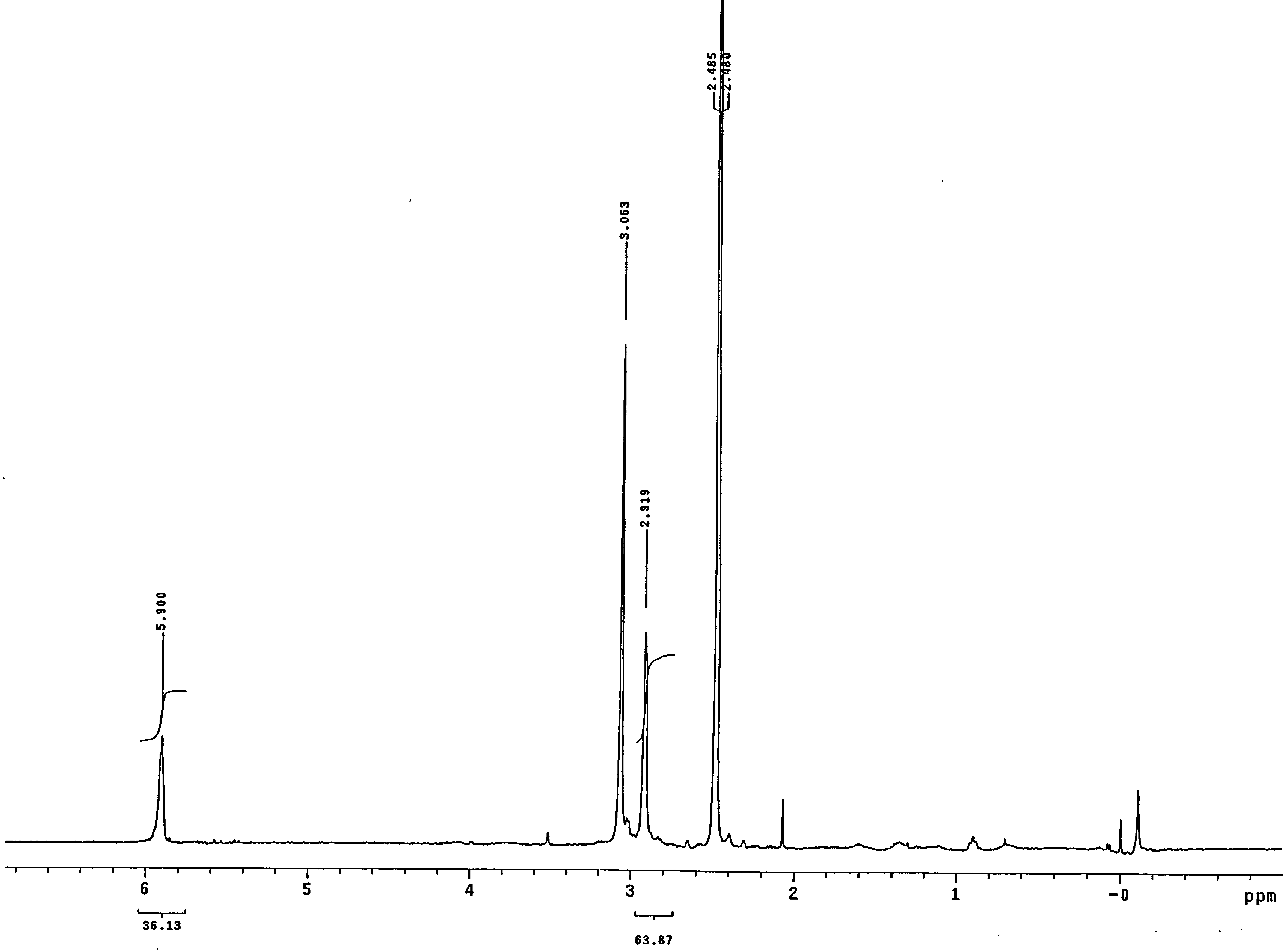
Molecular Weight Averages

Mp = 189099
Mz = 336979
Mn = 123734
Mz+1 = 466751
Mw = 213017
Mv = 200237
Polydispersity = 1.717
Peak Area = 21715

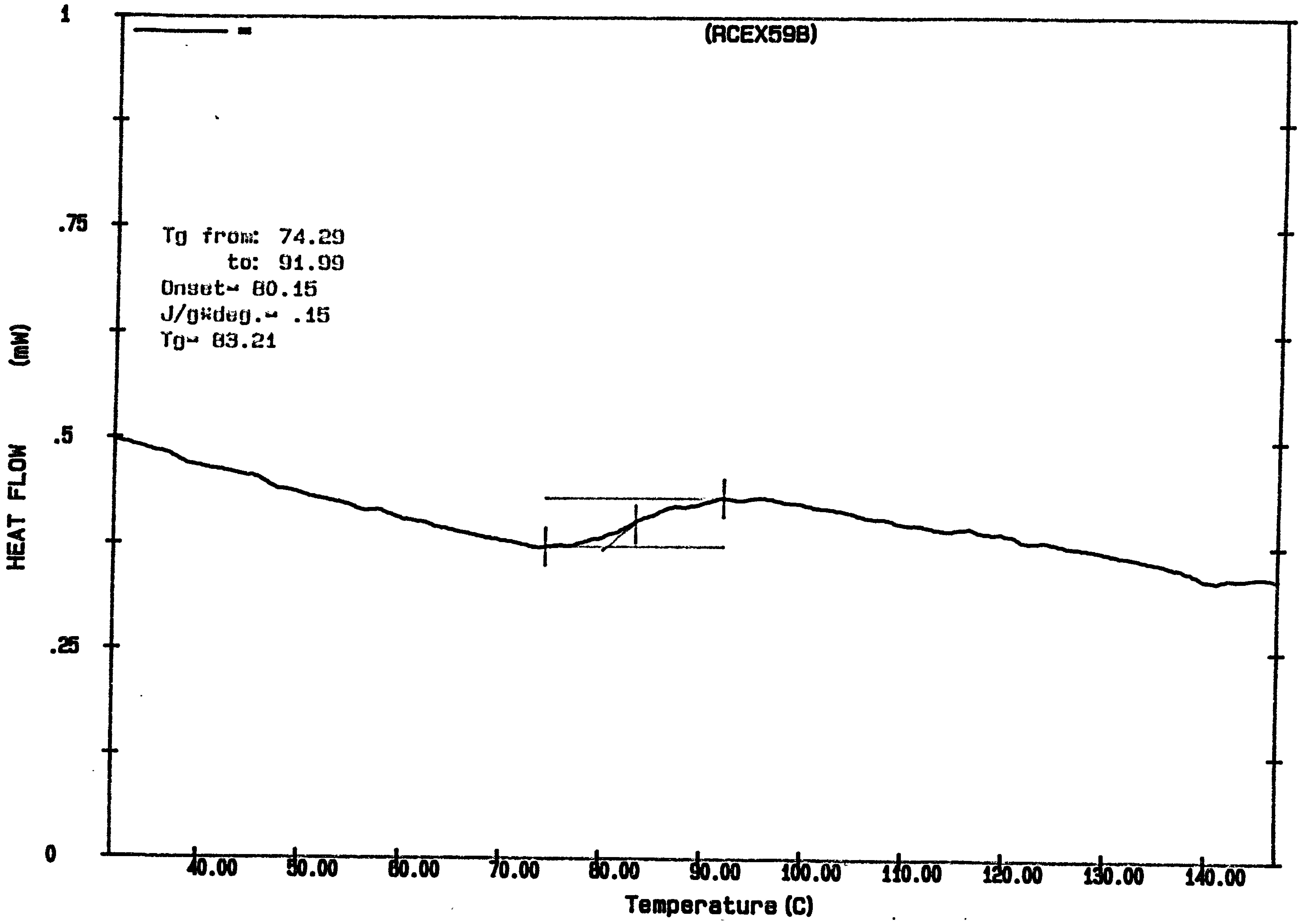
Appendix 3.10 GPC trace of polymer formed in the attempted copolymerisation of butyl acrylate (4.5 g) and 1,1-dicyano-2-vinylcyclopropane (0.5 g)



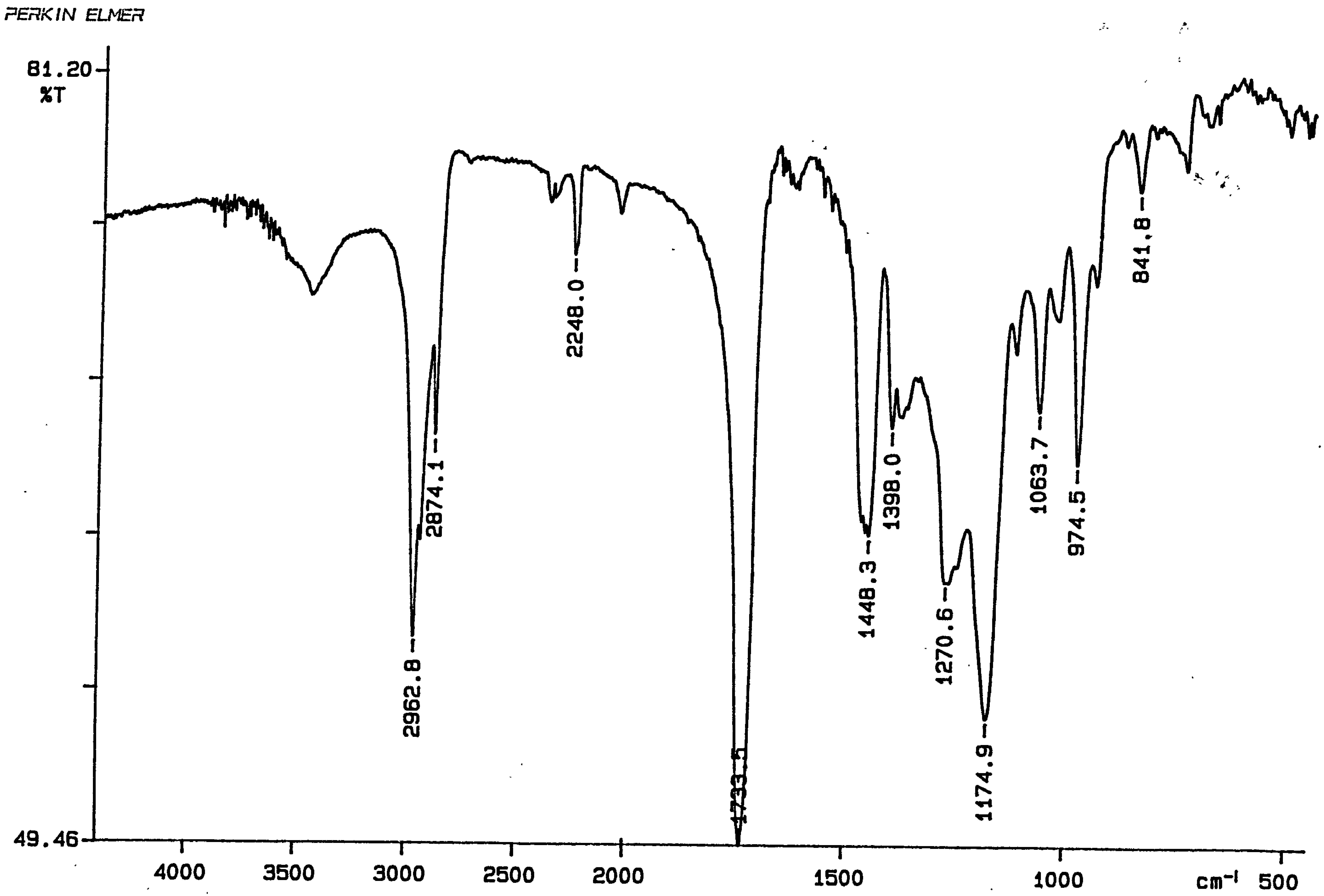
Appendix 3.11 Infra-red spectrum of polymer formed in the attempted copolymerisation of butyl



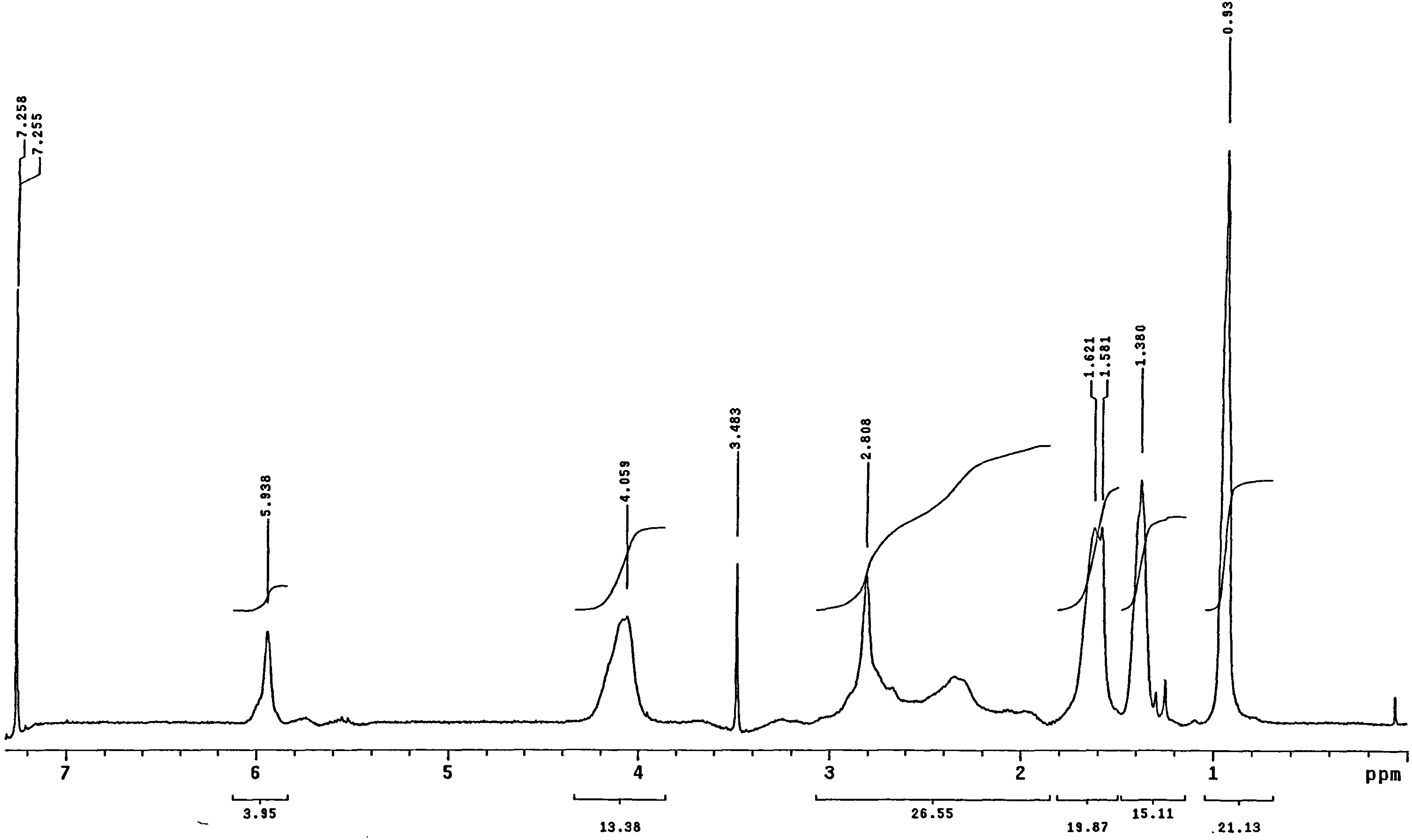
Appendix 3.12 ^{1}H NMR of polymer formed in the attempted copolymerisation of butyl acrylate (0.5 g) and 1,1-dicyano-2-vinylcyclopropane (4.5 g)



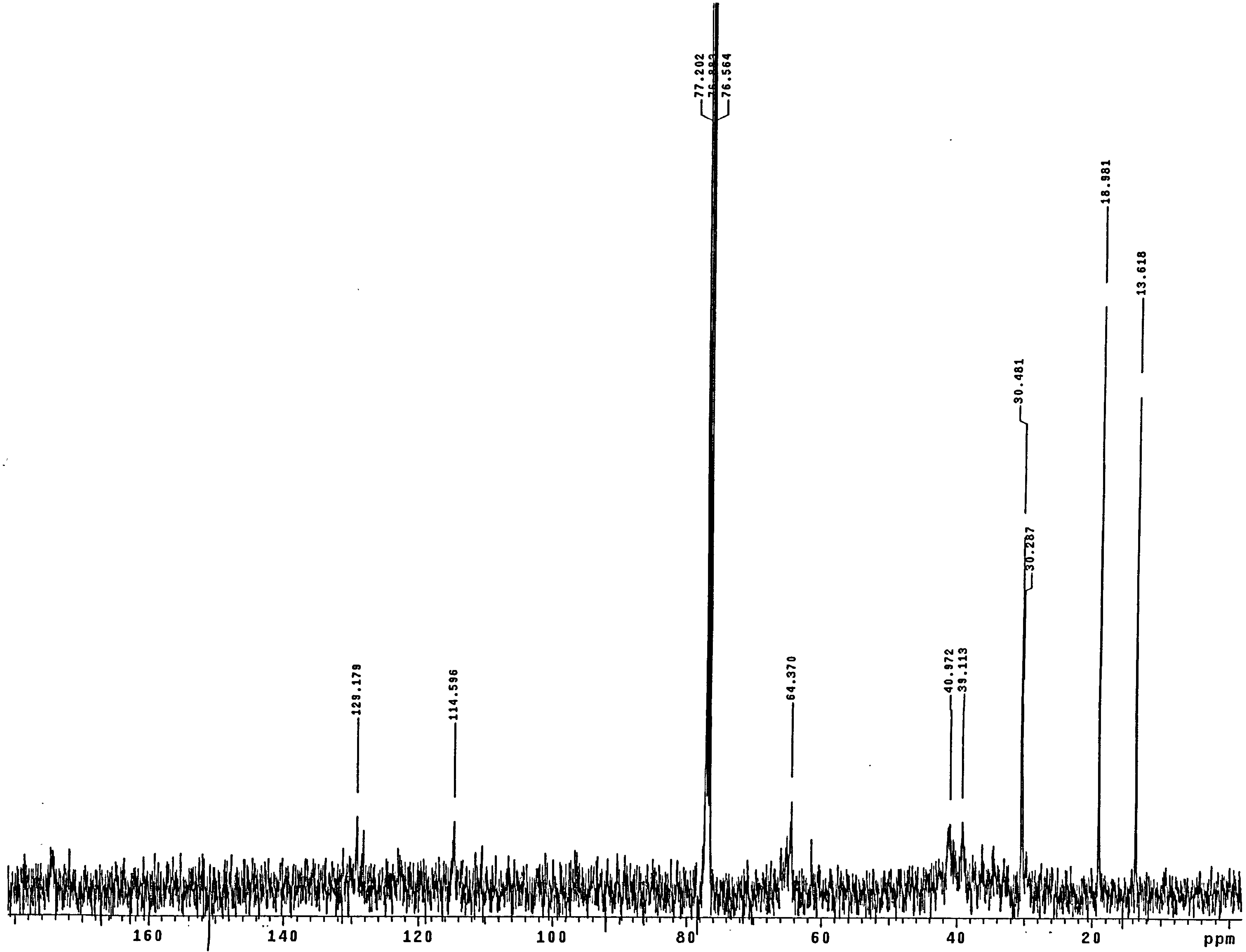
Appendix 3.13 DSC trace of polymer formed in the attempted copolymerisation of butyl acrylate (0.5 g) and 1,1-dicyano-2-vinylcyclopropane (4.5 g)



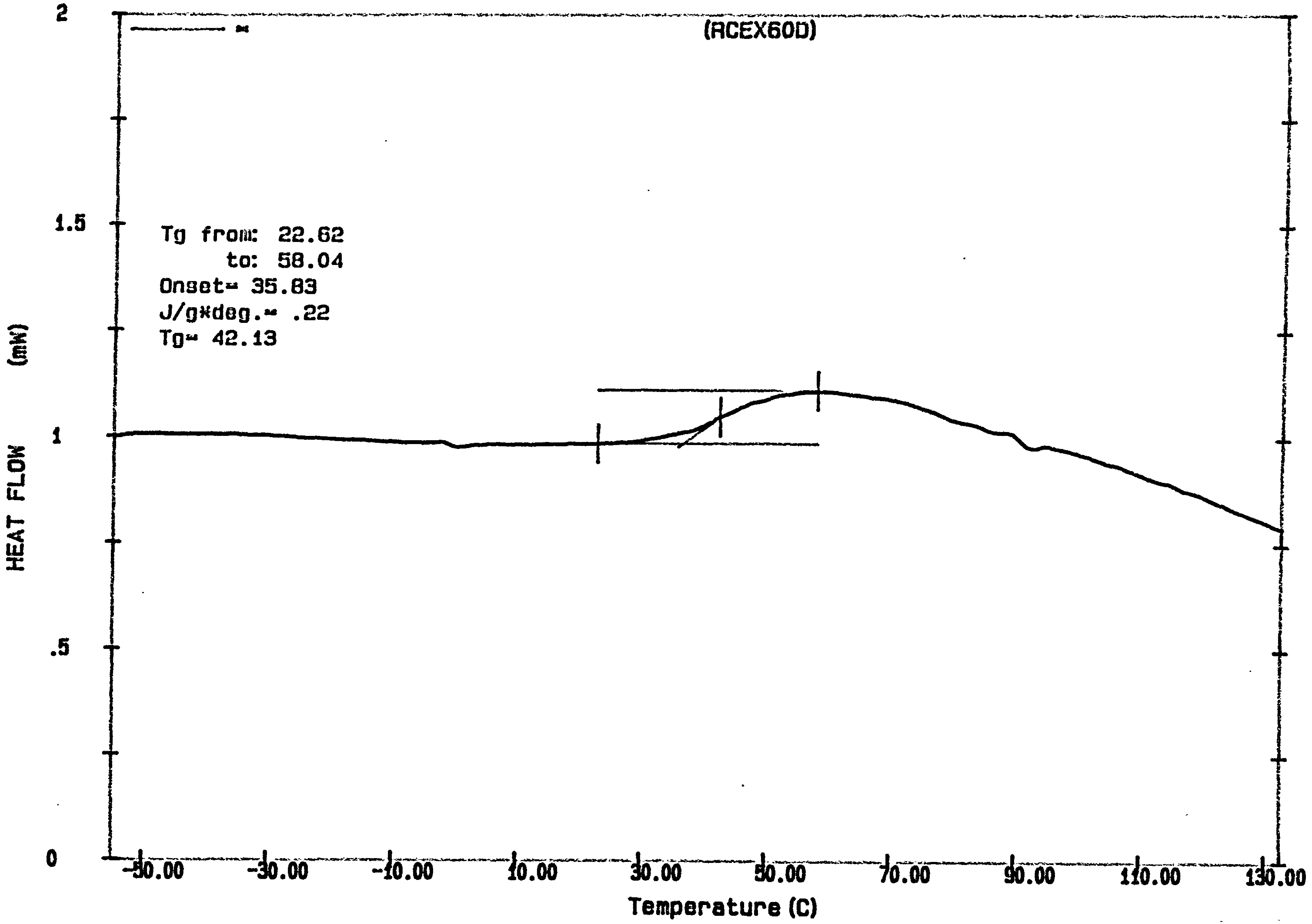
Appendix 3.14 Infra-red spectrum of polymer formed in the attempted solution free-radical



Appendix 3.15 ^{1}H NMR spectrum of polymer formed in the attempted solution free-radical polymerisation of butyl acrylate and 1,1-dicyano-2-vinylcyclopropane



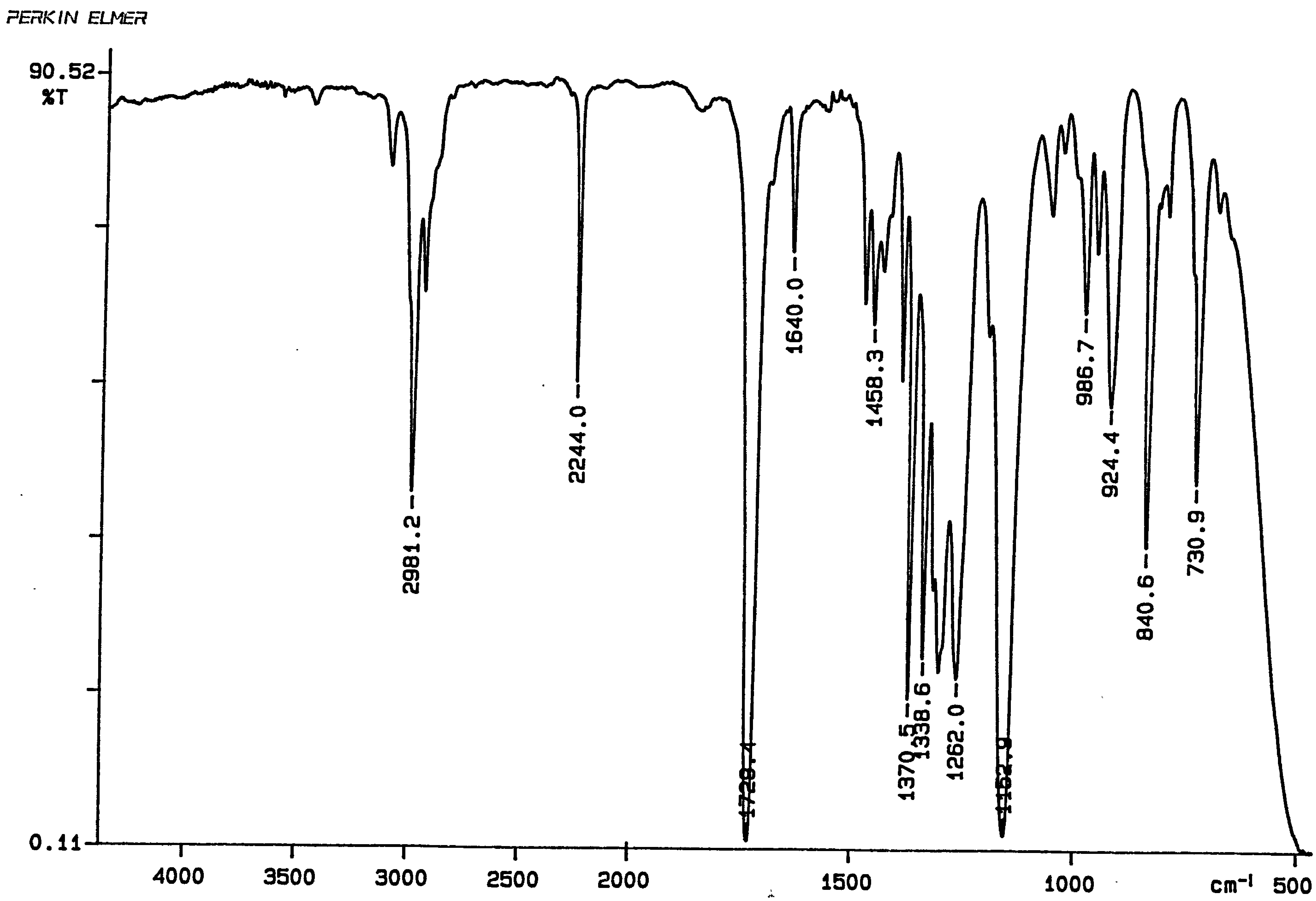
Appendix 3.16 ^{13}C NMR spectrum of polymer formed in the attempted solution free-radical



