The synthesis and properties of functionalised polymers

VALERIE NUBI

A thesis submitted for the degree of

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THE UNIVERSITY OF ASTON IN BIRMINGHAM

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SUMMARY

The aim of this project was to synthesise fluorinated polymers that might act as host material in a guest-host system for use in non-linear optical applications. These polymers would be expected to have the advantage over materials such as poly(vinylidene fluoride) which is known to be incompatible with many nlo active materials.

A series of bicyclic fluorinated monomers was prepared by the reaction of fluorinated dienophiles with cyclopentadiene in a series of Diels-Alder reactions. The monomers were purified and then used in ring opening metathesis polymerisation. The materials were then characterised by gel permeation chromatography and nuclear magnetic resonance spectroscopy and cast as films for determination of their activities as nlo materials using a Nd/YAG laser system. The second harmonic intensity of each was measured relative to quartz. However no materials of significant activity were produced.

In an attempt to produce polymers that might subsequently be functionalised the polymerisation of 1,2-methylenedioxybenzene and 1,4-benzodioxane was investigated.

KEYWORDS: METATHESIS, RING OPENING POLYMERISATION, NON-LINEAR OPTICAL MATERIALS, Nd/YAG LASER, SECOND HARMONIC GENERATION.

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Abbreviations

NLO- non-linear optics

PVDF- polyvinylidene fluoride

DANS- p,p'-dimethylaminonitrostilbene

MNA- 2-methyl-4-nitroaniline

SHG- second harmonic generation

MMONS- 3-methyl-4-methoxy-4'-nitrostilbene

DSC- differential scanning calorimeter

STP- standard temperature and pressure

GLC- gas liquid chromatography

DMA- dynamic mechanical analysis

BSA- bis(trimethylsilyl)acetamide

BSTFA- bis(trimethylsilyl)trifluoroacetamide

AZBN- azoisobutyronitrile

GPC- gel permeation chromatography

TMS- tetramethylsilane

Nd/YAG- neodynium/yttrium aluminium garnet

EFISH- electric field induced second harmonic

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CHAPTER 1

POLYMERS FOR NON-LINEAR OPTICS

1.1 INTRODUCTION

The field of non-linear optics had previously been dominated by inorganic compounds, such as lithium niobate, and polymers were regarded only as insulators. But since being recognised as an important class of materials for electronics applications, polymers have developed significantly. Until the 1980's the chemical industry focused all resources and intellectual property on structural and elastomeric applications of polymers rather than the more sophisticated properties required by the electronics industry.

1.2 THE APPLICATION OF POLYMERS IN NON-LINEAR OPTICS.(NLO)

Non-linear polymers find increasing use in devices such as:-

a) cladding and coatings for optical fibres

b) piezoelectricity and optical fibres sensors,

c) frequency doublers and thin films for integrated optics applications,

d) in organic dyes for lasers, holographic media and photo conductors,

e) liquid crystals in displays and optical switches,

f) conducting and superconducting organic solids.

The application of polymers in optics technology to date has been mostly to inexpensive lenses, prisms, fibre optics, anti reflection coatings, filters etc., but this is rapidly changing. The attraction of polymer based non-linear optical materials lies in the very large non-linear responses possible over a broad frequency range, rapid response times and high laser damage thresholds. The scientific challenge lies in the design and synthesis of materials with high non-linear optical properties.

Non-linear optical devices are desirable to process light derived from lasers, so that systems capable of rapid, high information content communications or computing may be developed. Non linear optical devices are also required for controlled delivery of energy at appropriate wavelengths and currently available NLO inorganic crystalline materials are not adequate for the desired device characteristics. The potential use and applications of very sophisticated nlo processes in optical telecommunications and integrated optics have put requirements on the nlo optical materials which cannot all be met with the currently used inorganic crystals such as, $LiNbO_3$, KDP (lithium niobate, potassium dihydrogen phosphate).

1.2.1 Materials utilised for non-linear optics

Polyvinylidene fluoride (PVDF)[1,2] has been studied extensively as a non-linear optical material since such research efforts began in 1969. Polyvinylidene fluoride may be subjected to high electric fields in the stretched state, i.e. poled. When molecules that possess non linear optical properties are poled electro-optic property is enhanced. Bergmann et. al.[3] showed that it was possible to induce pyroelectricity and nlo properties in such polymer films as PVDF.