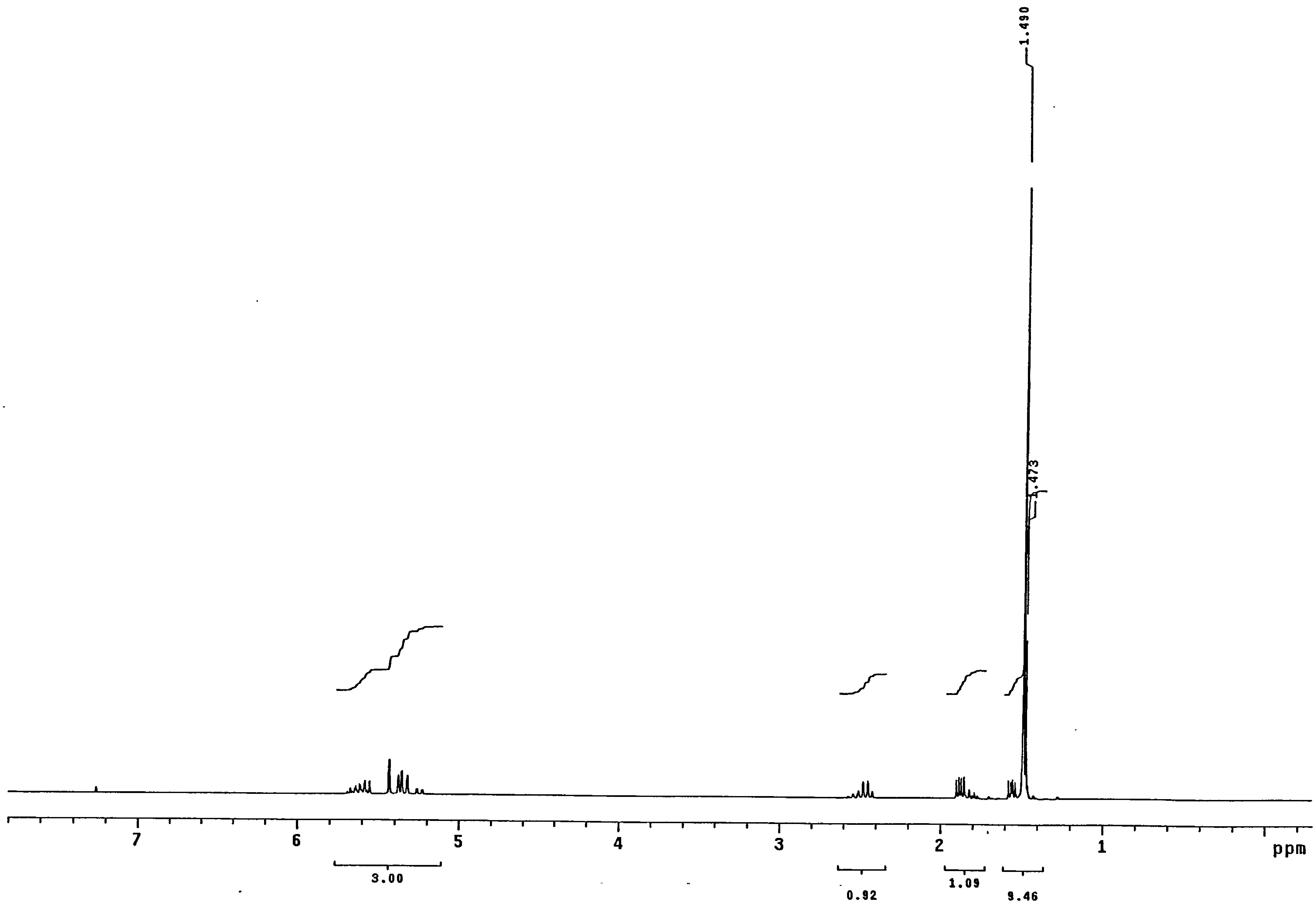
Appendix 3.17 DSC trace of polymer formed in the attempted solution free-radical *polymerisation of butyl acrylate and 1,1-dicyano-2-vinylcyclopropane*

Appendix 4

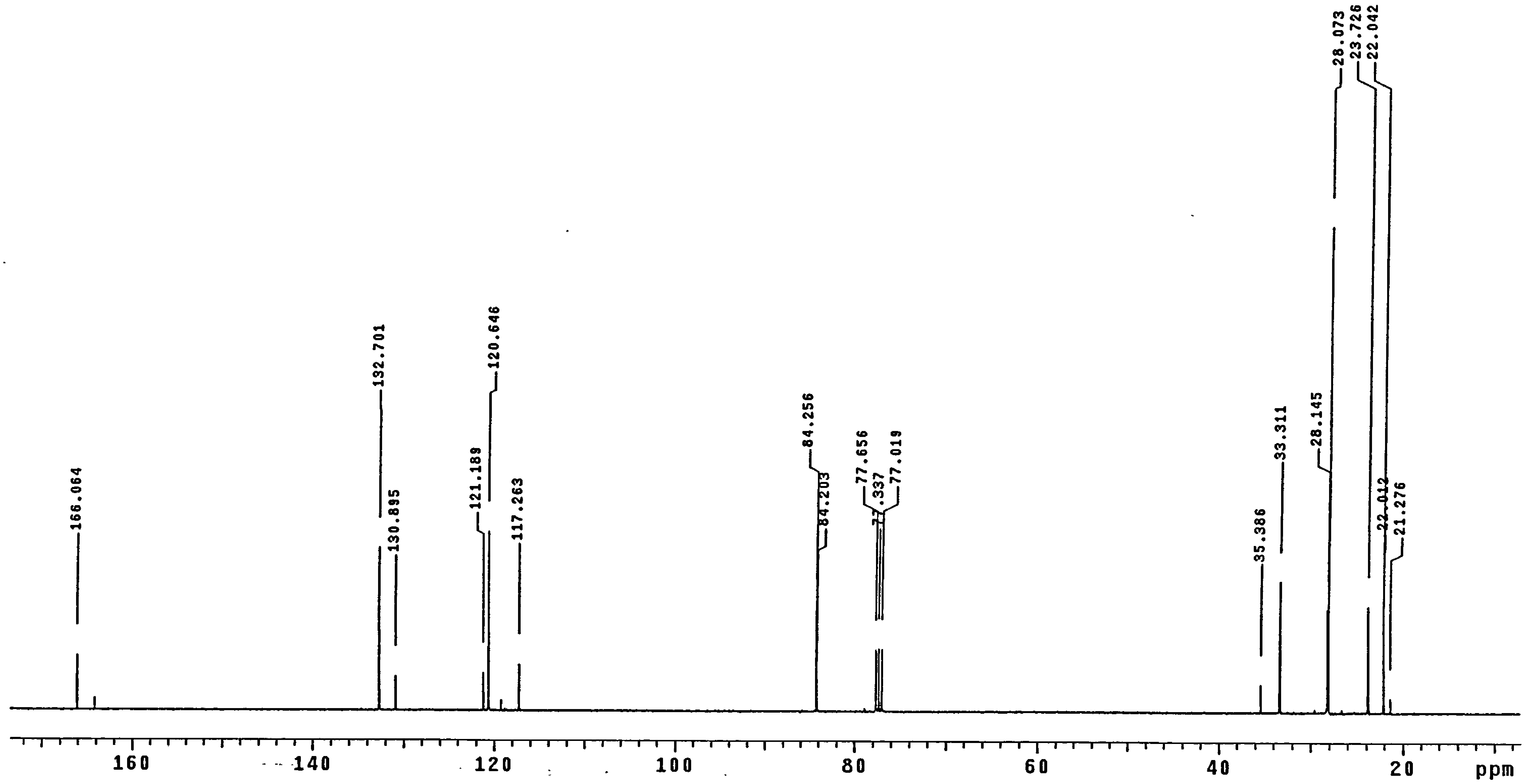
Analytical data for chapter 5



Appendix 4.1 Infra-red spectrum of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane



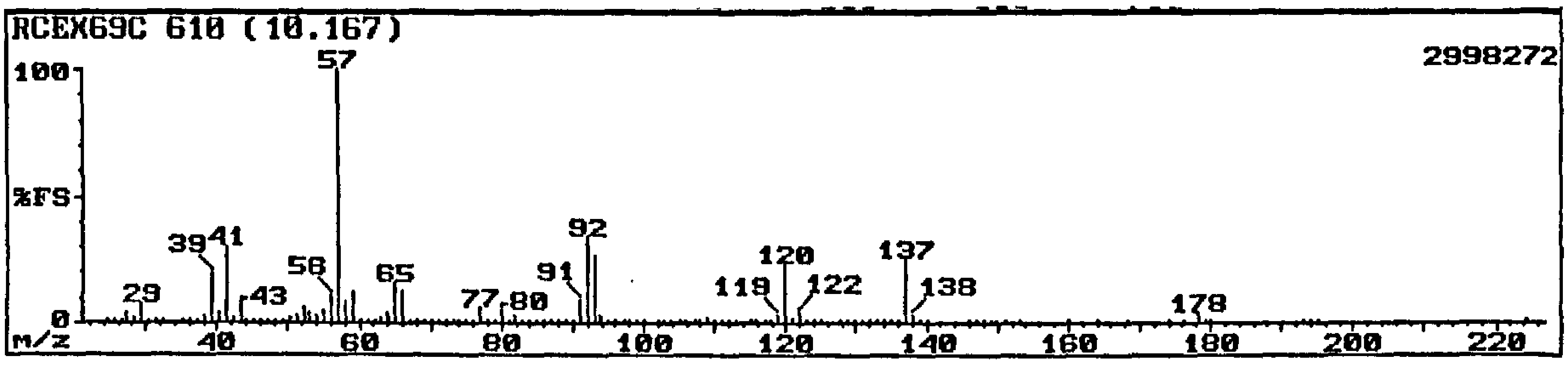
Appendix 4.2 ^{1}H NMR spectrum of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane



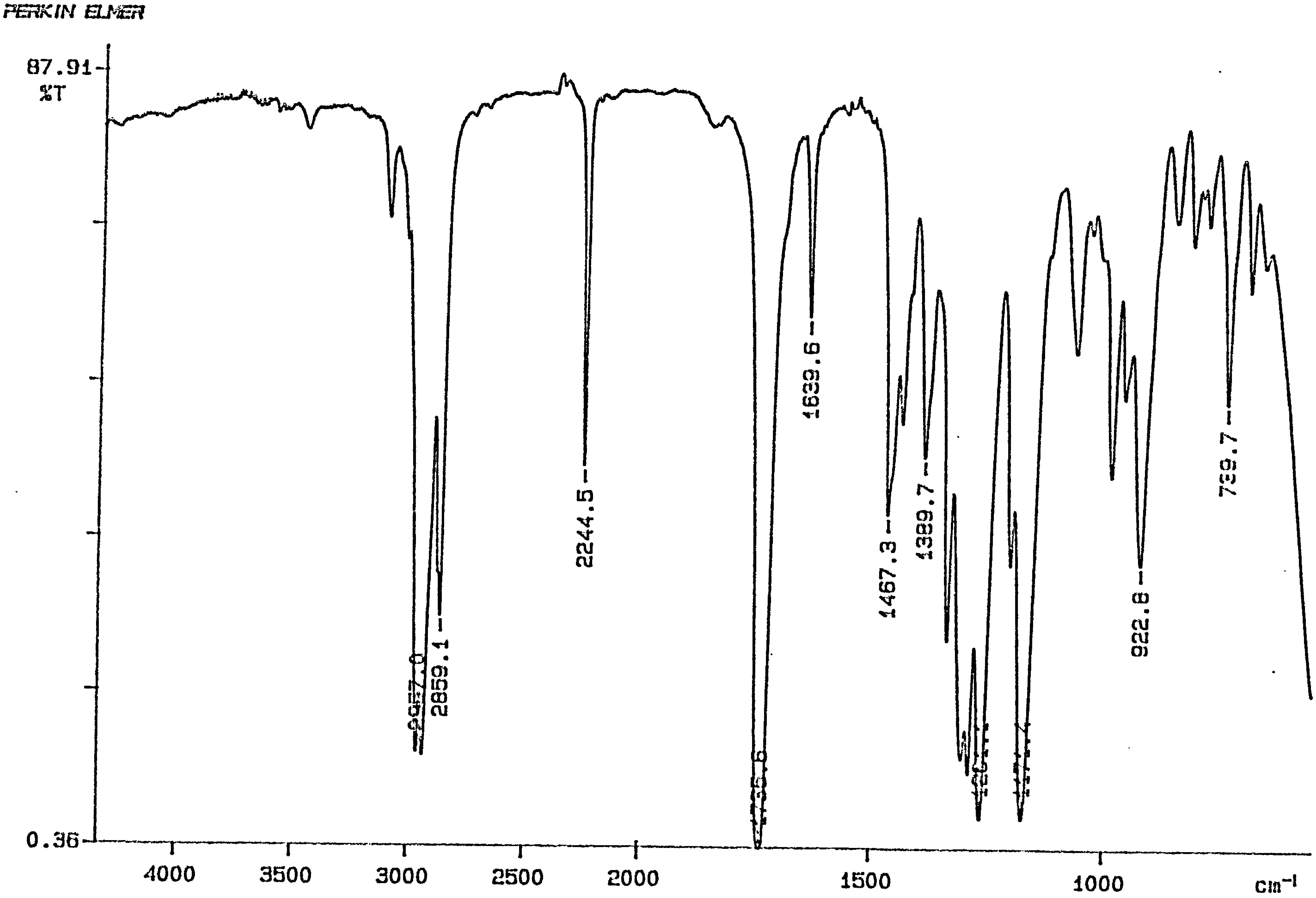
Appendix 4.3 ^{13}C NMR spectrum of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane

RCEX69C 610 (10.167) 2998272

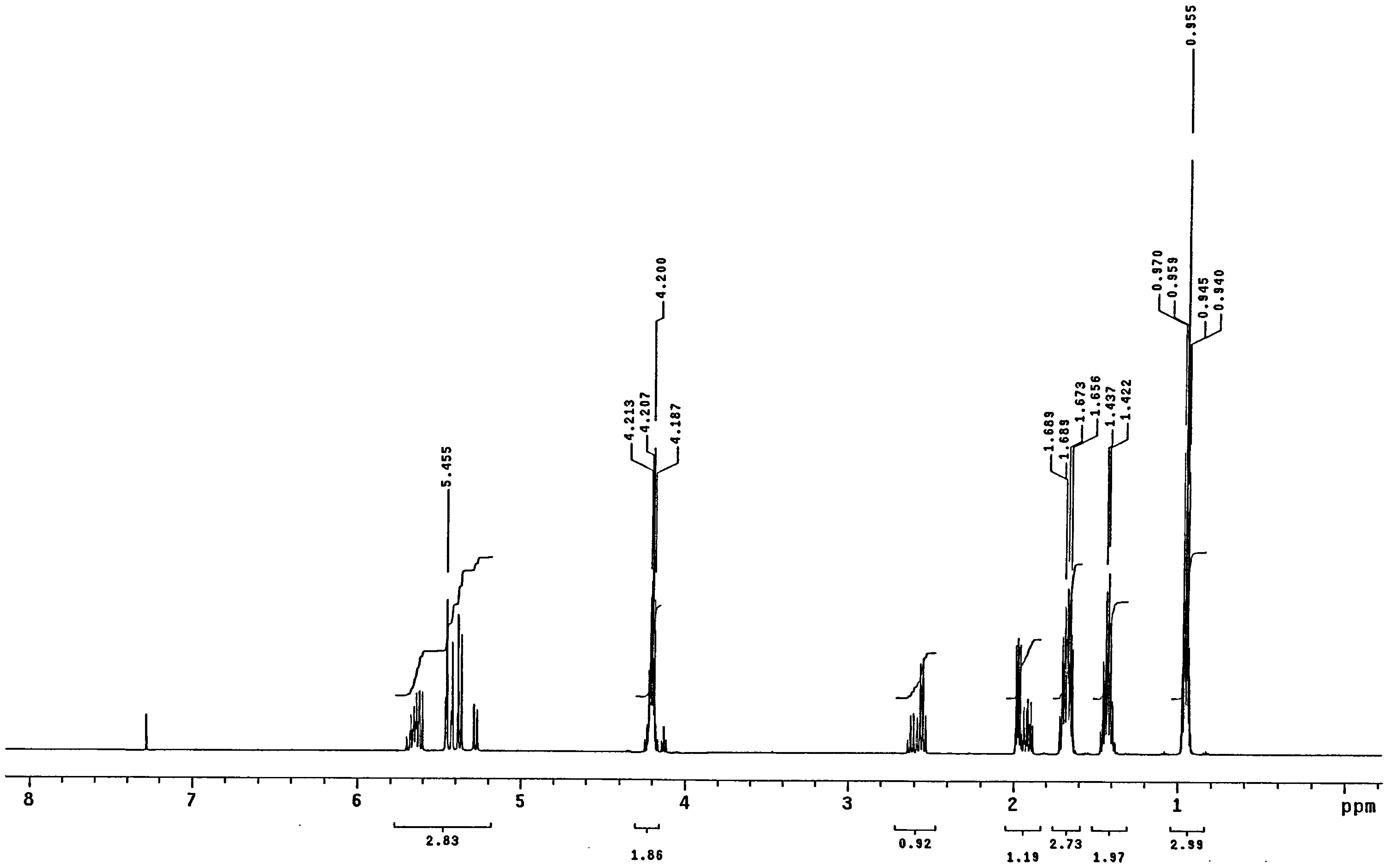
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
24	0.01	59	11.20	92	33.88	129	0.02
25	0.04	60	0.48	93	26.09	130	0.04
26	0.59	61	0.35	94	2.97	131	0.02
27	3.52	62	0.61	95	0.33	132	0.04
28	1.83	63	2.15	96	0.15	133	0.04
29	7.41	64	4.13	97	0.16	134	0.03
30	0.21	65	15.98	98	0.38	135	0.03
31	0.34	66	12.84	99	0.04	136	0.36
32	0.16	67	1.41	100	0.02	137	25.55
35	0.02	68	0.45	102	0.40	138	3.21
36	0.18	69	0.19	103	0.07	139	0.33
37	1.05	70	0.16	104	0.13	140	0.04
38	2.60	71	0.12	105	0.06	146	0.03
39	19.40	72	0.05	106	0.16	147	0.04
40	3.59	73	0.22	107	0.07	148	0.05
41	30.46	74	0.07	108	0.55	149	0.07
42	1.90	75	0.25	109	1.89	150	0.03
43	6.39	76	0.51	110	0.83	151	0.02
44	0.88	77	5.74	111	0.20	153	0.02
45	1.19	78	0.79	112	0.15	160	0.02
46	0.07	79	0.31	113	0.03	164	0.02
47	0.02	80	5.09	115	0.02	168	0.04
48	0.04	81	1.39	116	0.01	174	0.01
49	0.27	82	3.31	117	0.02	176	0.01
50	1.61	83	0.55	118	0.07	178	3.76
51	2.46	84	0.09	119	3.18	179	0.39
52	5.50	85	0.10	120	23.36	180	0.03
53	4.00	86	0.06	121	2.02	193	0.02
54	3.14	87	0.14	122	3.52	194	0.16
55	4.71	88	0.18	123	0.27	195	0.01
56	10.52	89	0.08	124	0.05	224	0.02
57	100.00	90	0.61	125	0.03		
58	8.67	91	9.15	128	0.02		



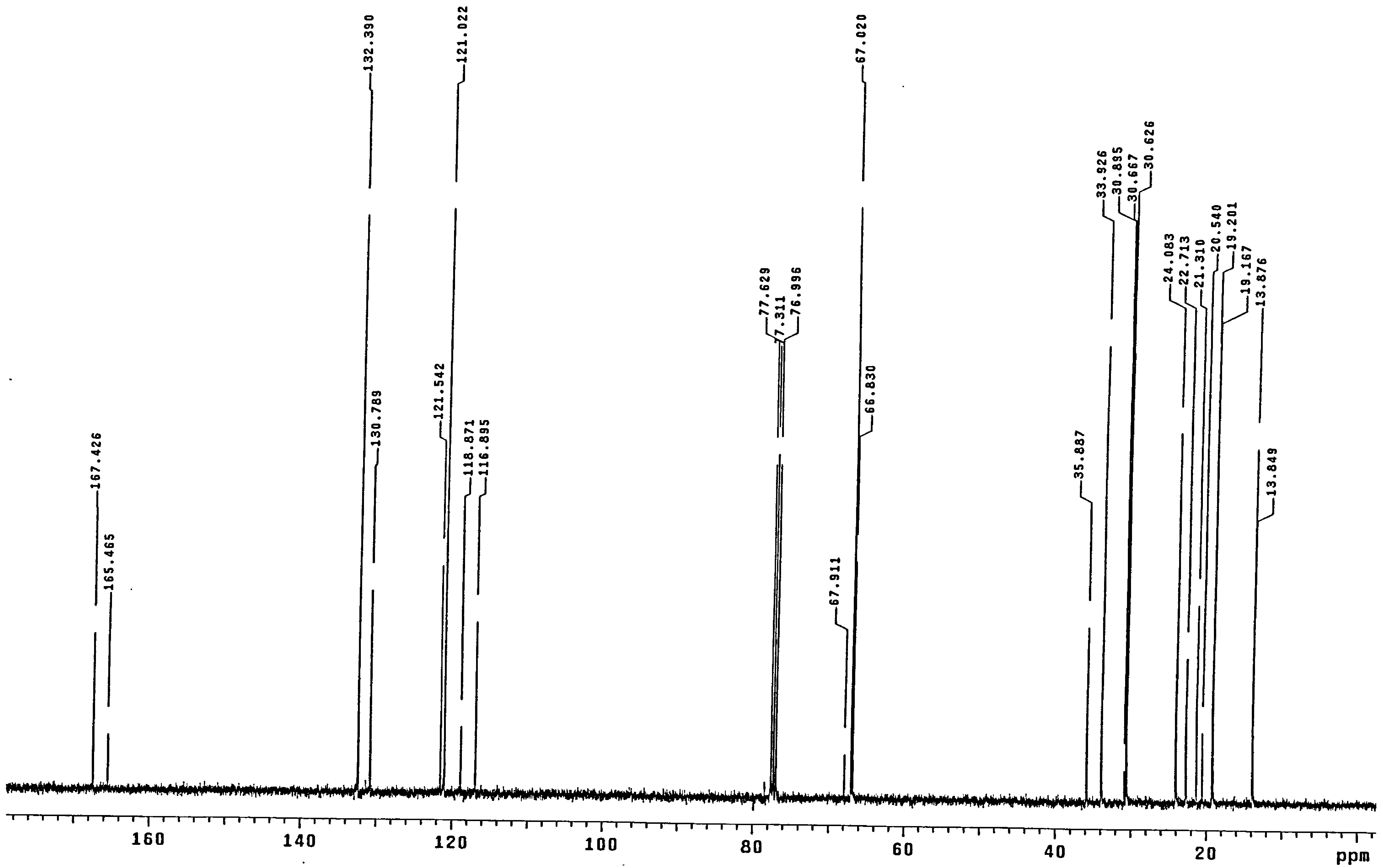
Appendix 4.4 Mass spectrum of 1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane



Appendix 4.5 Infra-red spectrum of 1-cyano-1-n-butoxycarbonyl-2-vinylcyclopropane



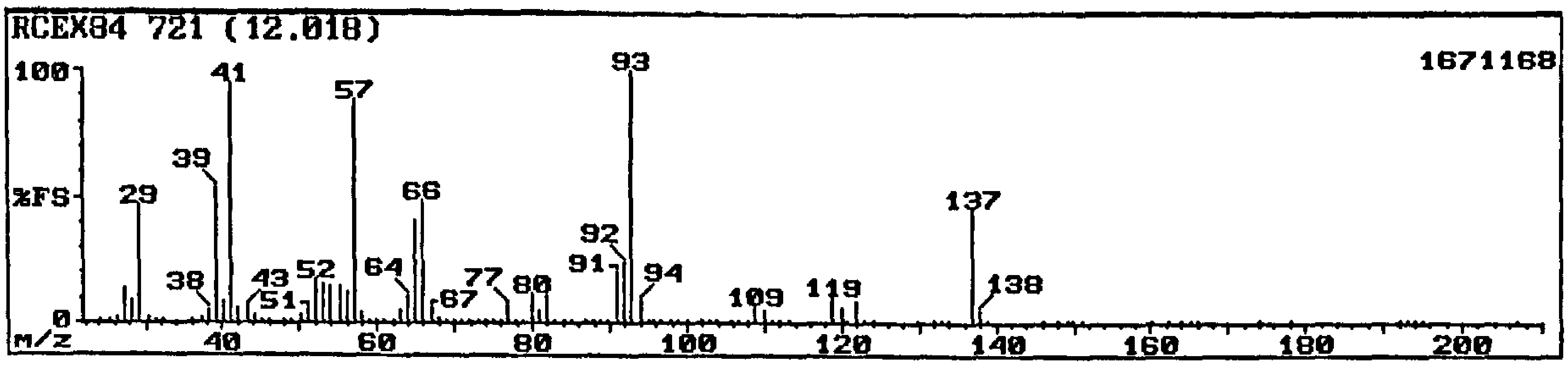
Appendix 4.6 ^{1}H NMR spectrum of 1-cyano-1-n-butoxycarbonyl-2-vinylcyclopropane



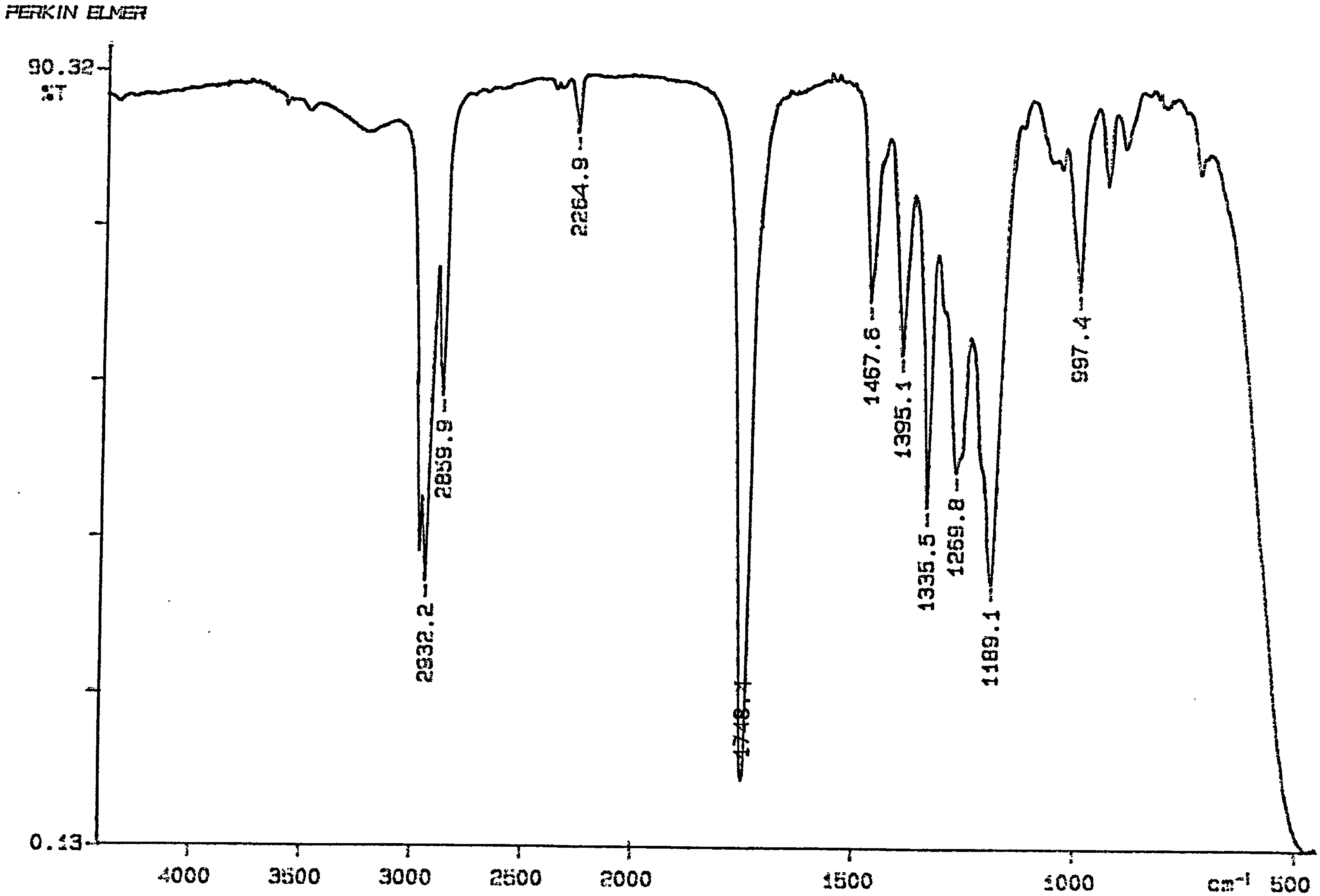
Appendix 4.7 ^{13}C NMR spectrum of 1-cyano-1-n-butoxycarbonyl-2-vinylcyclopropane

RCEX84 721 (12.018) 1671168

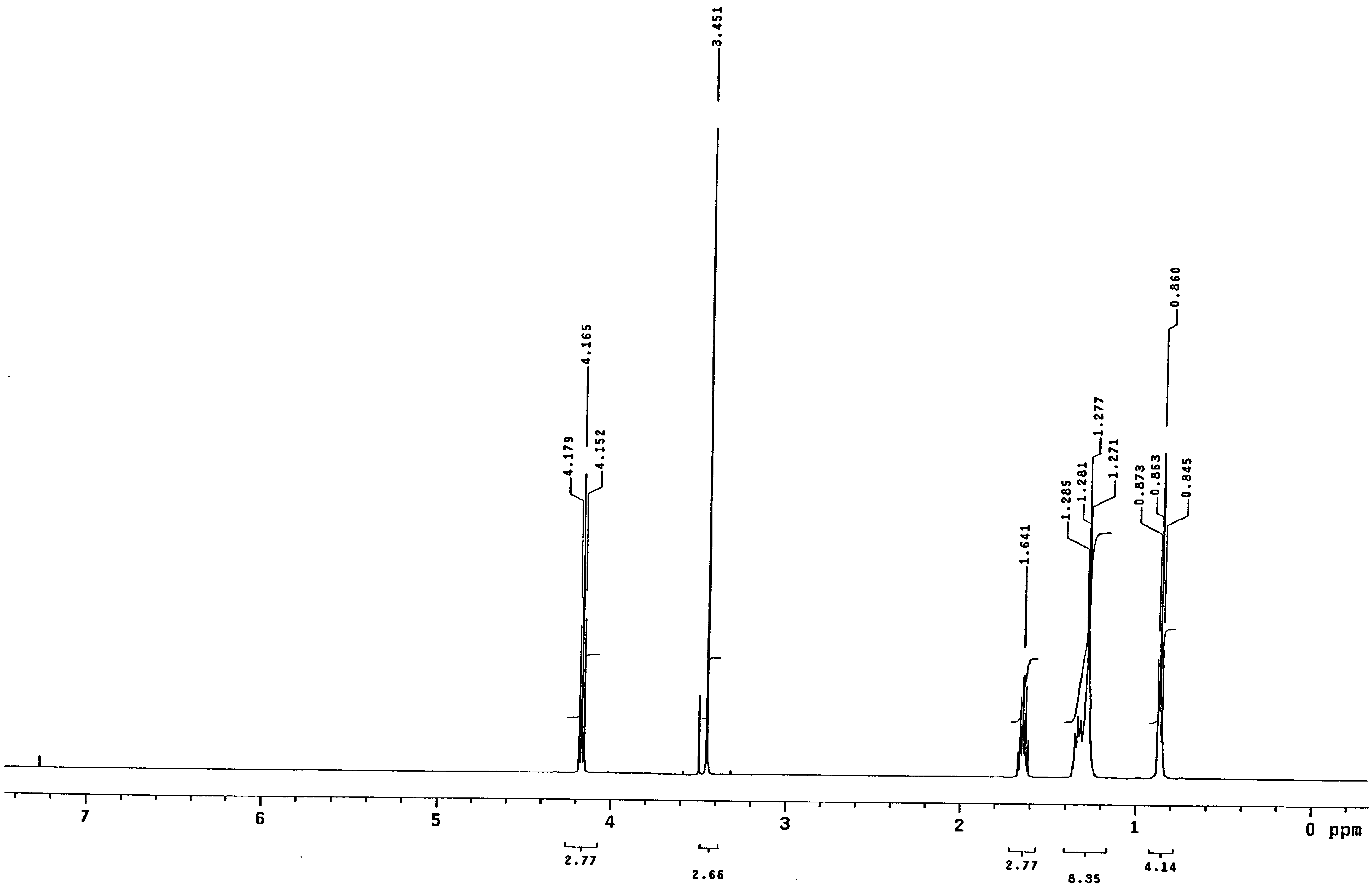
Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
24	0.02	57	88.24	87	0.14	123	0.41
25	0.05	58	4.11	88	0.22	124	0.11
26	1.49	59	0.25	89	0.06	130	0.04
27	13.91	60	0.07	90	0.52	132	0.18
28	8.70	61	0.47	91	20.10	133	0.07
29	47.06	62	1.15	92	24.75	134	0.13
30	1.47	63	5.02	93	100.00	137	45.59
31	1.06	64	10.72	94	9.01	138	5.21
32	1.07	65	41.18	95	0.67	139	0.44
36	0.09	66	48.77	96	0.10	146	0.18
37	1.90	67	6.00	97	0.14	148	0.48
38	5.33	68	1.78	98	0.57	149	0.06
39	53.68	69	0.50	99	0.02	150	0.23
40	8.95	70	0.80	100	0.05	151	0.11
41	95.10	71	0.59	102	0.28	160	0.11
42	5.45	72	0.11	103	0.06	162	0.05
43	5.94	73	0.13	104	0.13	164	0.26
44	2.45	74	0.08	106	0.52	165	0.04
45	1.41	75	0.41	107	0.10	166	0.03
46	0.14	76	0.89	108	0.86	174	0.06
48	0.04	77	6.37	109	6.74	178	0.17
49	0.25	78	1.19	110	4.96	192	0.16
50	2.76	79	0.77	111	0.47	193	0.33
51	5.33	80	11.70	112	0.06	194	0.91
52	17.89	81	4.47	113	0.02	195	0.08
53	15.69	82	11.09	119	10.54	207	0.04
54	14.09	83	1.39	120	6.00		
55	15.01	84	0.20	121	0.38		
56	12.87	85	0.09	122	8.46		



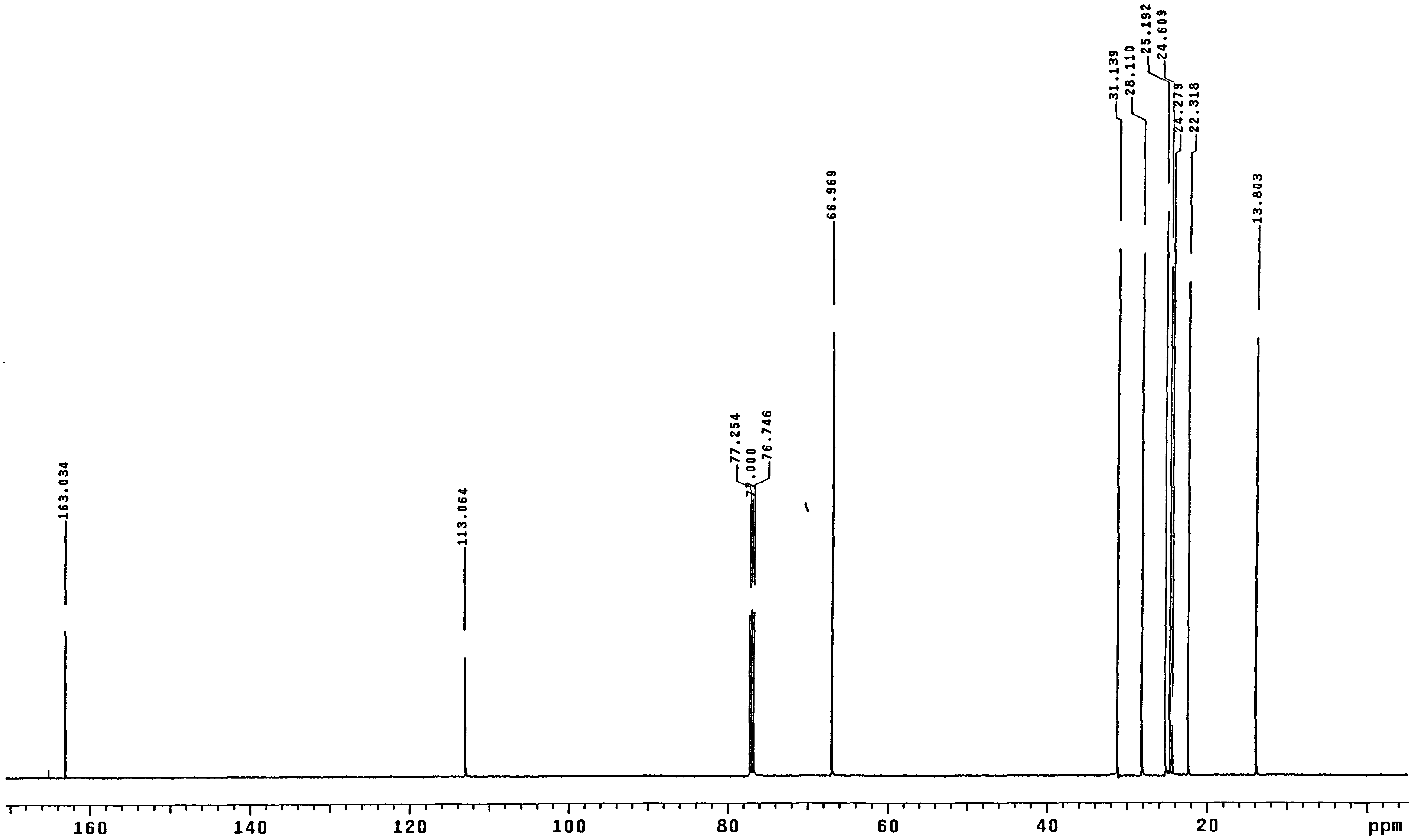
Appendix 4.8 Mass spectrum of 1-cyano-1-n-butoxycarbonyl-2-vinylcyclopropane



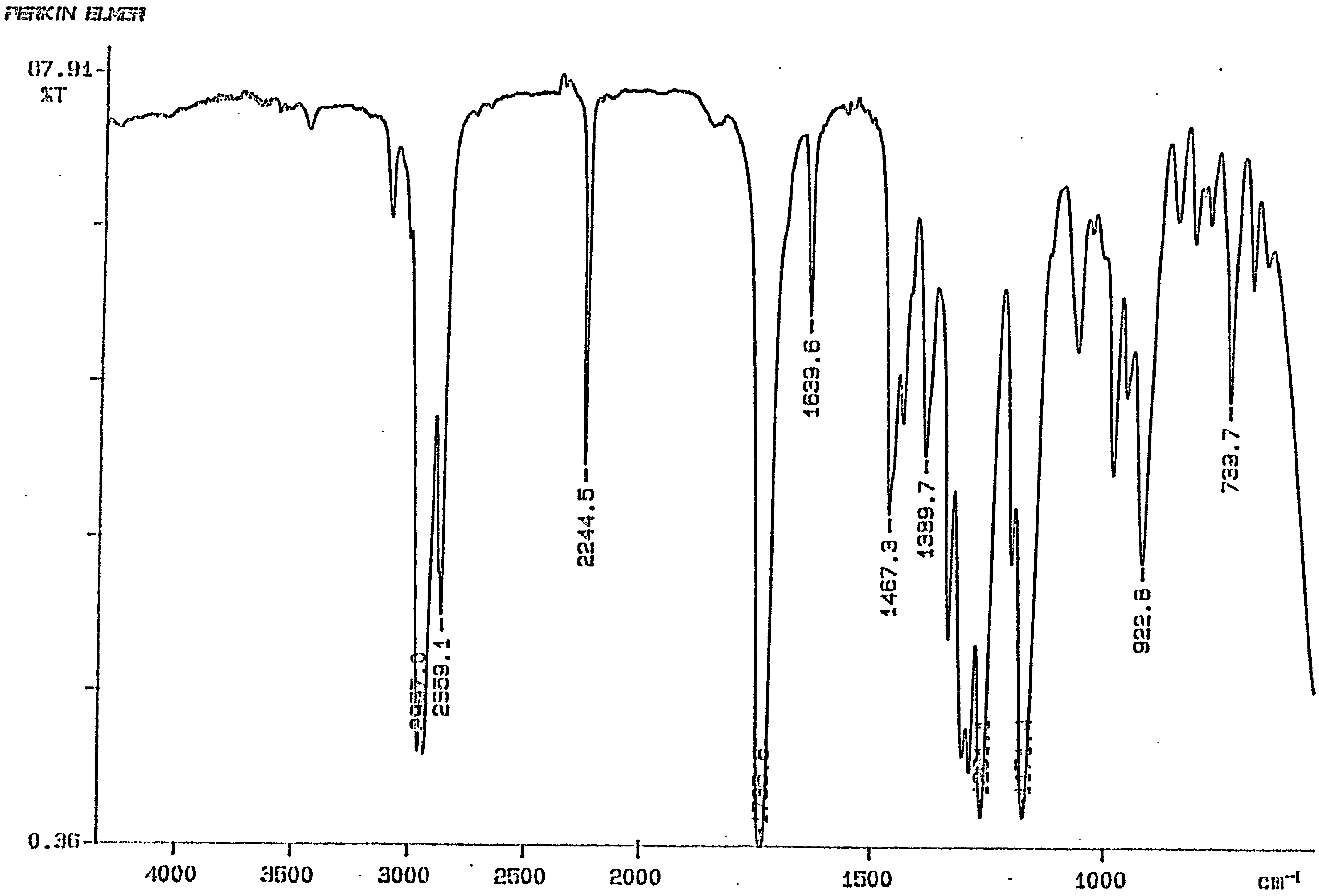
Appendix 4.9 Infra-red spectrum of hexyl-cyanoacetate



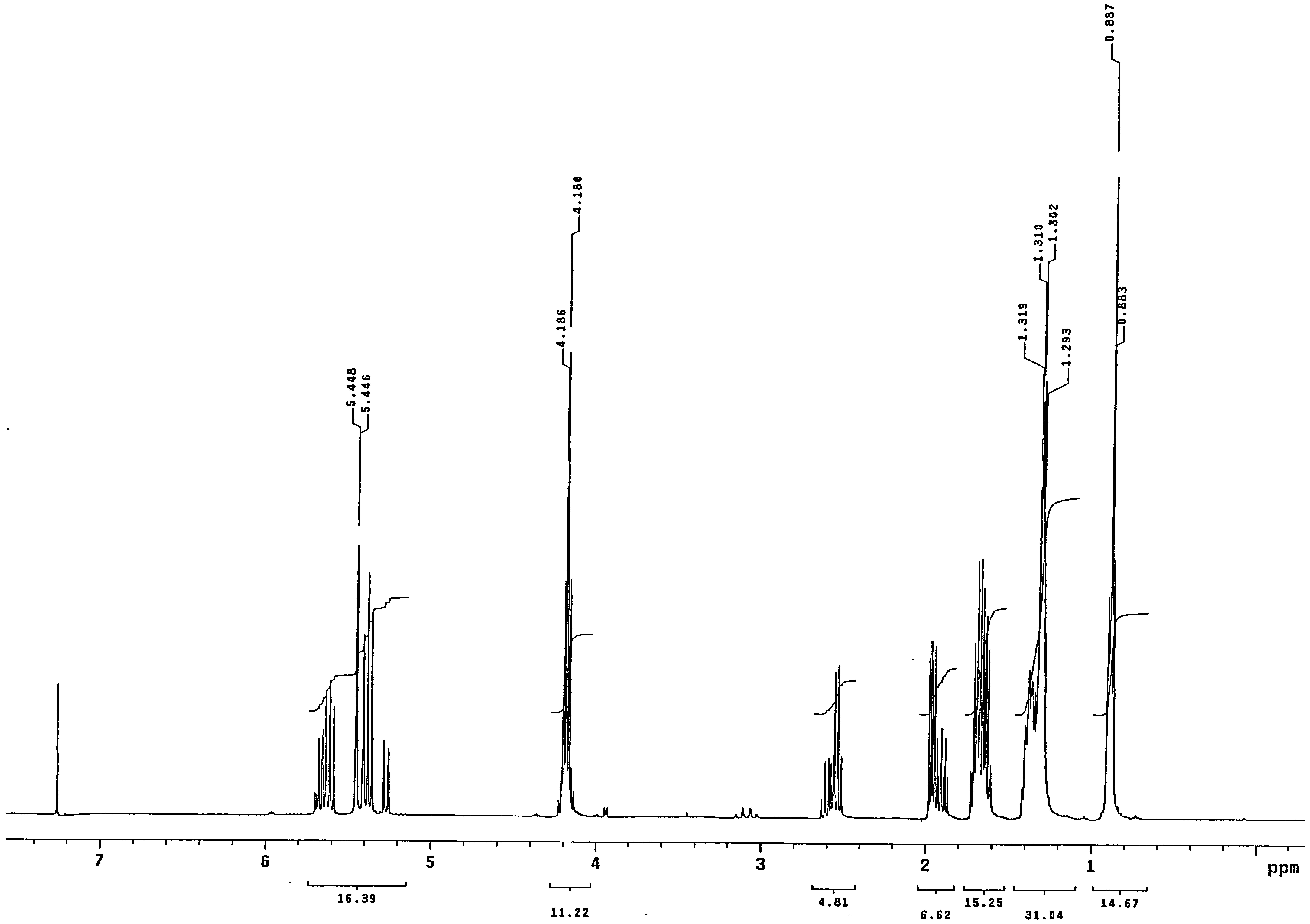
Appendix 4.10 ¹H NMR *spectrum of hexyl-cyanoacetate*



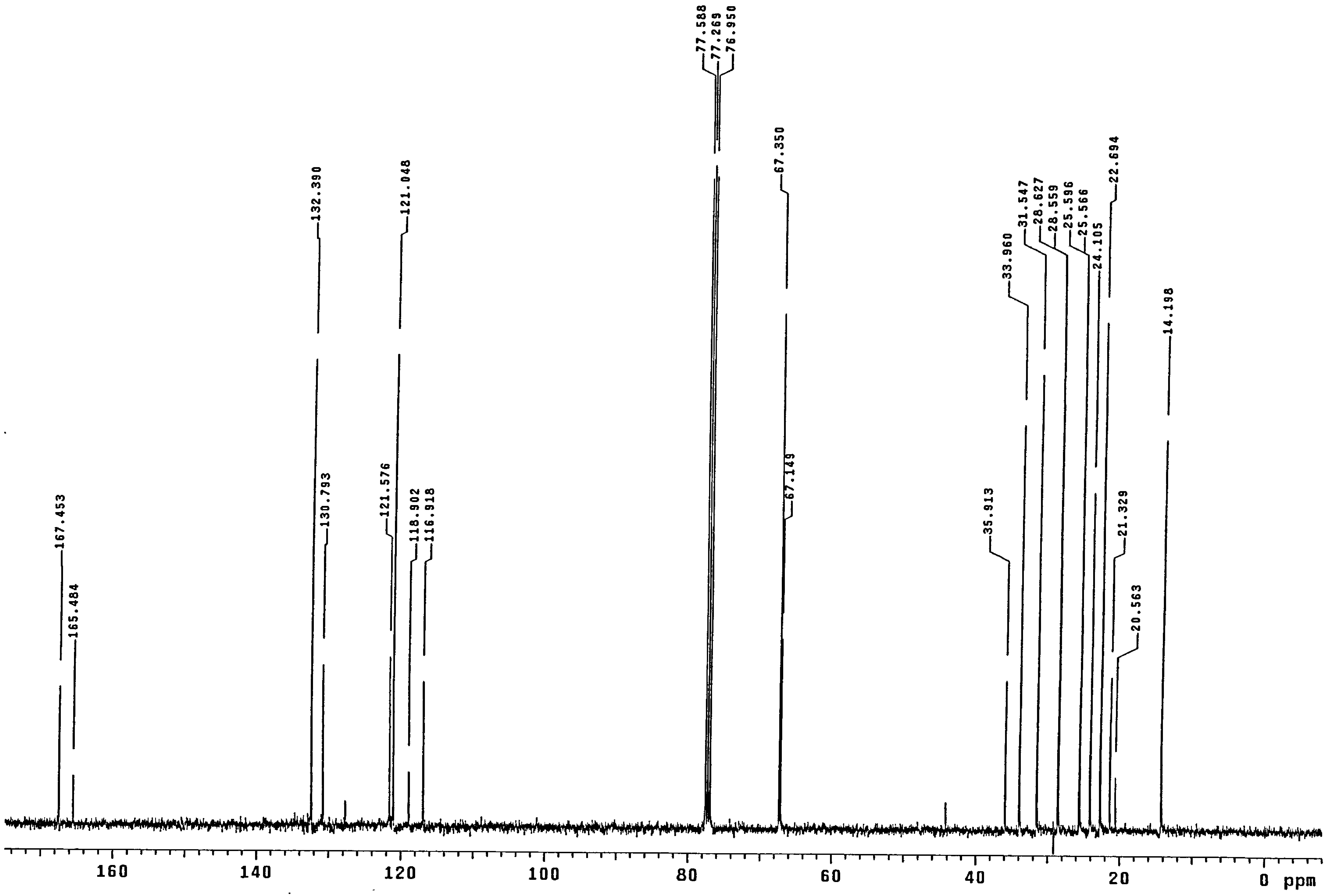
Appendix 4.11 ^{13}C NMR spectrum of hexyl-cyanoacetate



Appendix 4.12 Infra-red spectrum of 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane



Appendix 4.13 ^{1}H NMR spectrum of 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane



Appendix 4.14 ^{13}C NMR spectrum of 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane

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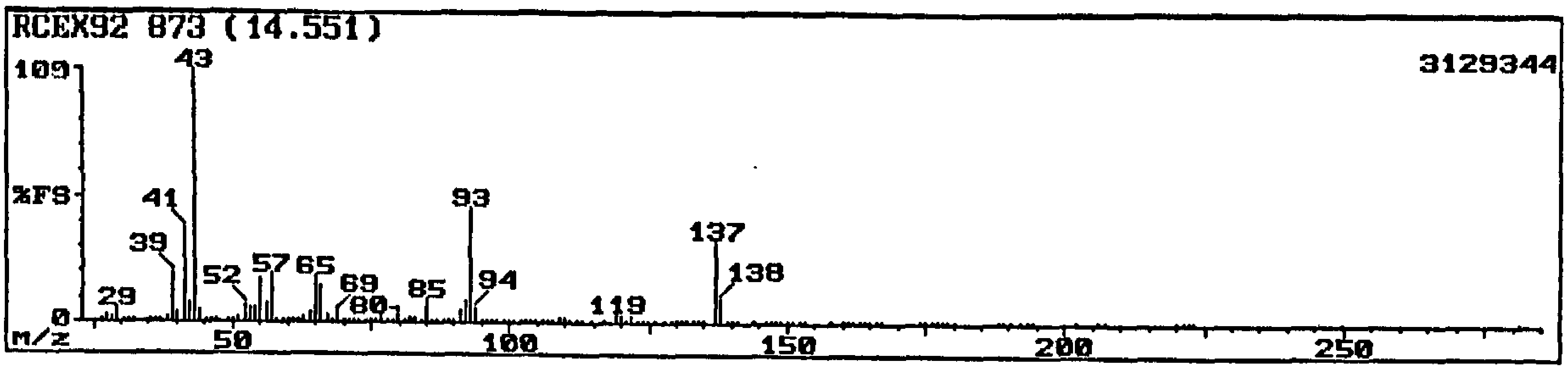
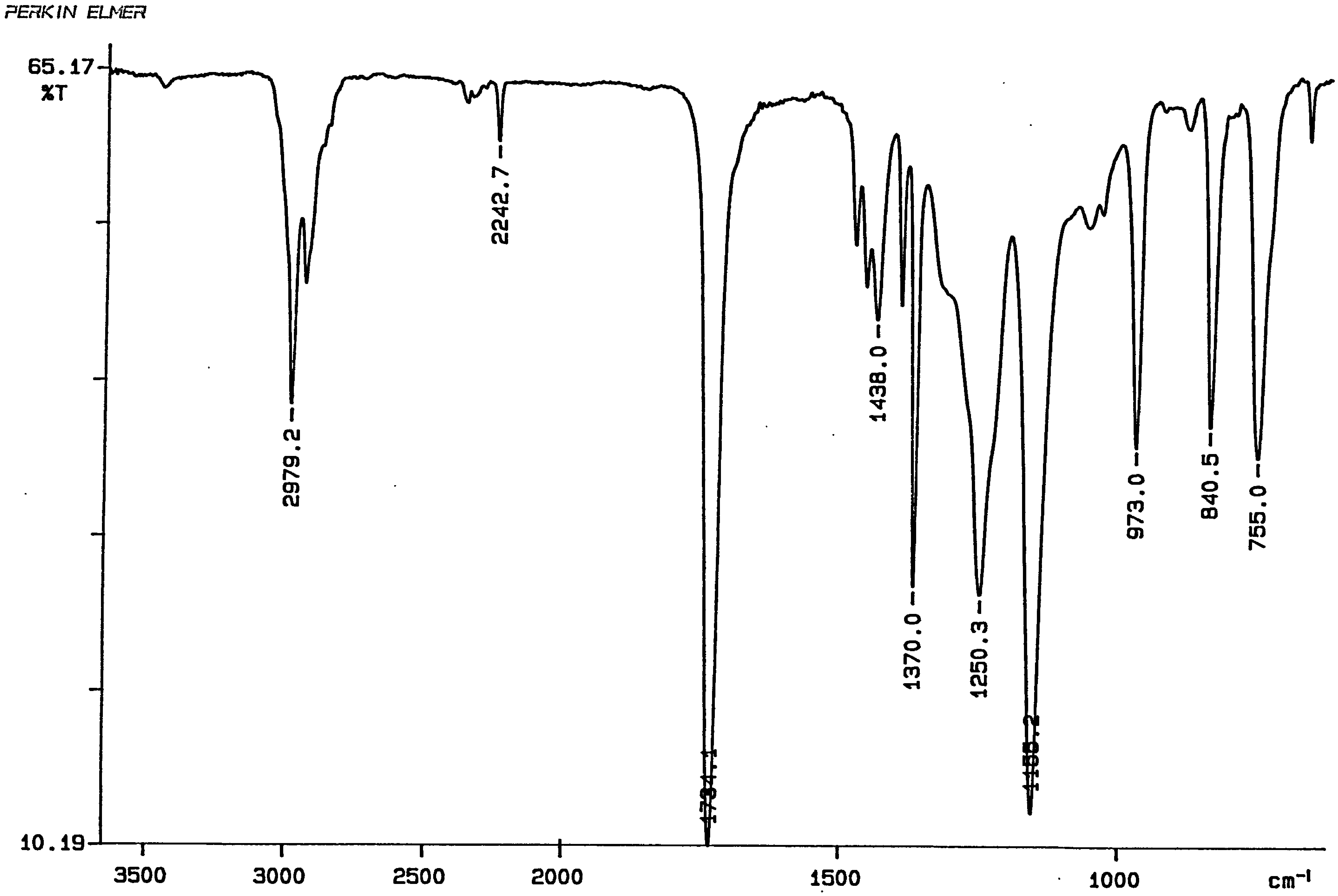
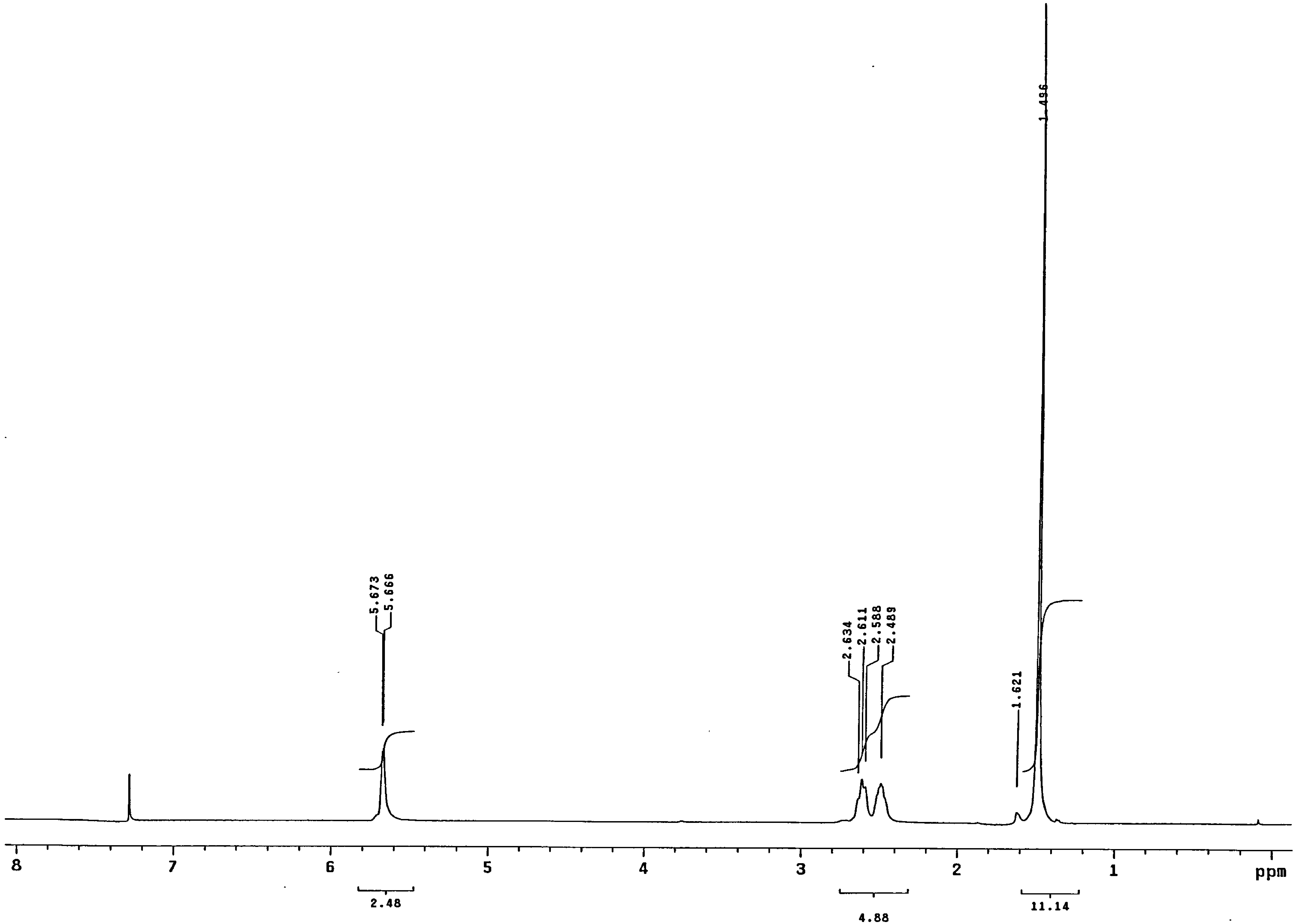
 ----------------------------------------------------------------------------
 RCEX92 873 (14.551)                                                  3129344
-------------------+-------------------+-------------------+-----------------
 Mass    Rel Int   | Mass    Rel Int   | Mass    Rel Int   | Mass    Rel Int
-------------------+-------------------+-------------------+-----------------
  26       0.18    |  66      14.79    | 103       0.04    | 148       0.28
  27       2.91    |  67       3.30    | 104       0.08    | 149       0.09
  28       1.75    |  68       0.86    | 105       0.09    | 150       0.20
  29       5.43    |  69       3.47    | 106       0.29    | 151       0.10
  30       0.19    |  70       0.45    | 107       0.16    | 152       0.10
  31       0.25    |  71       0.30    | 108       0.31    | 153       0.02
  32       0.37    |  72       0.03    | 109       2.09    | 158       0.02
  35       0.02    |  73       0.06    | 110       2.29    | 160       0.11
  36       0.17    |  74       0.03    | 111       0.28    | 161       0.04
  37       0.50    |  75       0.13    | 112       0.06    | 162       0.21
  38       1.59    |  76       0.33    | 113       0.01    | 163       0.06
  39      18.98    |  77       2.65    | 115       0.02    | 164       0.40
  40       3.50    |  78       0.51    | 117       0.04    | 165       0.11
  41      37.17    |  79       0.42    | 119       3.99    | 166       0.03
  42       7.43    |  80       3.37    | 120       2.55    | 167       0.04
  43     100.00    |  81       1.21    | 121       0.92    | 174       0.10
  44       4.94    |  82       2.36    | 122       2.52    | 175       0.03
  45       0.59    |  83       1.66    | 123       0.27    | 176       0.97
  46       0.07    |  84       1.01    | 124       0.09    | 177       0.15
  47       0.03    |  85       9.95    | 125       0.02    | 178       0.30
  49       0.08    |  86       0.70    | 126       0.01    | 179       0.13
  50       0.91    |  87       0.09    | 128       0.06    | 180       0.04
  51       1.99    |  88       0.06    | 129       0.05    | 188       0.04
  52       6.54    |  89       0.03    | 130       0.03    | 189       0.02
  53       6.28    |  90       0.35    | 131       0.03    | 190       0.03
  54       5.76    |  91       5.17    | 132       0.13    | 192       0.33
  55      17.93    |  92       8.64    | 133       0.06    | 193       0.07
  56       7.43    |  93      46.07    | 134       0.35    | 194       0.02
  57      19.63    |  94       5.63    | 135       0.12    | 202       0.06
  58       0.92    |  95       0.59    | 137      33.12    | 206       0.22
  59       0.10    |  96       0.11    | 138       9.42    | 207       0.08
  60       0.03    |  97       0.08    | 139       0.91    | 220       0.32
  61       0.17    |  98       0.23    | 140       0.11    | 221       0.21
  62       0.45    |  99       0.06    | 141       0.03    | 222       1.01
  63       2.09    | 100       0.02    | 144       0.02    | 223       0.14
  64       4.12    | 101       0.08    | 146       0.16    | 281       0.01
  65      18.85    | 102       0.14    | 147       0.06    |
-------------------+-------------------+-------------------+-----------------
```



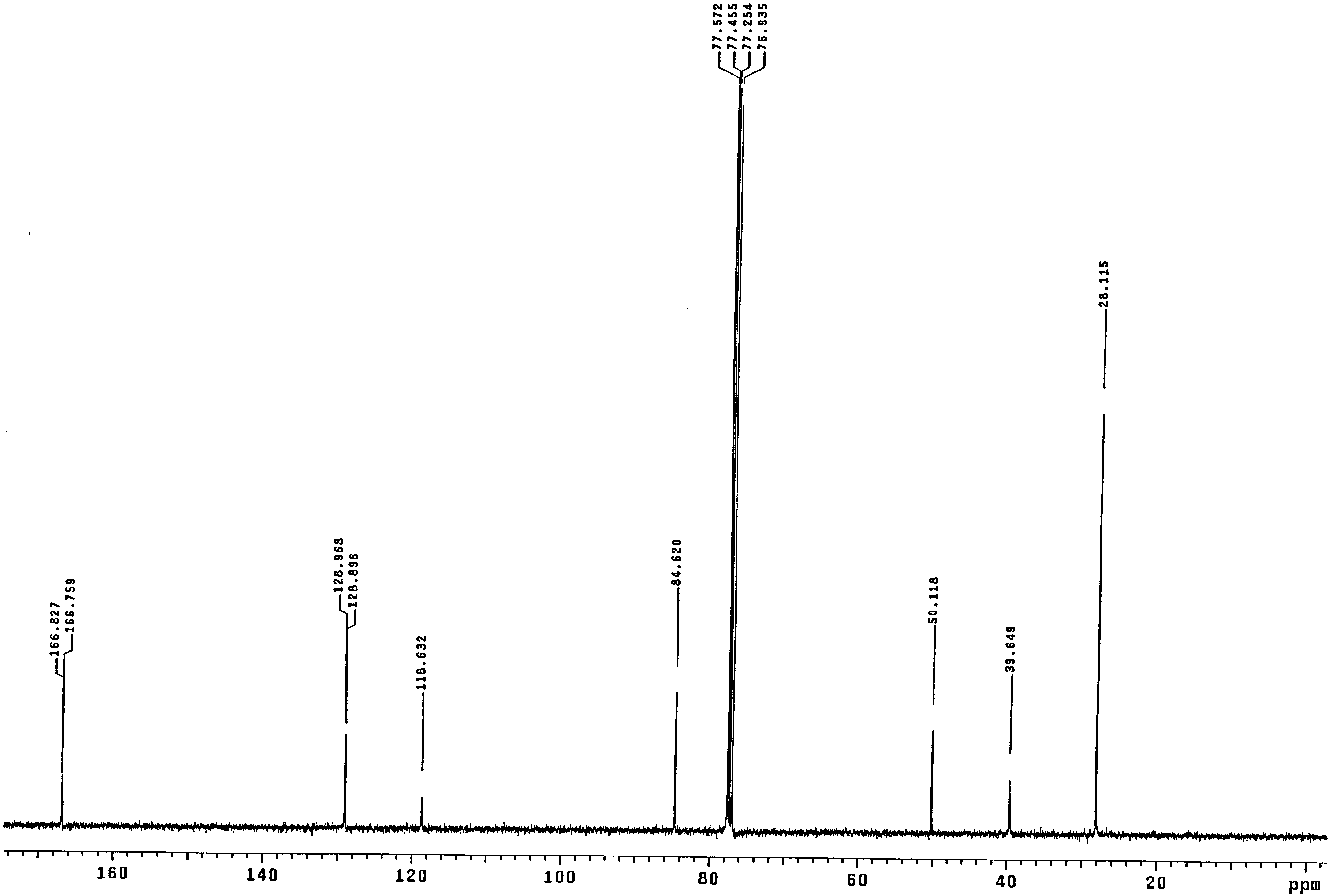
Appendix 4.15 Mass spectrum of 1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane



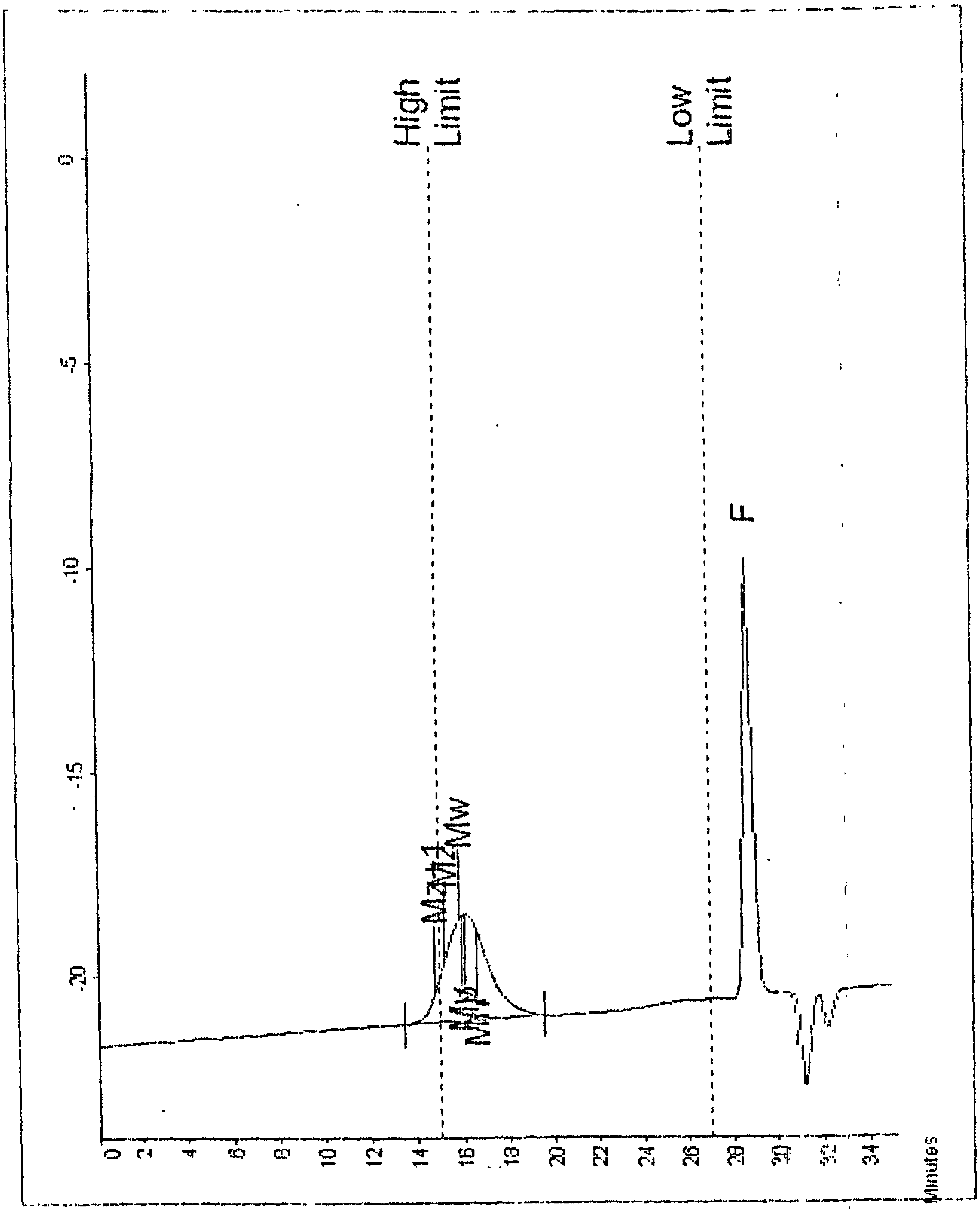
Appendix 4.16 Infra-red spectrum of poly(1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane)



Appendix 4.17 ^{1}H NMR spectrum of poly(1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane)



Appendix 4.18 ^{13}C NMR spectrum of poly(1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane)



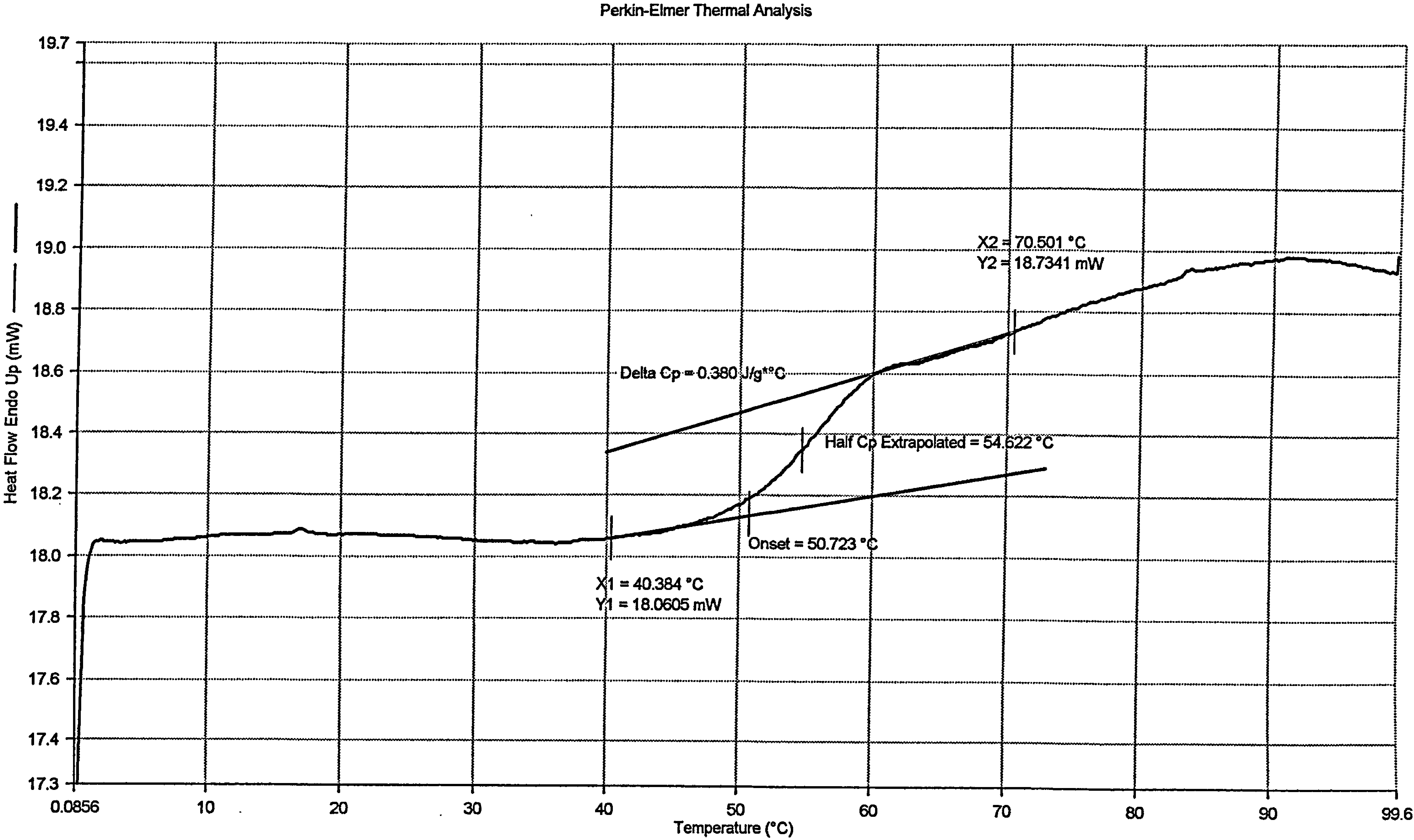
Molecular Weight Averages

Mp =	321625	Mz =	782884
Mn =	201788	Mz+1 =	1307166
Mw =	418690	Mv =	378511
Polydispersity =	2.075	Peak Area =	70567

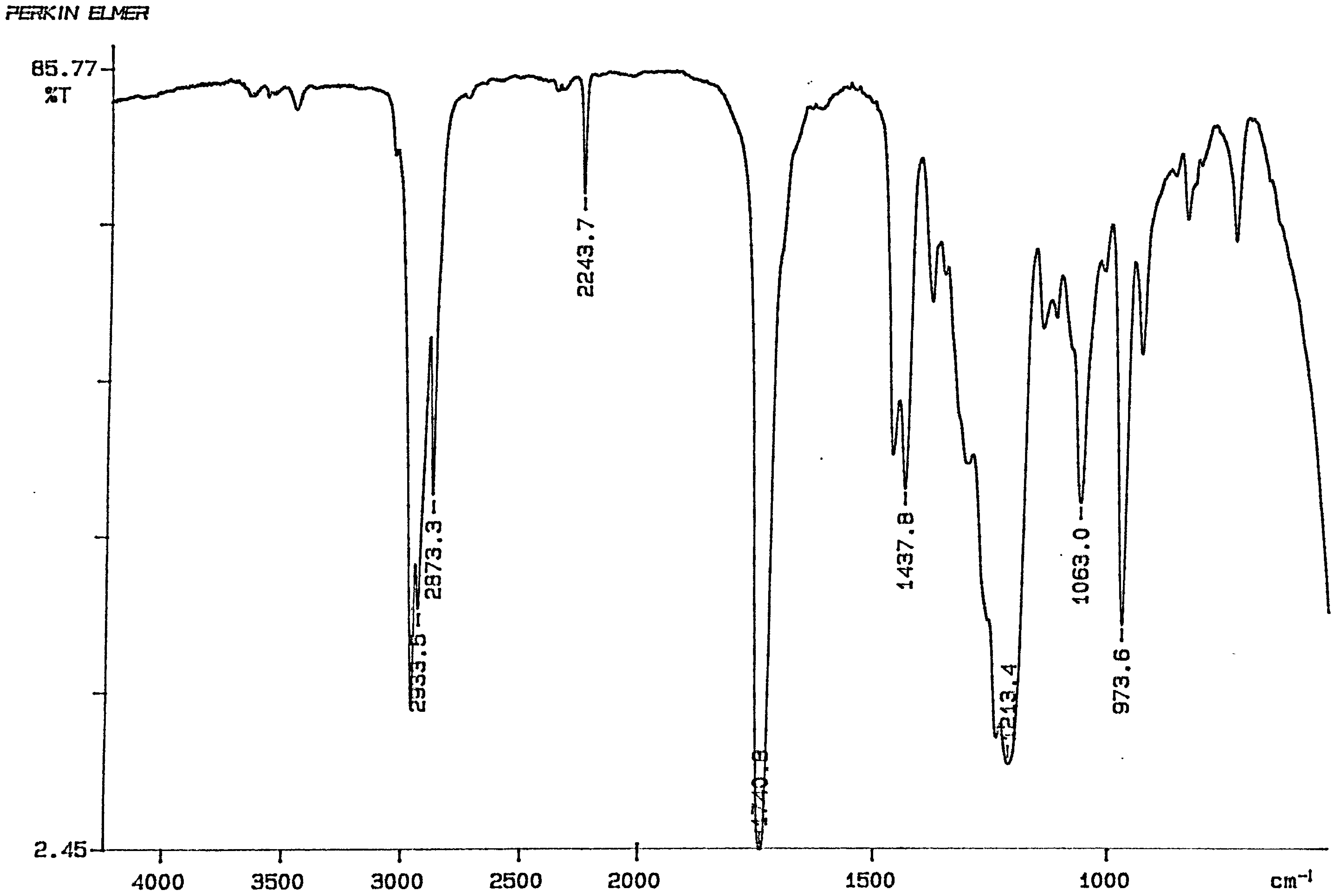
Appendix 4.19 GPC trace of poly(1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane)

Filename: c:\pe\pyris\data\wjf da...\rcex79f.dcd - 3/25/98 1:26:38 PM
Operator ID: tb
Sample ID: rcex79f
Sample Weight: 5.711 mg
Comment: Rachel Cochlin
decomposition according to TGA at T>100-150C

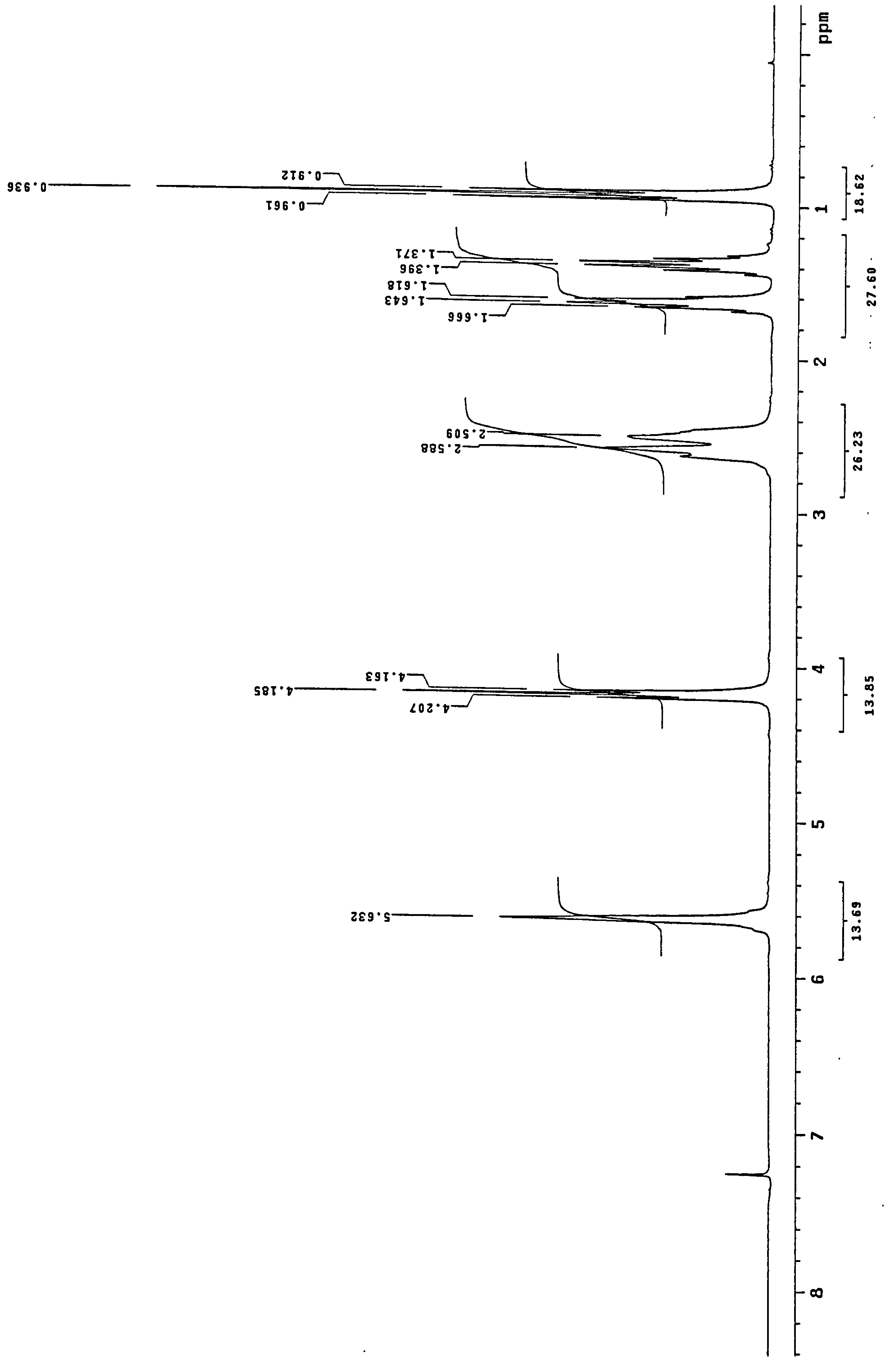
rcex79f: rcex79f
Heat Flow Endo Up (mW) : Step: 4



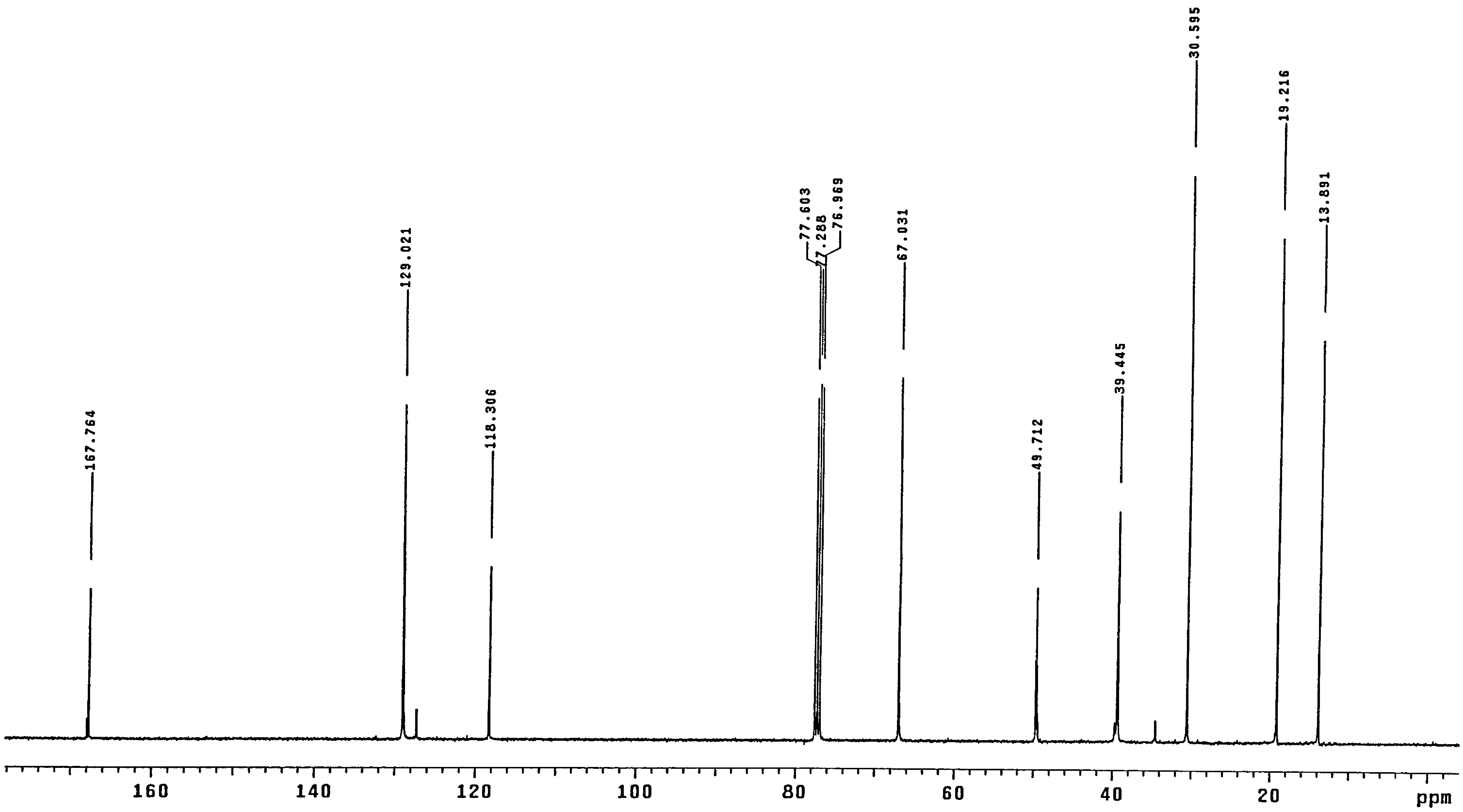
Appendix 4.20 DSC trace of poly(1-cyano-1-*tert*-butoxycarbonyl-2-vinylcyclopropane)



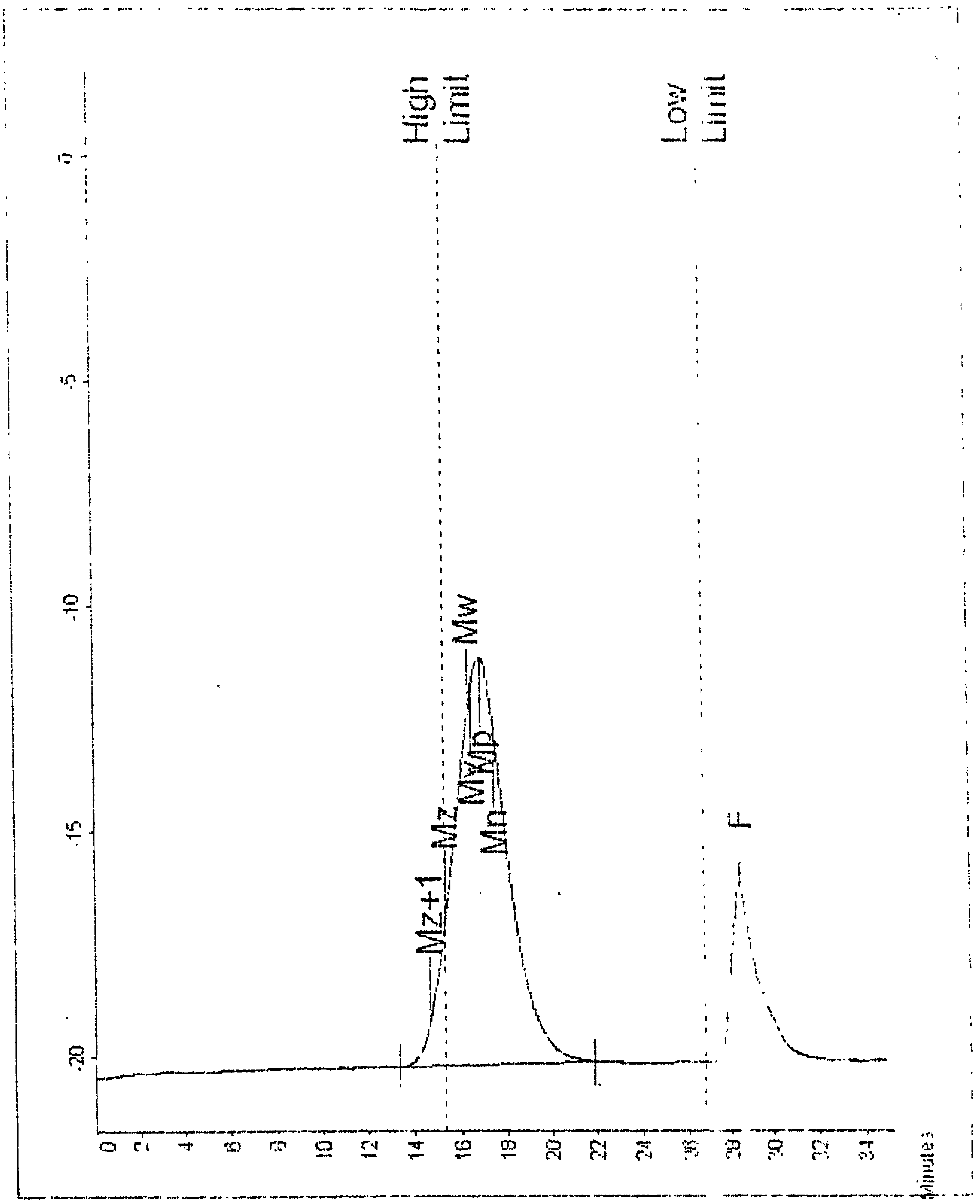
Appendix 4.21 Infra-red spectrum of poly(1-cyano-1-n-butoxycarbonyl-2-vinylcyclopropane)



Appendix 4.22 ^{1}H NMR spectrum of poly(1-cyano-1-n-butoxycarbonyl-2-vinylcyclopropane)



Appendix 4.23 ^{13}C NMR spectrum of poly(1-cyano-1-n-butoxycarbonyl-2-vinylcyclopropane)



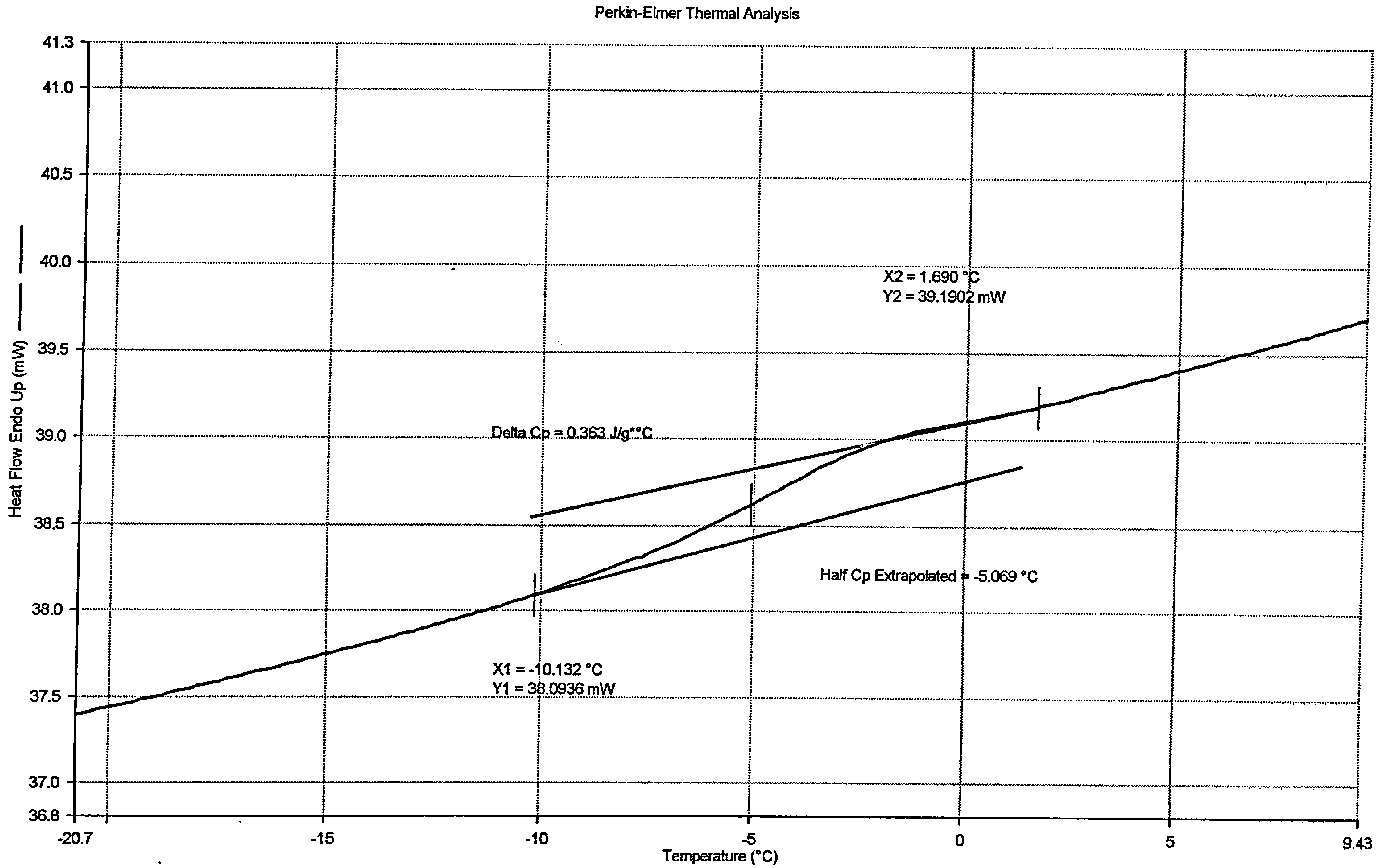
Molecular Weight Averages

Mp =	195874	Mz =	971342
Mn =	109270	Mz+1 =	2164421
Mw =	339804	Mv =	287687
Polydispersity =	3 110	Peak Area =	296017

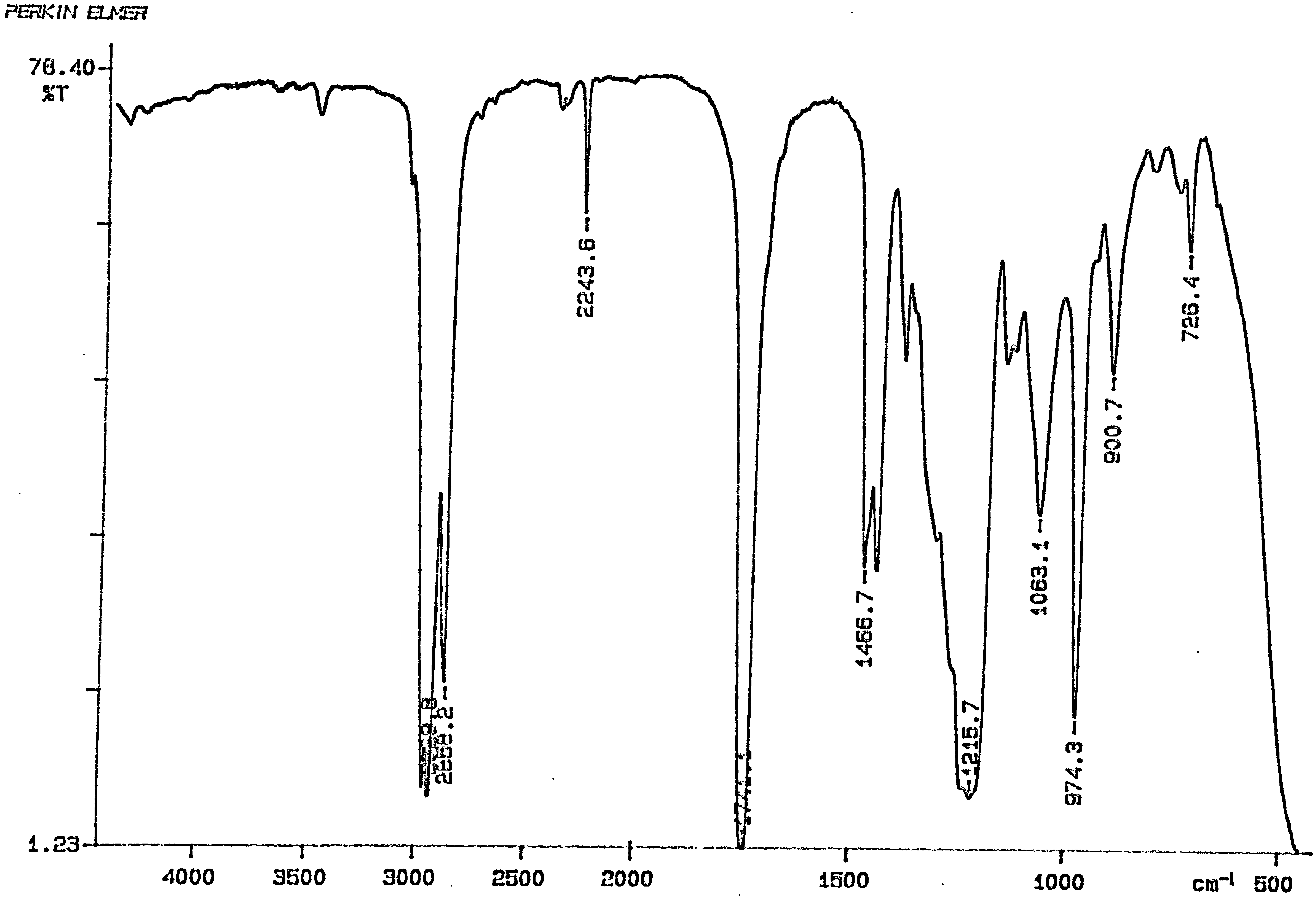
Appendix 4.24 GPC trace of poly(1-cyano-1-n-butoxycarbonyl-2-vinylcyclopropane)

Filename: c:\pe\pyris\data\rwr da...\rcex91f.dcd - 6/10/98 2:57:21 PM
Operator ID: BOZZ
Sample ID: RCEX91~~C~~F
Sample Weight: 6.672 mg
Comment:

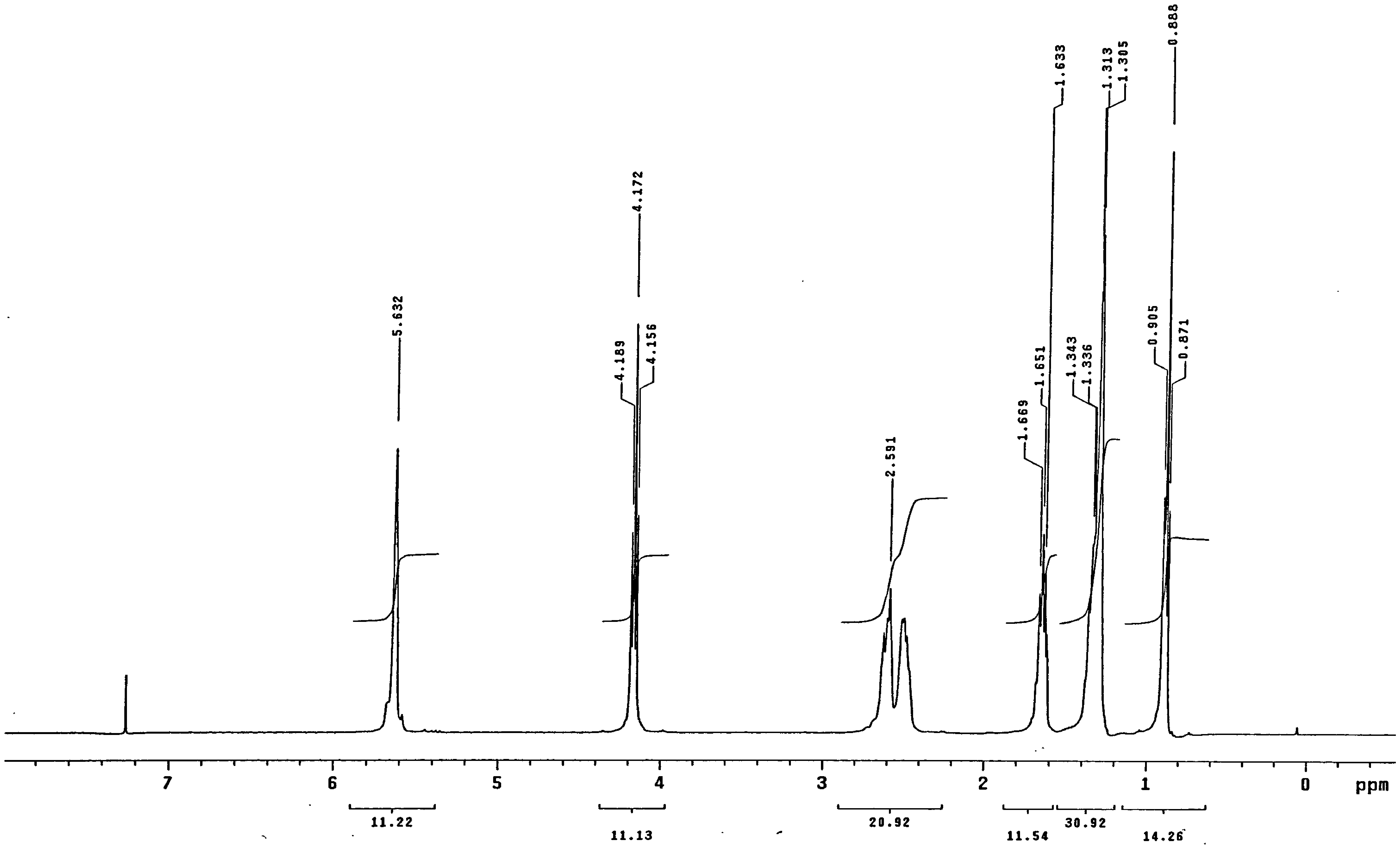
RCEX91C: RCEX91f
Unsubtracted Heat Flow Endo Up (mW) : Step: 1



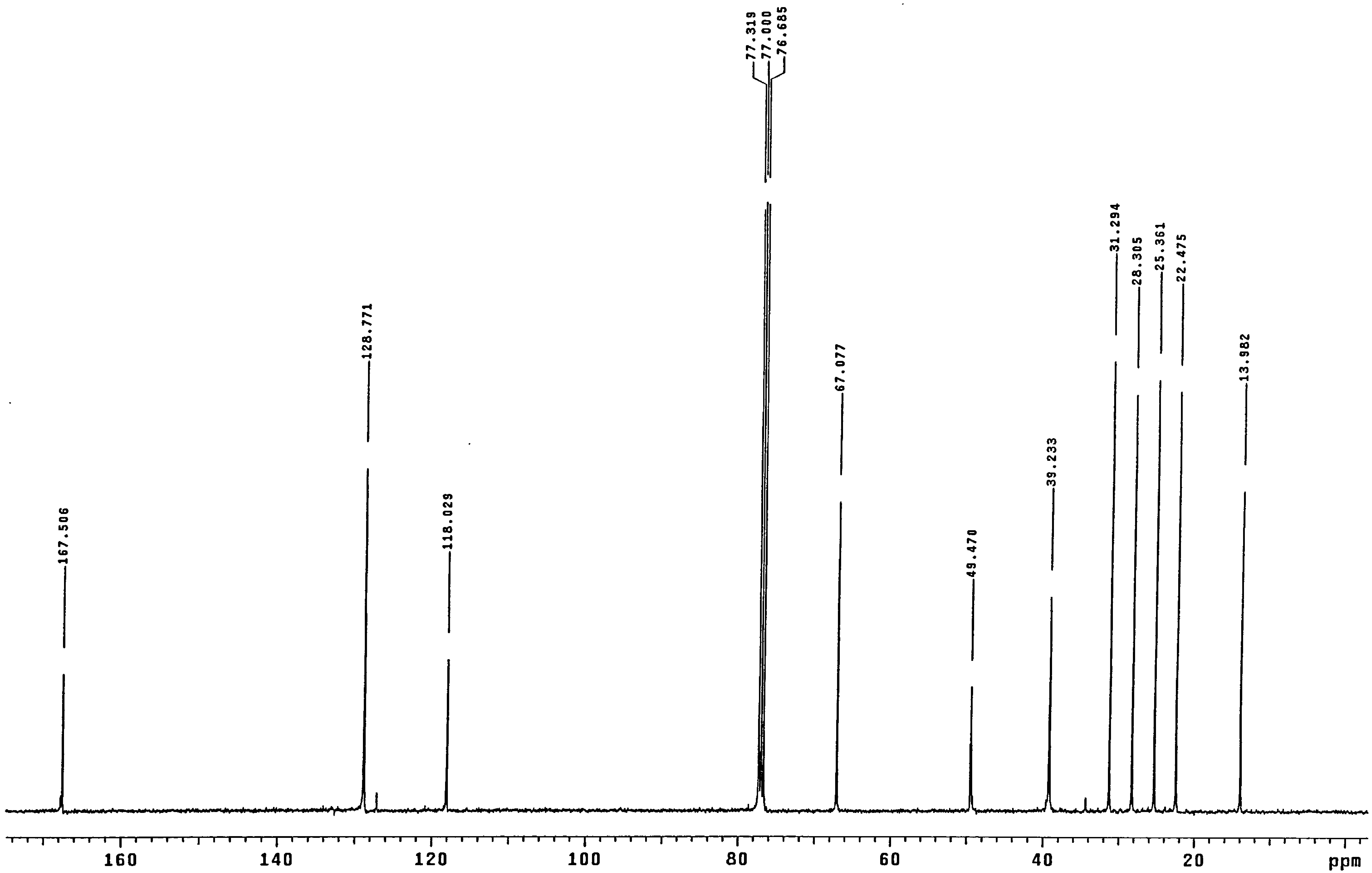
Appendix 4.25 DSC trace of poly(1-cyano-1-n-butoxycarbonyl-2-vinylcyclopropane)



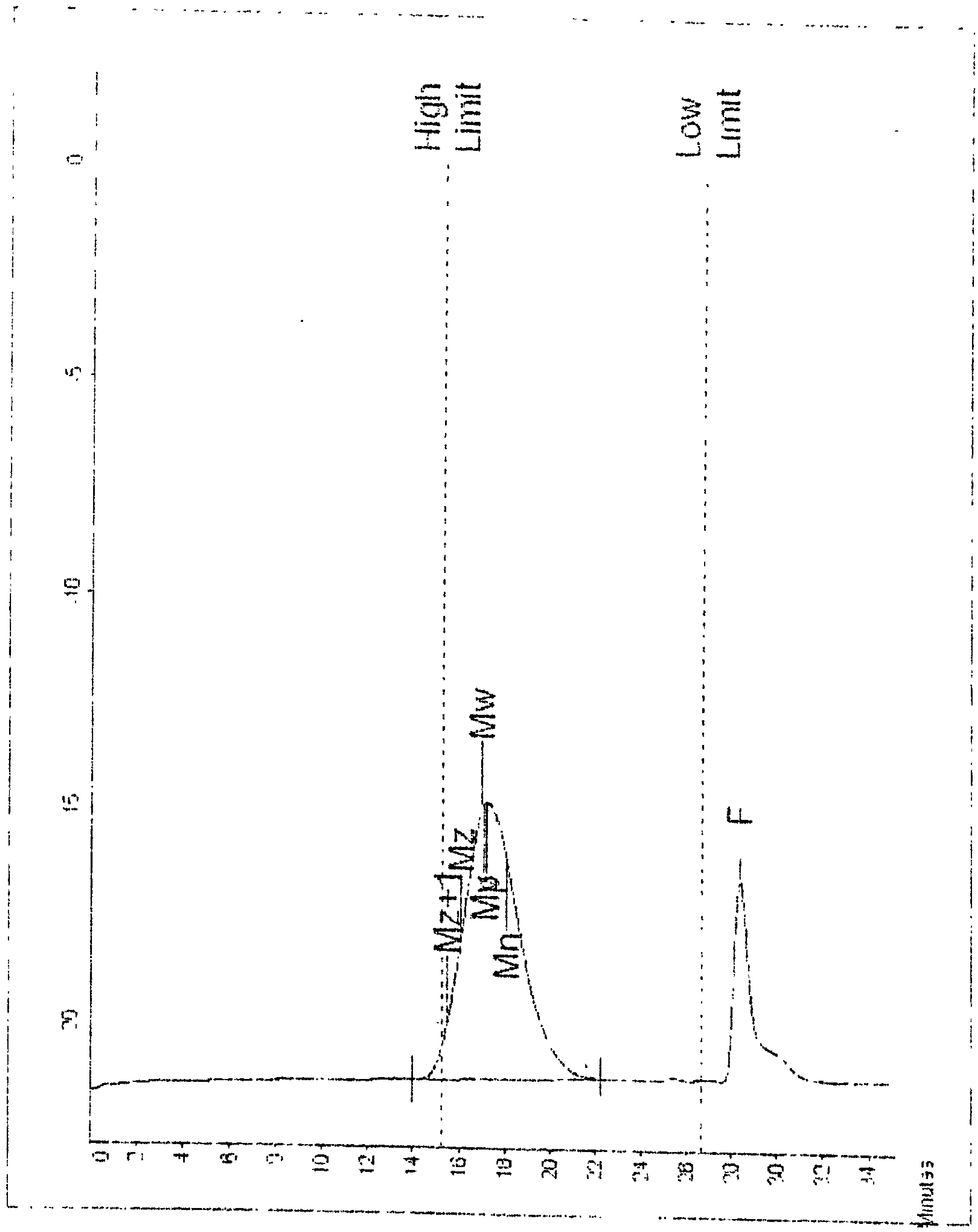
Appendix 4.26 Infra-red spectrum of poly(1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane)



Appendix 4.27 ¹H NMR spectrum of poly(1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane)



Appendix 4.28 ^{13}C NMR spectrum of poly(1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane)



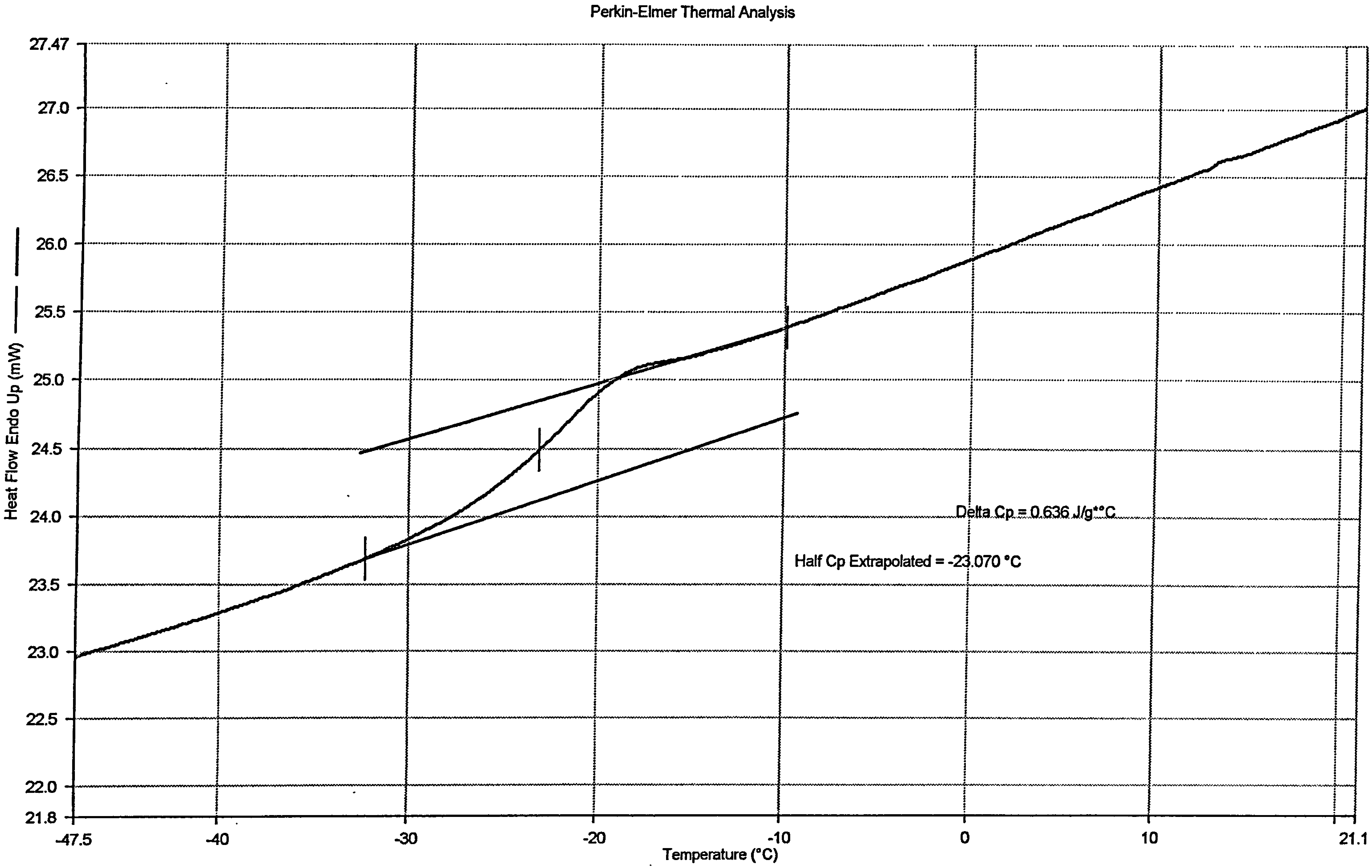
Molecular Weight Averages

Mp =	143120	Mz =	428728
Mn =	64912	Mz+1 =	791361
Mw =	182034	Mv =	157901
Polydispersity =	2.804	Peak Area =	221923

Appendix 4.29 GPC trace of poly(1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane)

Filename: c:\pe\pyris\data\wjf data\rcex95h - 6/2/98 2:12:00 PM
Operator ID: RJP
Sample ID: RCEX95~~G~~H
Sample Weight: 6.642 mg
Comment: No Comment...

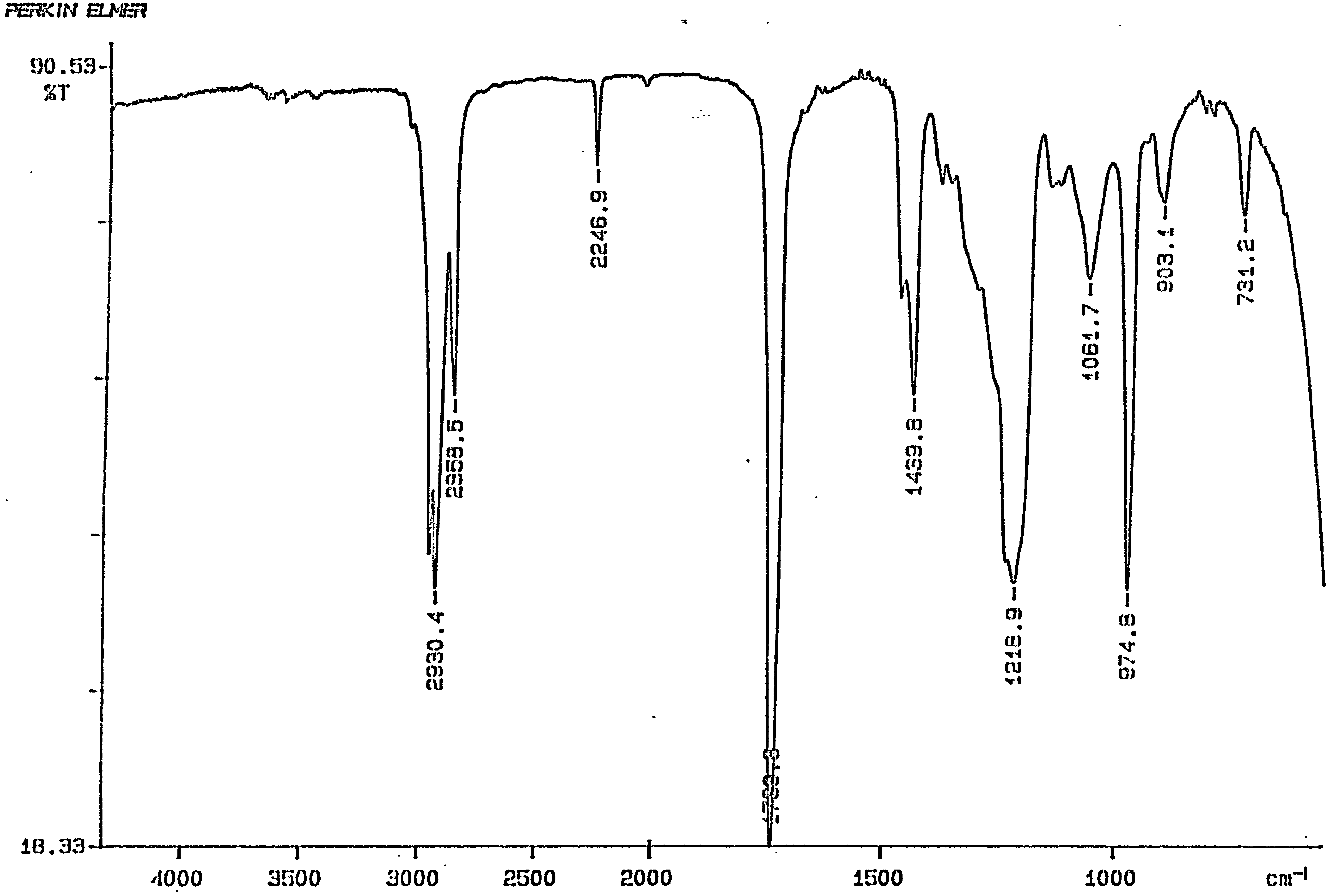
RCEX95G: RCEX95G@980602140230
Unsubtracted Heat Flow Endo Up (mW) : Step: 1



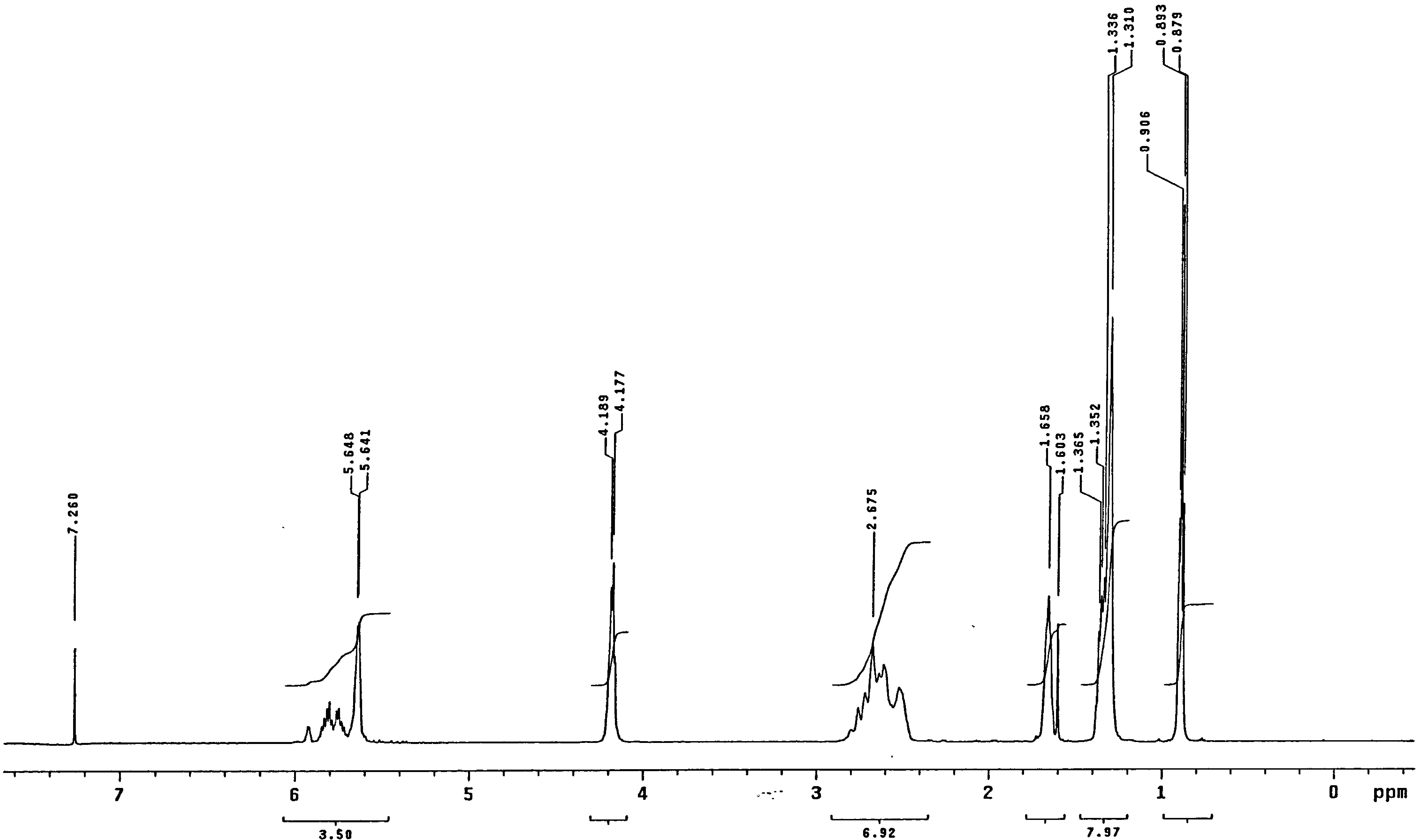
Appendix 4.30 DSC trace of poly(1-cyano-1-hexoxycarbonyl-2-vinylcyclopropane)

Appendix 5

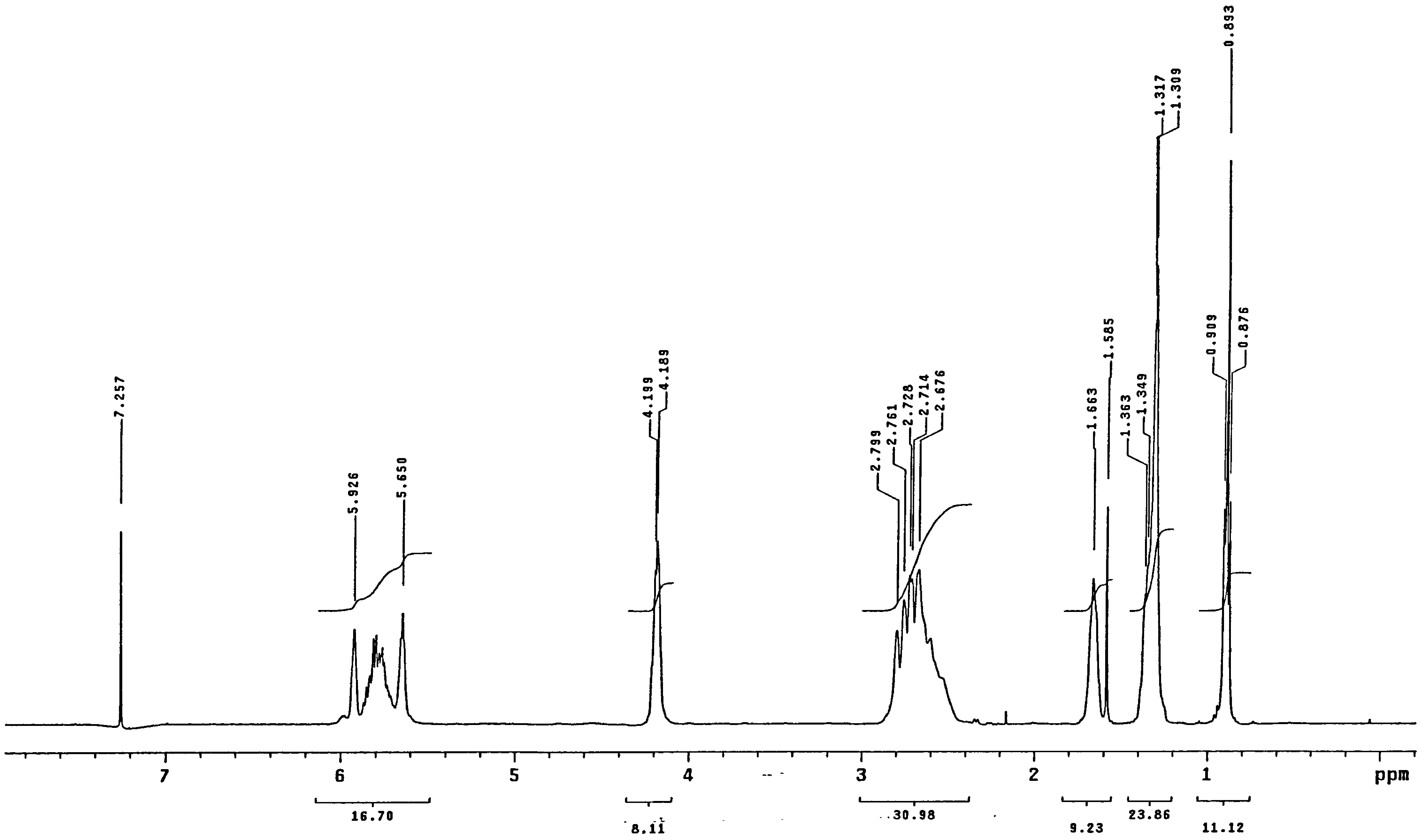
Analytical data for chapter 6



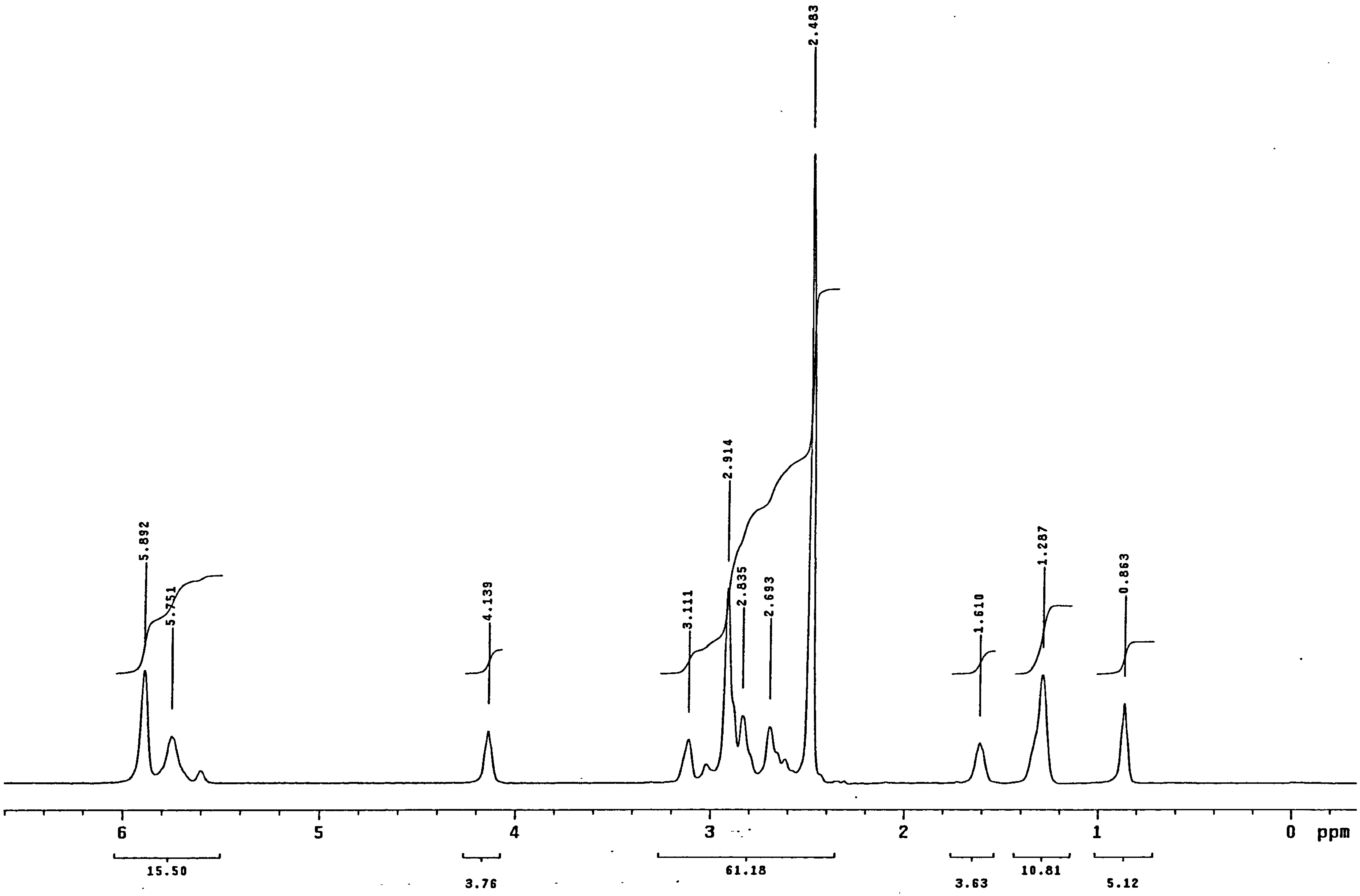
Appendix 5.1 Infra-red spectrum of copolymer A



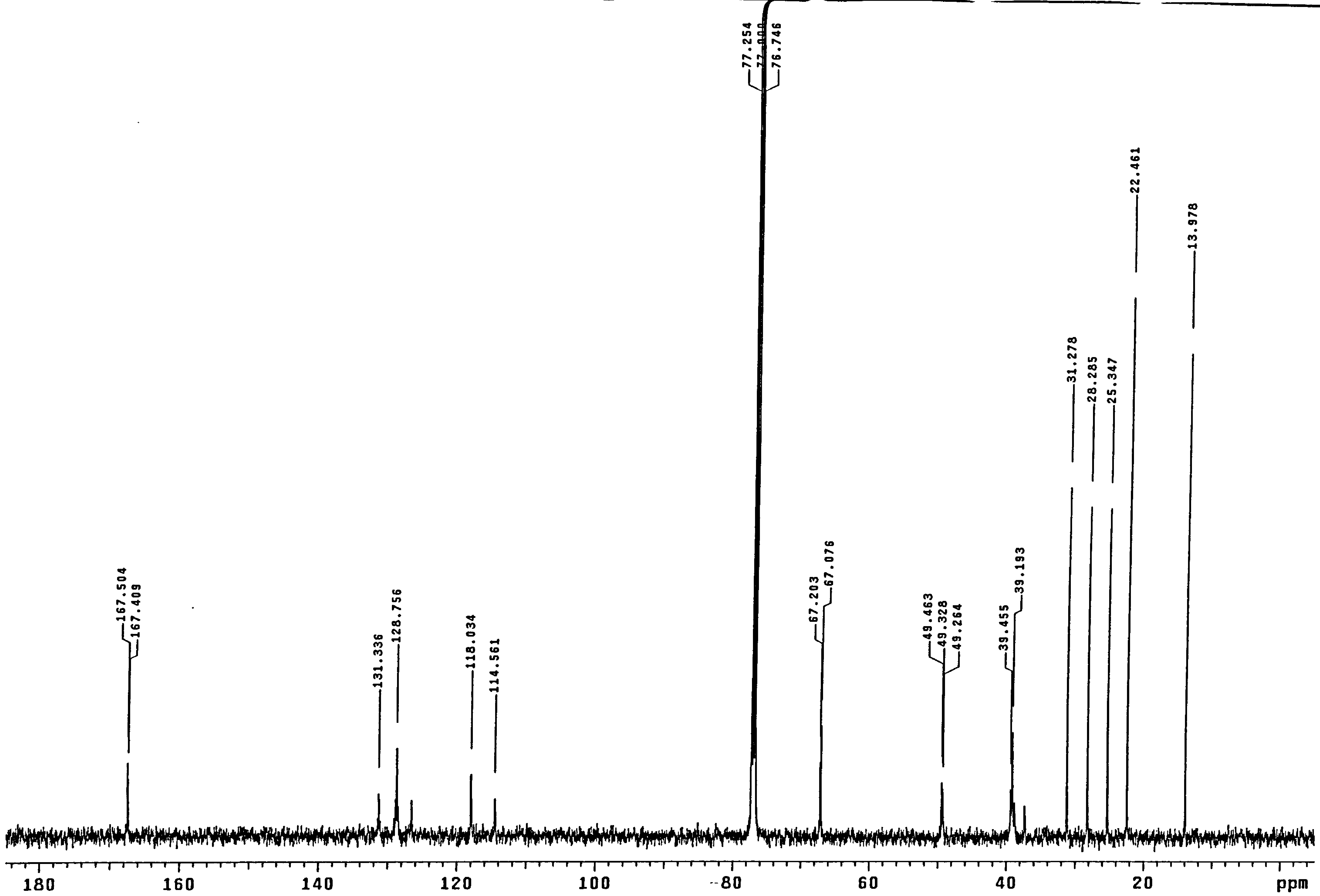
Appendix 5.2 Proton NMR spectrum of copolymer A



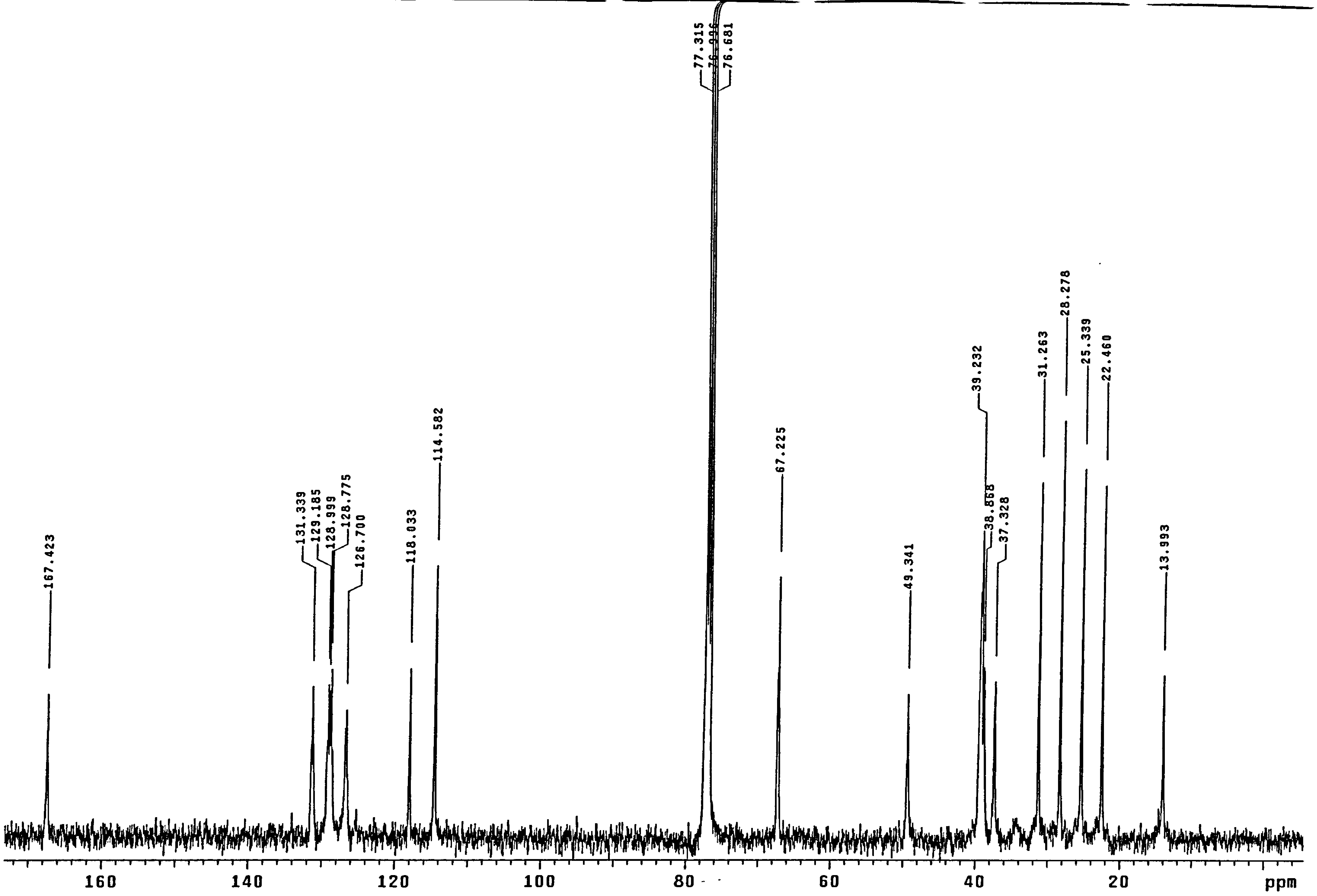
Appendix 5.3 Proton NMR spectrum of copolymer B



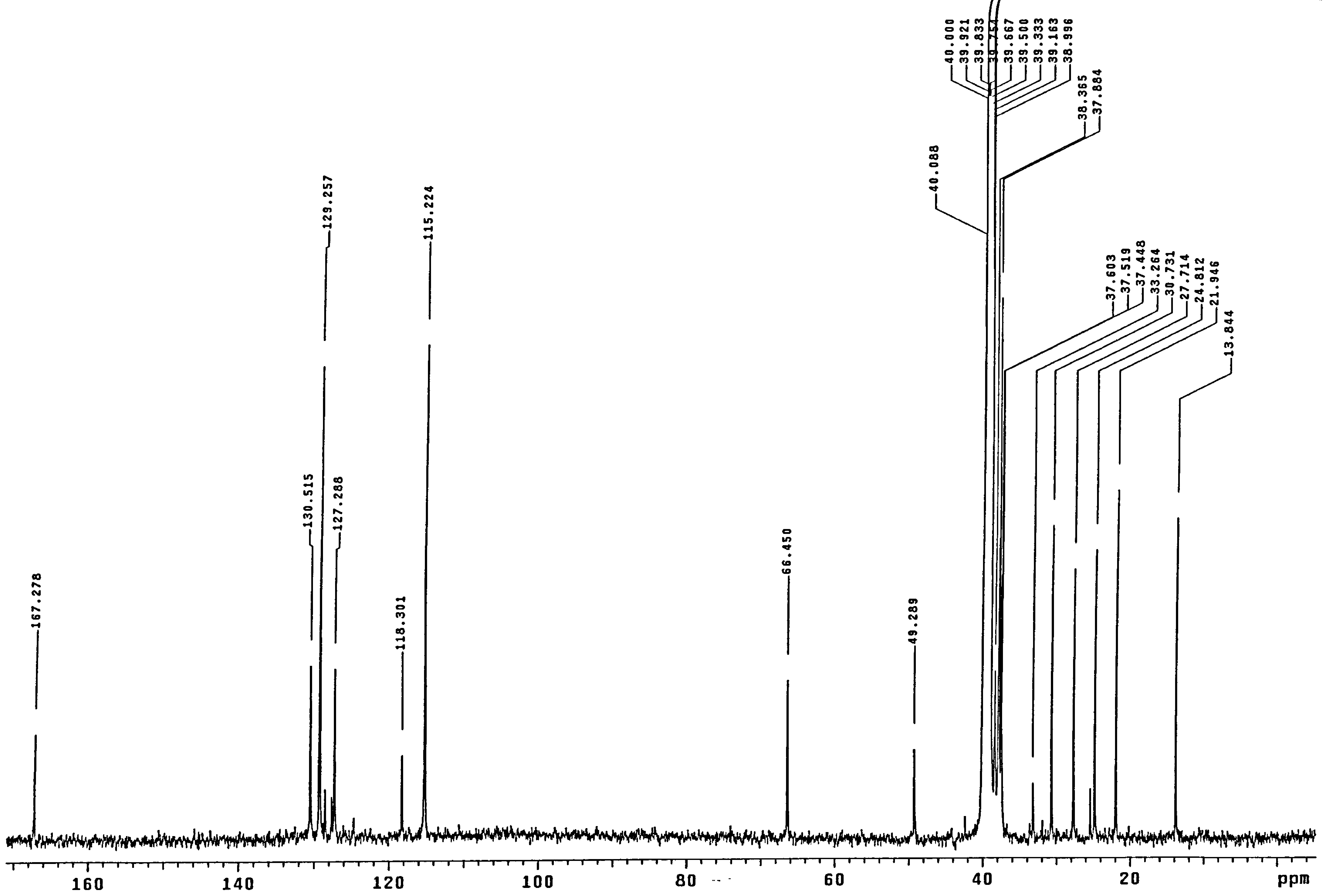
Appendix 5.4 Proton NMR spectrum of copolymer C



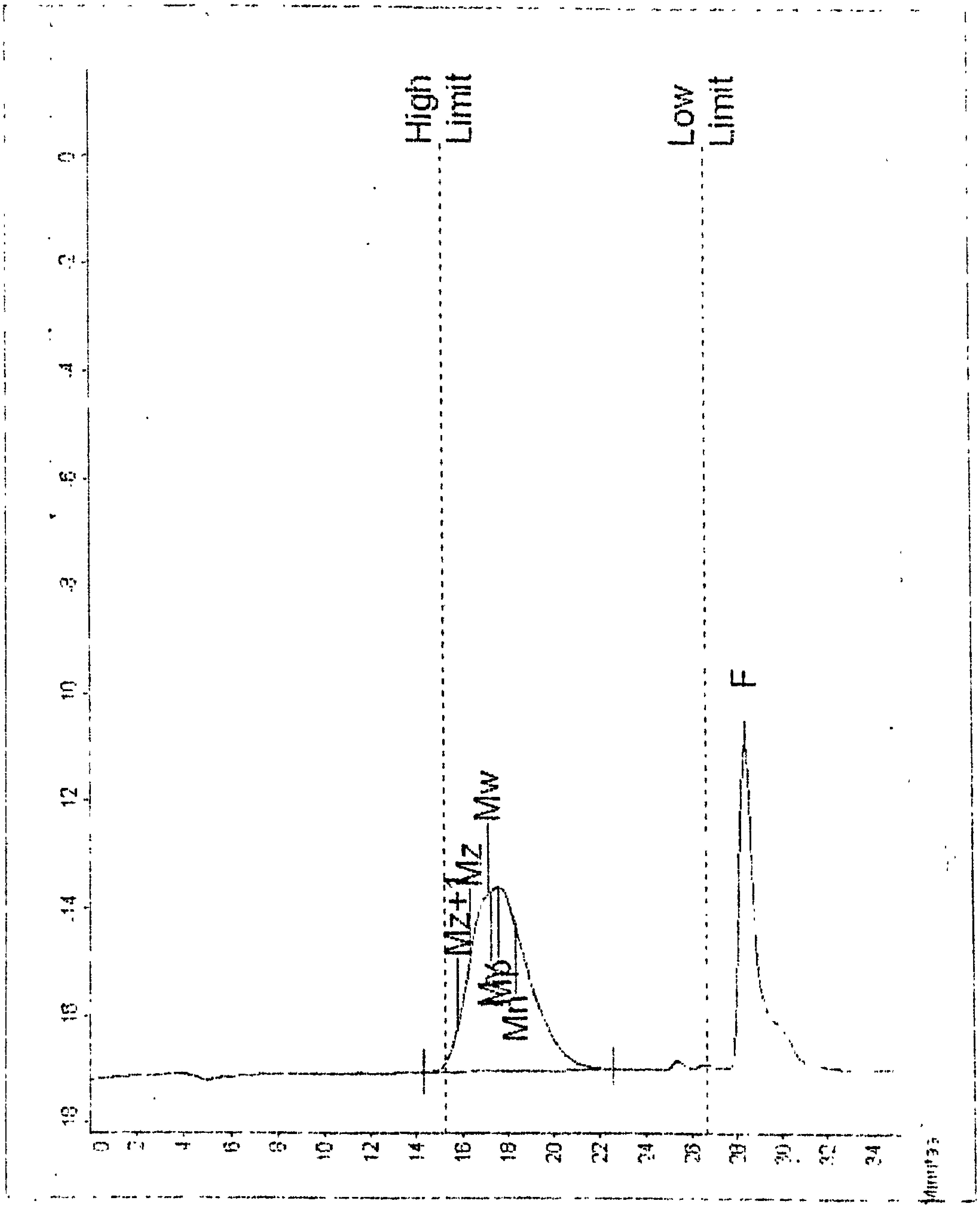
Appendix 5.5 Carbon NMR spectrum of copolymer A



Appendix 5.6 Carbon NMR spectrum of copolymer B



Appendix 5.7 Carbon NMR spectrum of copolymer C



Molecular Weight Averages

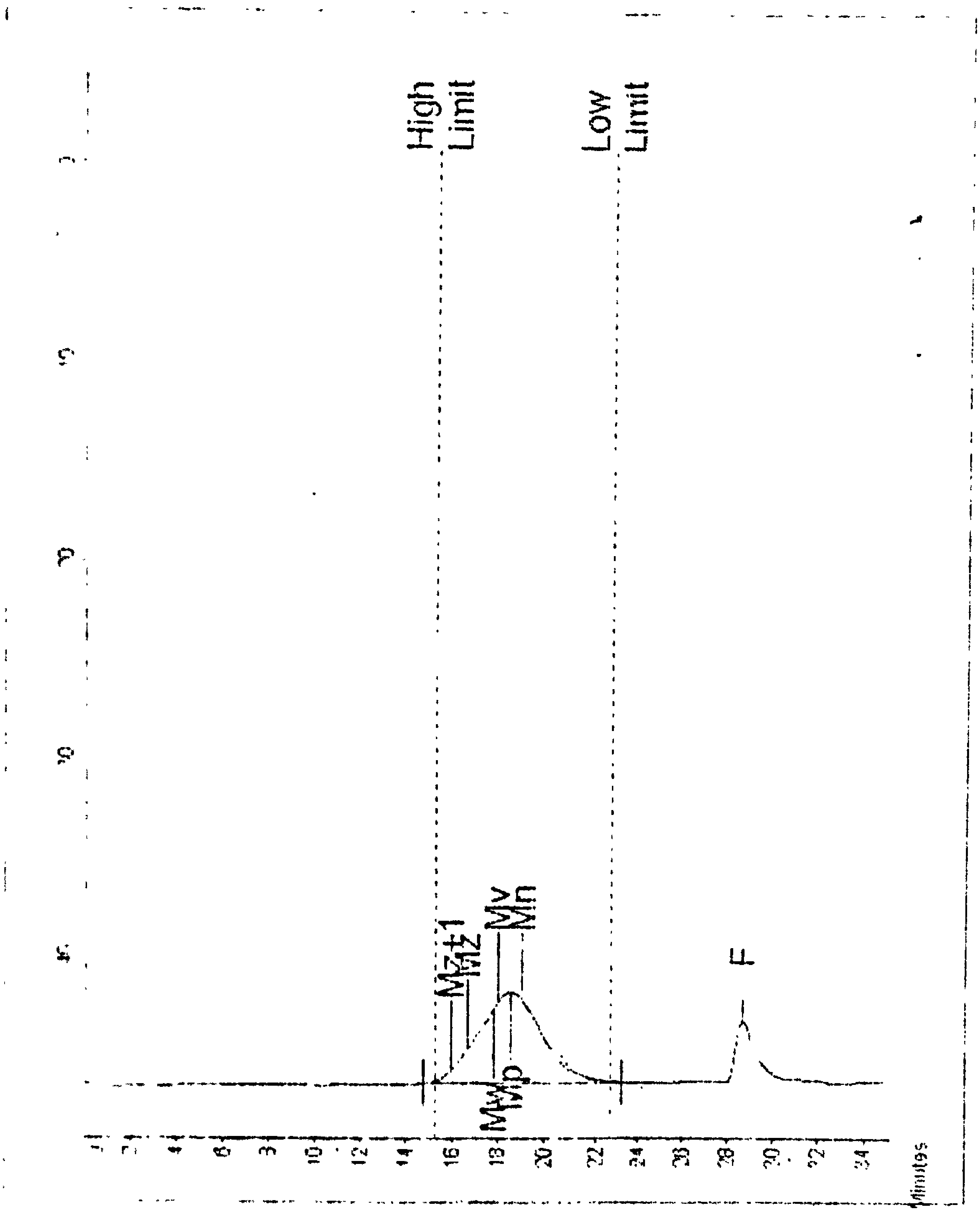
Mp = 99810 Mz = 317765

Mn = 53247 Mz+1 = 558057

Mw = 146608 Mv = 125432

Polydispersity = 2.753 Peak Area = 123738

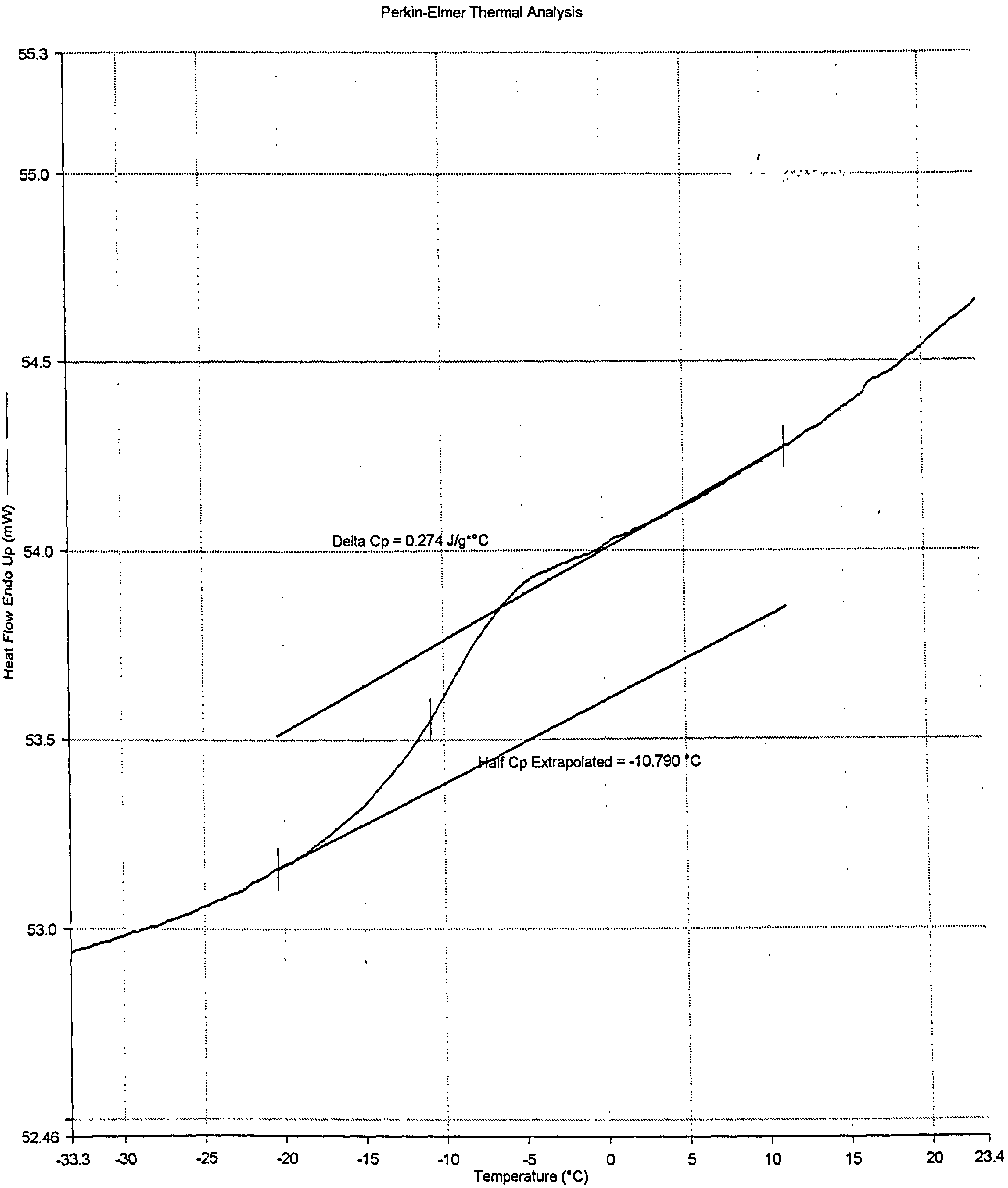
Appendix 5.8 GPC trace of copolymer A



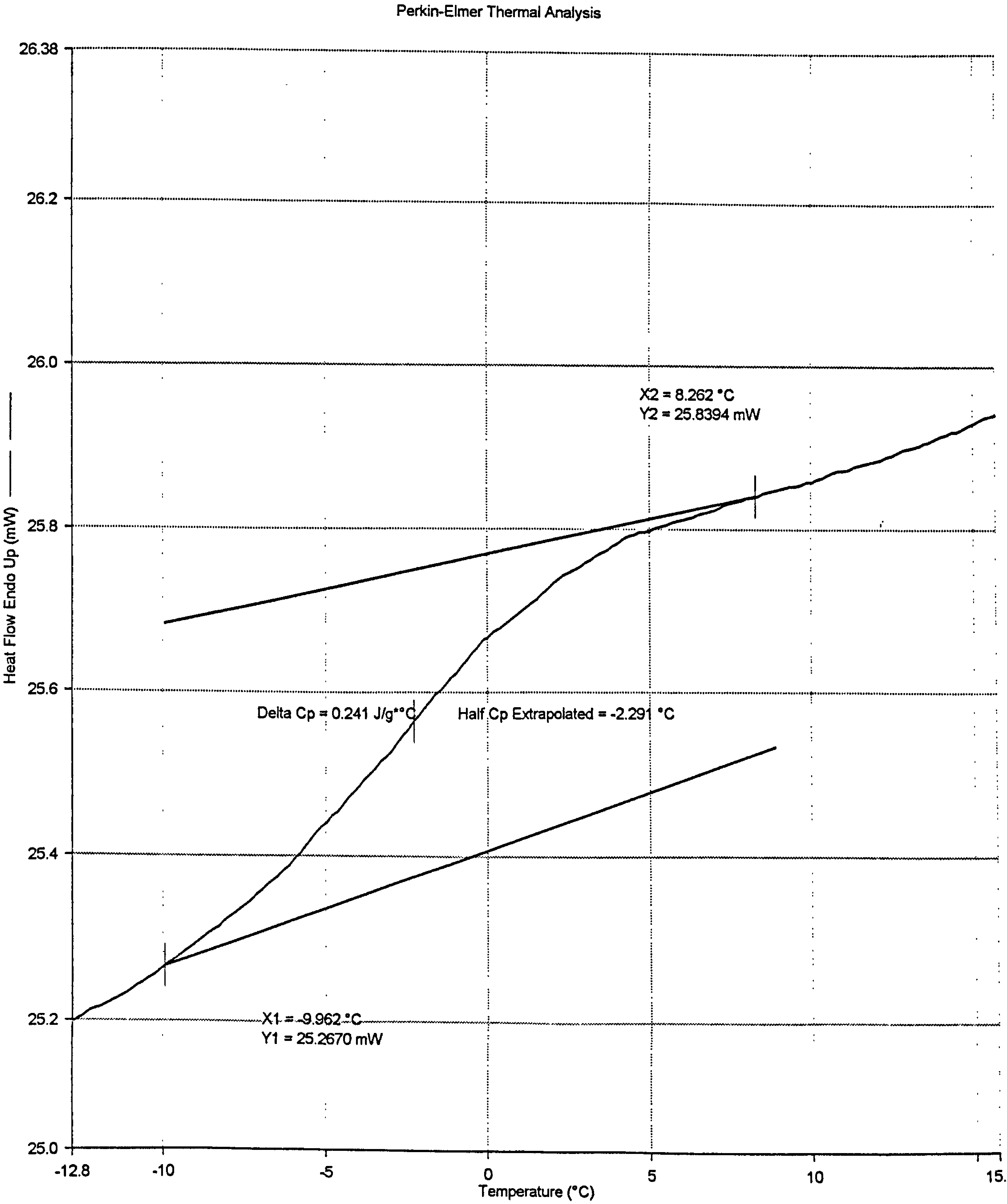
Molecular Weight Averages

Mp =	47378	Mz =	220862
Mn =	31848	Mz+1 =	440803
Mw =	83554	Mv =	71883
Polydispersity =	2.624	Peak Area =	170880

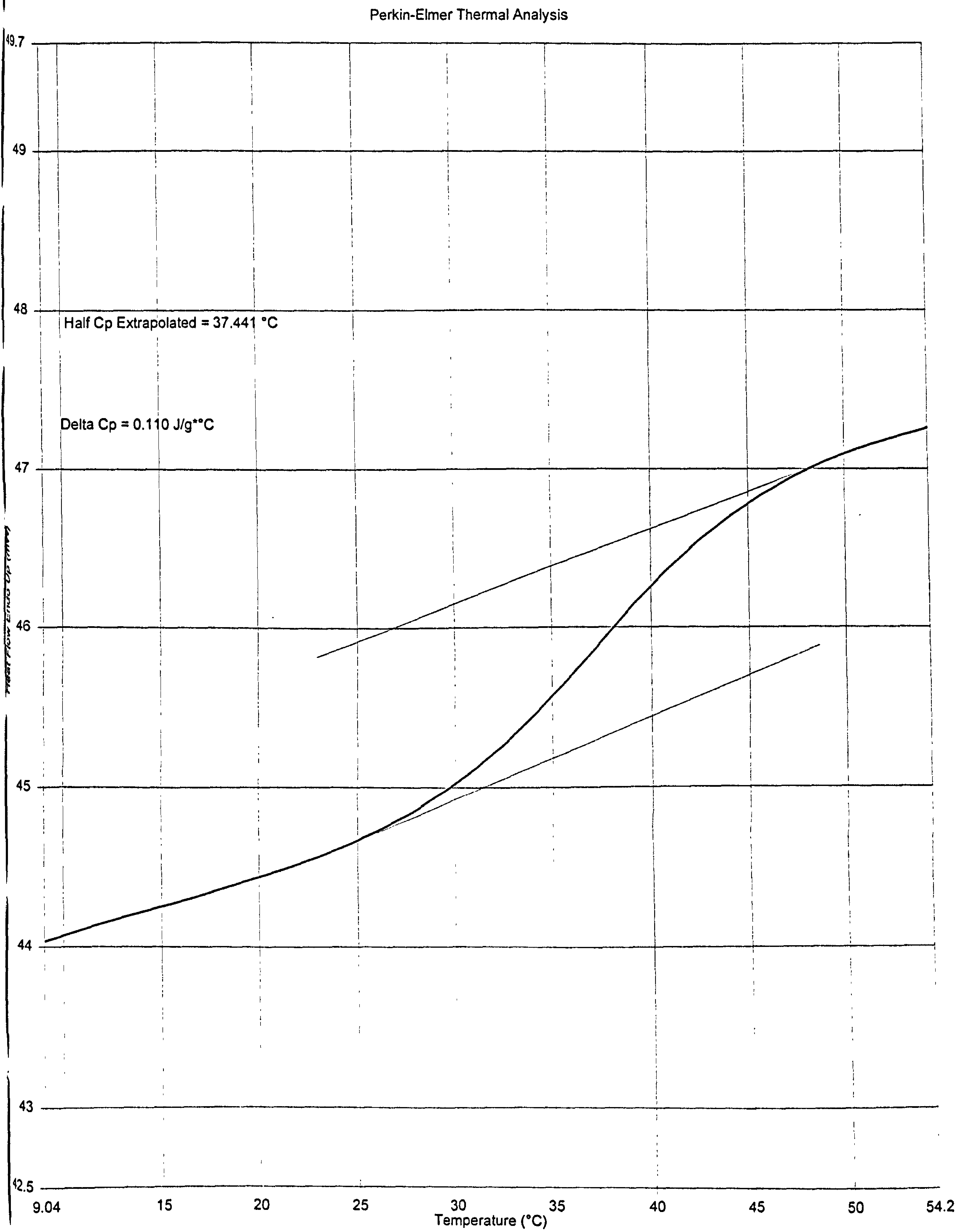
Appendix 5.9 GPC trace of copolymer B

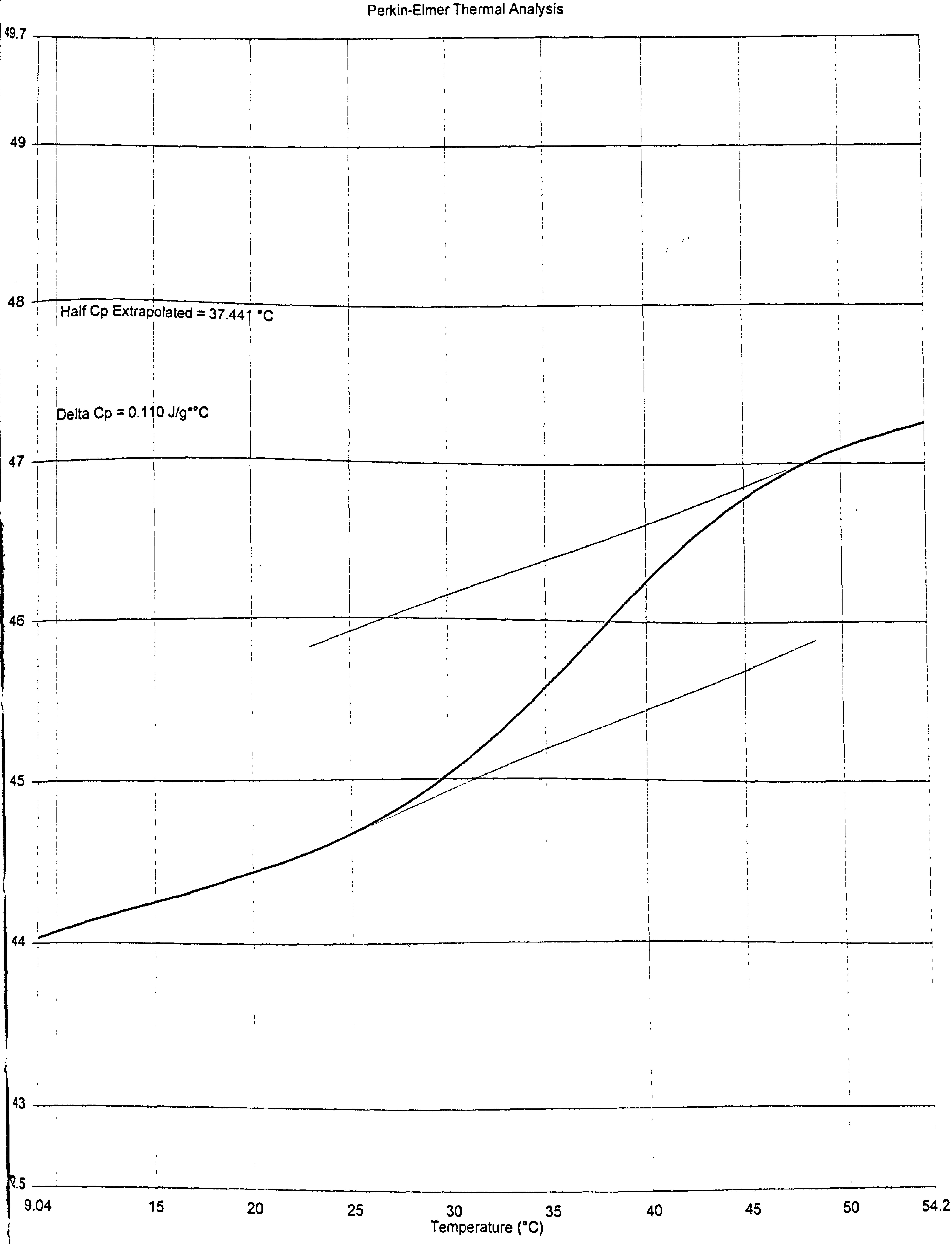


Appendix 5.10 DSC trace for copolymer A



Appendix 5.11 DSC trace for copolymer B

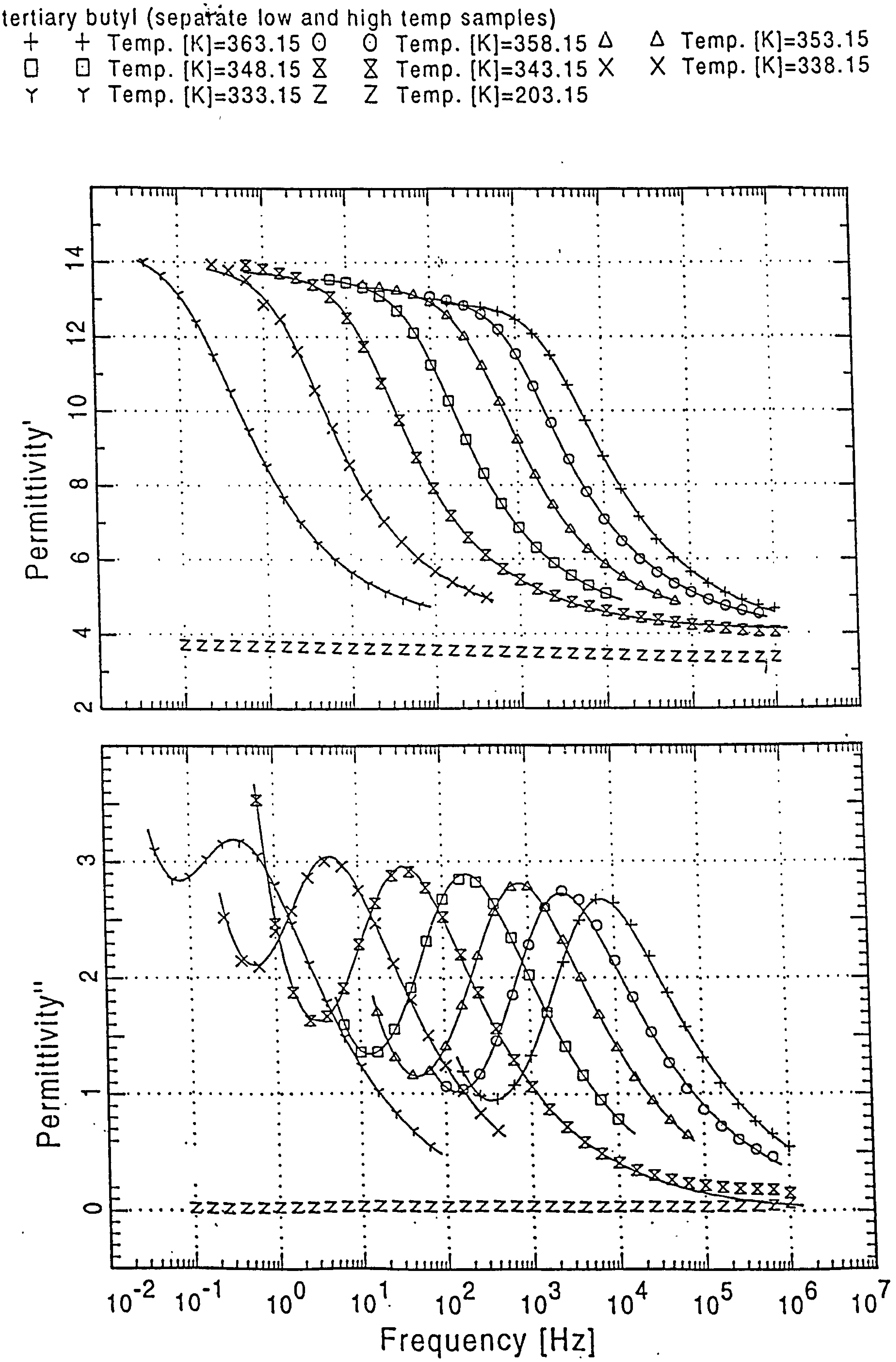

Perkin-Elmer Thermal Analysis
Half Cp Extrapolated = 37.441 °C
Delta Cp = 0.110 J/g*°C
Heat Flow Endo Up (mW)
49.7
49
48
47
46
45
44
43
42.5
9.04
15
20
25
30
35
40
45
50
54.2
Temperature (°C)



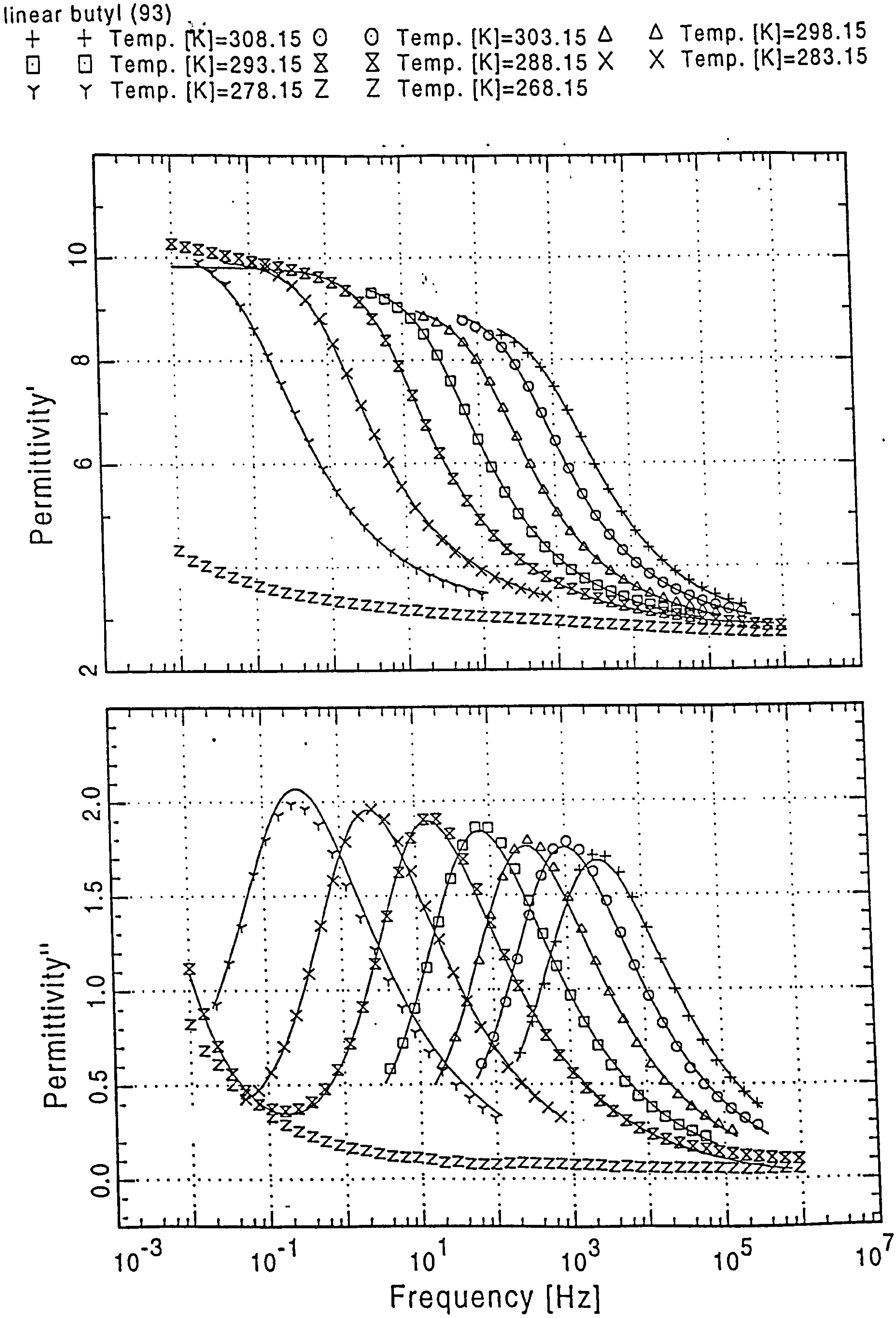
Appendix 5.12 DSC trace for copolymer C

Appendix 6

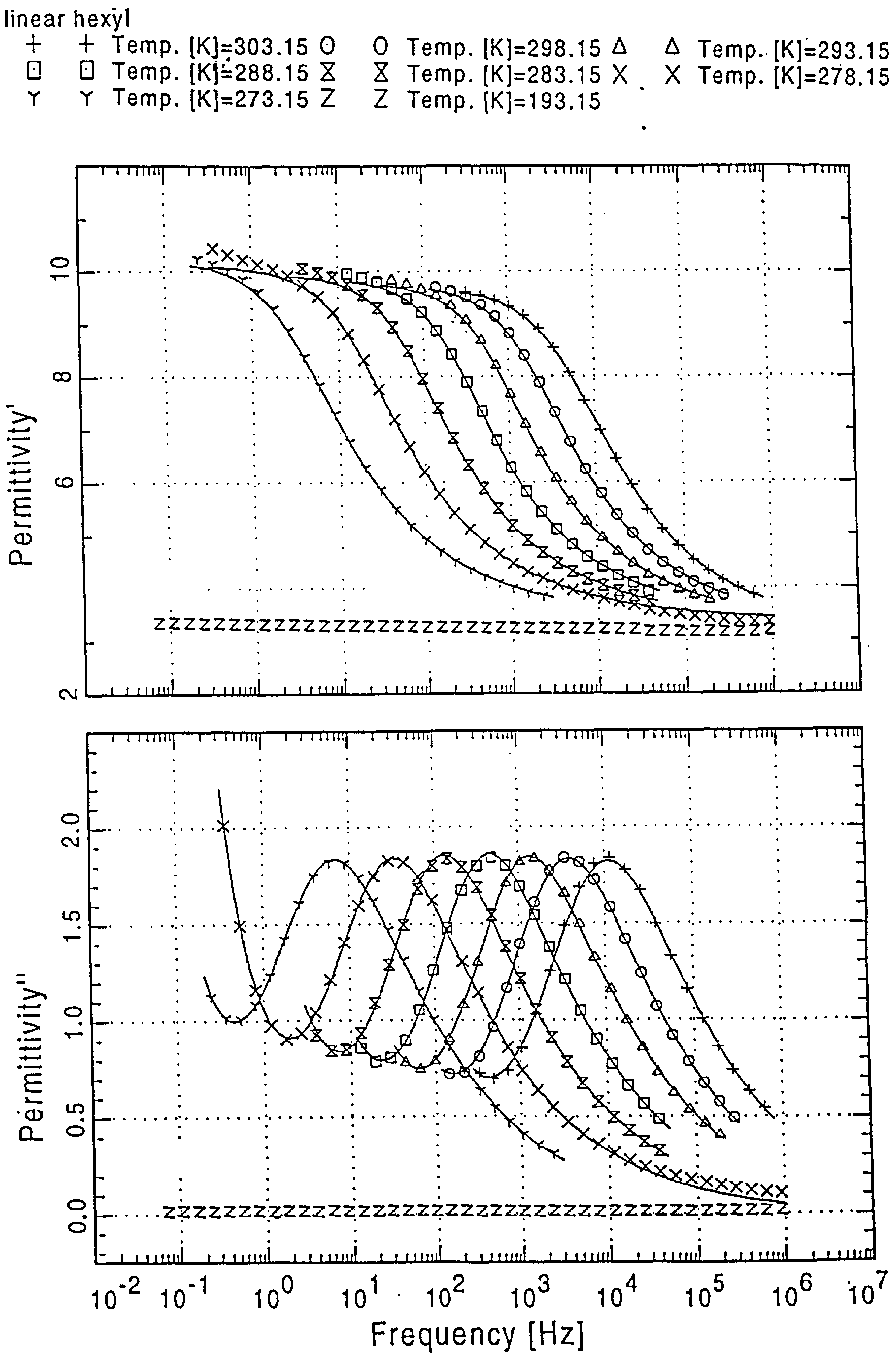
Dielectric measurement data for chapter 7



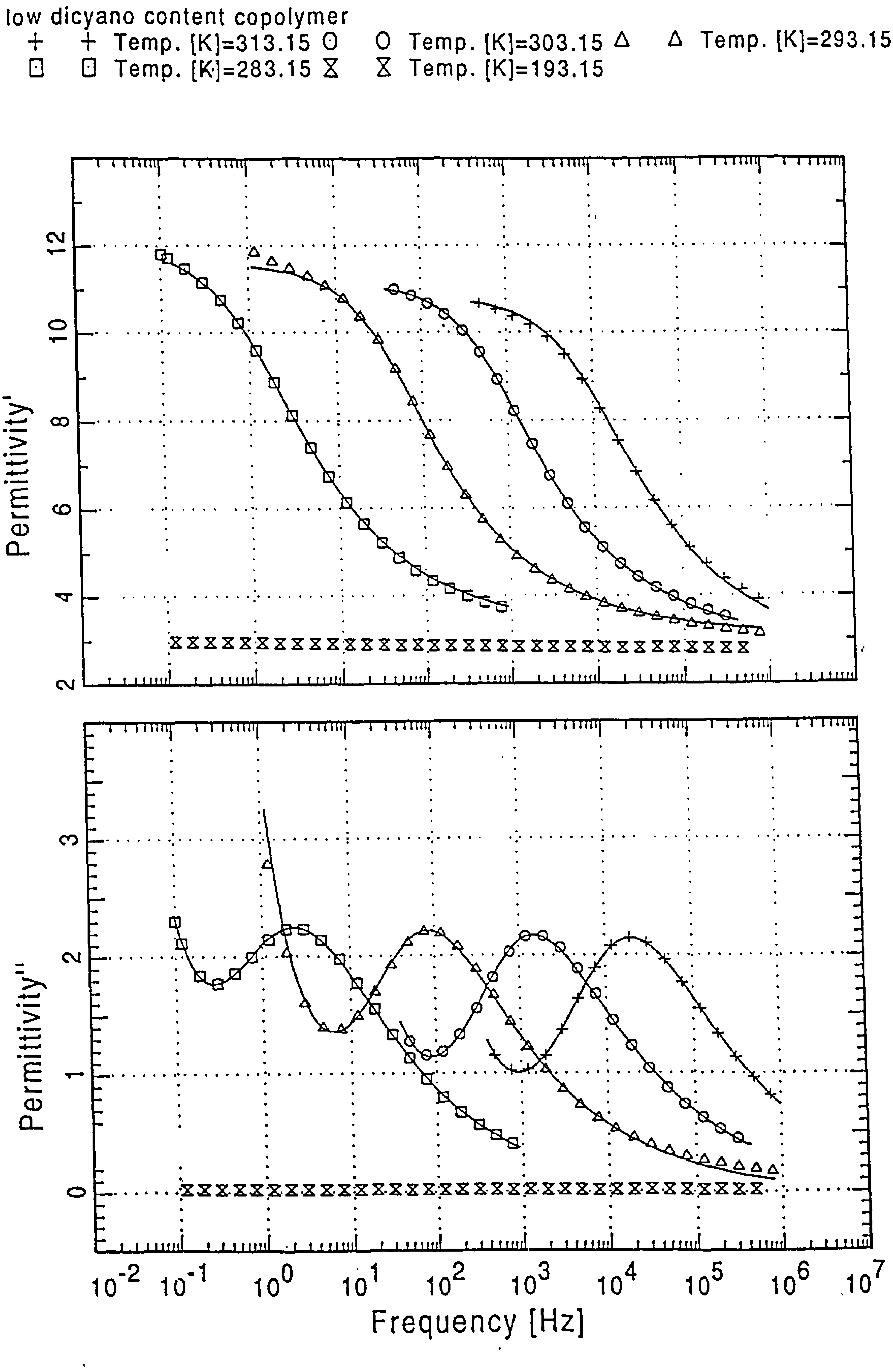
Appendix 6.1 Graphs of real and imaginary permittivity against frequency for the *tert*-butyl ester homopolymer



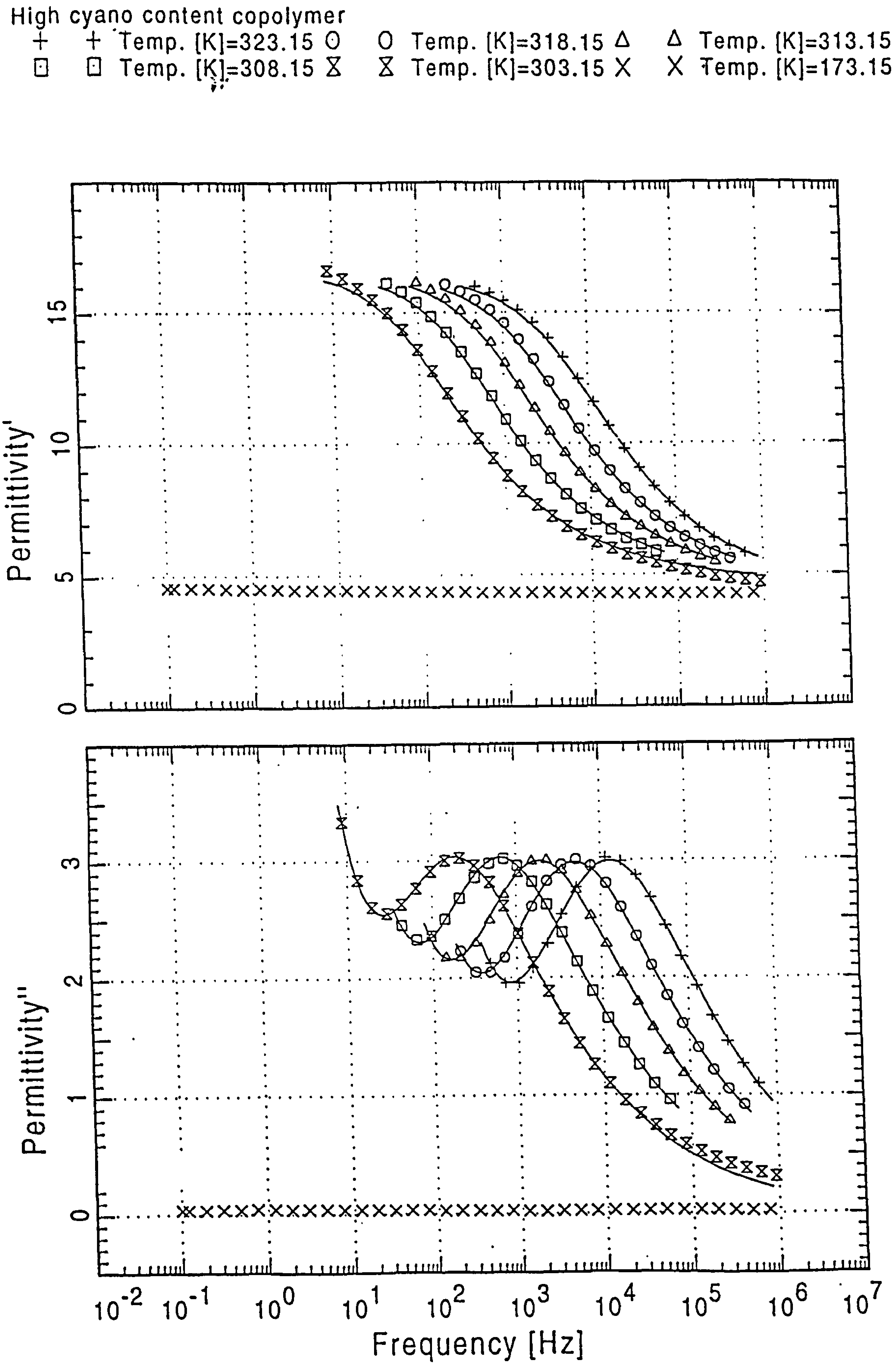
Appendix 6.2 Graphs of real and imaginary permittivity against frequency for the butyl ester homopolymer



Appendix 6.3 Graphs of real and imaginary permittivity against frequency for the hexyl ester homopolymer



Appendix 6.4 Graphs of real and imaginary permittivity against frequency for the 24% dicyano copolymer (A)



Appendix 6.5 Graphs of real and imaginary permittivity against frequency for the 48% dicyano copolymer (**B**)

Appendix 7

Lectures and conferences attended by the author

University of Durham - Board of Studies in Chemistry

Colloquia, Seminars and Lectures given by invited speakers

1995

October 18 Prof. A. Alexakis, Univ. Pierre et Marie Curie, Paris,
Synthetic and Analytical Uses of Chiral Diamines

October 25 Dr.D.Martin Davies, University of Northumbria
Chemical Reactions in Organised Systems

November 1 Prof. W. Motherwell, UCL London
New Reactions for Organic Synthesis

November 8 Dr. D. Craig, Imperial College, London
New Stategies for the Assembly of Heterocyclic Systems

November 17 Prof. David Bergbreiter, Texas A&M, USA
Design of Smart Catalysts, Substrates and Surfaces from Simple Polymers

November 22 Prof. I Soutar, Lancaster University
A Water of Glass? Luminescence Studies of Water-Soluble Polymers.

1996

January 10 Dr Bill Henderson, Waikato University, NZ
Electrospray Mass Spectrometry - a new Sporting Technique

January 17 Prof. J. W. Emsley , Southampton University
Liquid Crystals: More than Meets the Eye

January 24 Dr Alan Armstrong, Nottingham Univesity
Alkene Oxidation and Natural Product Synthesis

January 31 Dr J. Penfold, Rutherford Appleton Laboratory,
Soft Soap and Surfaces

February 14 Dr J. Rohr, Univ Gottingen, FRG
Goals and Aspects of Biosynthetic Studies on Low Molecular Weight Natural Products

February 28 Prof. E. W. Randall, Queen Mary & Westfield College
New Perspectives in NMR Imaging

March 12	RSC Endowed Lecture - Prof. V. Balzani, Univ of Bologna Supramolecular Photochemistry
March 13	Prof. Dave Garner, Manchester University Mushrooming in Chemistry
October 22	Professor B. J. Tighe, Department of Molecular Sciences and Chemistry, University of Aston Making Polymers for Biomedical Application - Can we meet Nature's Challenge? Joint lecture with the Institute of Materials
October 23	Professor H. Ringsdorf (Perkin Centenary Lecture), Johannes Gutenberg-Universitat, Mainz, Germany Function Based on Organisation
November 12	Professor R. J. Young, Manchester Materials Centre, UMIST New Materials - Fact or Fantasy? Joint Lecture with Zeneca & RSC
November 13	Dr G. Resnati, Milan Perfluorinated Oxaziridines: Mild Yet Powerful Oxidising Agents
November 18	Professor G. A. Olah, University of Southern California, USA Crossing Conventional Lines in my Chemistry of the Elements
November 19	Professor R. E. Grigg, University of Leeds Assembly of Complex Molecules by Palladium-Catalysed Queueing Processes
November 27	Dr Richard Templer, Imperial College, London Molecular Tubes and Sponges
December 3	Professor D. Phillips, Imperial College, London A Little Light Relief
December 11	Dr Chris Richards, Cardiff University Sterochemical Games with Metallocenes

1997

January 15	Dr V. K. Aggarwal, University of Sheffield Sulfur Mediated Asymmetric Synthesis
January 21	Mr D. Rudge, Zeneca Pharmaceuticals High Speed Automation of Chemical Reactions

January 22	Dr Neil Cooley, BP Chemicals, Sunbury Synthesis and Properties of Alternating Polyketones
January 29	Dr Julian Clarke, UMIST What can we learn about Polymers and Biopolymers from Computer-generated Nanosecond Movie-clips?
February 4	Dr A. J. Banister, University of Durham From Runways to Non-metallic Metals - A New Chemistry Based on Sulphur
February 5	Dr A. Haynes, University of Sheffield Mechanism in Homogeneous Catalytic Carbonylation
February 12	Dr Geert-Jan Boons, University of Birmingham New Developments in Carbohydrate Chemistry
February 18	Professor Sir James Black, Foundation/King's College London My Dialogues with Medicinal Chemists
February 19	Professor Brian Hayden, University of Southampton The Dynamics of Dissociation at Surfaces and Fuel Cell Catalysts
February 26	Dr Tony Ryan, UMIST Making Hairpins from Rings and Chains
March 4	Professor C. W. Rees, Imperial College Some Very Heterocyclic Chemistry
October 15	Dr. R. Mark Ormerod, Department of Chemistry, Keele University Studying Catalysts in Action
October 21	Prof. A. F. Johnson, IRC, Leeds Reactive Processing of Polymers: Science and Technology
October 23	Prof. M.R. Bryce, University of Durham, Inaugural Lecture New Tetrathiafulvalene Derivatives in Molecular, Supramolecular and Macromolecular Chemistry: Controlling the Electronic Properties of Organic Solids
October 28	Prof. A P de Silva, The Queen's University, Belfast Luminescent Signalling Systems
November 5	Dr Mimi Hii, Oxford University Studies of the Heck reaction
November 11	Prof. V Gibson, Imperial College, London Metallocene Polymerisation

November 20	Dr Leone Spiccia, Monash University, Melbourne, Australia Polynuclear Metal Complexes
November 26	Prof. R.W. Richards, University of Durham, Inaugural Lecture A Random Walk in Polymer Science
December 2	Dr C.J. Ludman, University of Durham Explosions
December 3	Prof. A.P. Davis, Department. of Chemistry, Trinity College Dublin. Steroid-based Frameworks for Supramolecular Chemistry
December 10	Prof. Mike Page, Department of Chemistry, University of Huddersfield The Mechanism and Inhibition of Beta-Lactamases

1998

January 14	Prof. David Andrews, University of East Anglia Energy Transfer and Optical Harmonics in Molecular Systems
January 27	Prof. Richard Jordan, Dept. of Chemistry, Univ. of Iowa, USA. Cationic Transition Metal and Main Group Metal Alkyl Complexes in Olefin Polymerisation
January 28	Dr Steve Rannard, Courtaulds Coatings (Coventry) The Synthesis of Dendrimers using Highly Selective Chemical Reactions
February 3	Dr J. Beacham, ICI Technology The Chemical Industry in the 21st Century
February 4	Prof. P. Fowler, Department of Chemistry, Exeter University Classical and Non-classical Fullerenes
February 18	Prof. Gus Hancock, Oxford University Surprises in the Photochemistry of Tropospheric Ozone
February 24	Prof. R. Ramage, University of Edinburgh The Synthesis and Folding of Proteins
March 4	Prof. T.C.B. McLeish, IRC of Polymer Science Technology, Leeds University The Polymer Physics of Pyjama Bottoms (or the Novel Rheological Characterisation of Long Branching in Entangled Macromolecules)

Conferences, Meetings and Courses attended by the author

1996

January	IRC Polymer Engineering Course, University of Bradford
January	IRC Polymer Physics Course, University of Leeds
April	Macro Group (UK) Family Meeting, University of Manchester

1997

April	Macro Group (UK) Family Meeting, Queens Hotel, Leeds
June	CRAC Course, Stirling University, Scotland

1998

July	IUPAC World Polymer Congress, Conrad Jupiters Hotel, Gold Coast, Queensland, Australia*
September	IRC Club Meeting, University of Durham

* Author presented a poster summarising the work described in this thesis