In designing polymers for electronic applications, various characteristics which are important in the small molecule such as delocalisation, the presence of heteroatoms or polar groups , lead to the appearance of unique electronic properties in polymers.

1.2.2 Properties of materials for non-linear optics

As many of the polymers of interest are conjugated and hence insoluble in common organic solvents. They lack the properties required for processing by conventional film casting techniques. This has proved to be a significant hurdle in the application of polymers in electronic and non-linear optics.

For organic materials and polymers to be employed in non-linear optics, the dipole moments of the molecules must all be aligned, whereas in the unpoled state, the dipole moments are randomly orientated. To optimise such polymers they are poled. Meredith et. al.[4] were the first to explore the properties of poled polymers. A χ_2 value of $3\mathrm{x}10^{-9}$esu was obtained for p,p'-dimethylaminonitrostilbene (DANS) poled in PVDF as host polymer.

Conjugated polymers are in general characterized by highly anisotropic optical, dielectric, conducting and mechanical properties[5]. This is because the valence electrons, responsible for these properties, respond more easily to pertubations along directions where conjugation occurs; their delocalisation in the other directions is hindered by sigma bonds.

Polymers are ideal for NLO applications because they are lightweight, strong, chemically resistant, tough, thermally stable, friction resistant and easily processable with regard to forming films, foils, fibres, coatings etc.

1.3 NON-LINEAR OPTICS

Non linear optics is a field of study concerned with the non-linear interaction of electromagnetic radiation and matter. These effects can occur in solids, liquids, gases and plasmas and may also involve more than one electromagnetic field[6]. The wavelength range of these effects generally coincides with the spectrum covered by lasers, extending from the far infra red to the vacuum ultra violet, but some non-linear interactions have been observed at wavelengths extending from the microwave to the x-ray ranges. Historically, non-linear optics preceded lasers but most of the work done in the field has made use of the high powers they make available[7].

1.3.1 Microscopic effects

The starting point for non-linear optics is the relationship between the polarization (P) induced in a molecule and the electric field components(F) of the incident electromagnetic waves. The non-linear optical effects occur at a molecular level because of the deviation of electronic and nuclear potential energies from a simple harmonic dependence on the electric field at the molecular site, thus:-

$$P = \alpha F + \beta FF + \gamma FFF + \ldots\ldots \qquad \text{Equation 1.1}$$

α,β, and γ determinine the nature of field dependence.[8,9,10]

1.3.2 Macroscopic effects

A similar expression can be written for the polarization induced in a medium, when high energy laser radiation propagates through matter, and the use of an intense electric field gives rise to a number of useful effects. These arise from non-linearities in the polarization (dipole moment per unit volume)(p) induced by the radiation. This can be expressed as:-

$$P = \chi_1 E + \chi_2 EE + \chi_3 EEE + \ldots\ldots \qquad \text{Equation 1.2}$$

where χ_1- linear susceptibility,

χ_2-second order susceptibility, and

χ_3-third order susceptibility.[11]

Oudar and Zyss[12,13]showed that the values of α,β,γ, could be related to χ_1, χ_2, and χ_3, using the molecular packing density, local field factors at molecular sites, and a detailed structural or crystallographic knowledge of the bulk material.

The macroscopic coefficients (χ_1, χ_2, χ_3) are readily related to the microscopic coefficients (α, β and γ) as follows[8,14,15]:-

$$\chi_1 = N\alpha F(\omega)^2 \qquad \text{Equation 1.3}$$

$$\chi_2 = N\beta F(\omega)F(\omega_2)F(\omega_3)0(\Omega) \qquad \text{Equation 1.4}$$

$$\chi_3 = N\gamma F(\omega)F(\omega_2)F(\omega_3)F(\omega_4) \qquad \text{Equation 1.5}$$

N- number density of molecules

$F(\omega_i)$ is a local field factor providing a correction to applied fields at frequency ω_i

$0(\omega)$is a statistical alignment factor

1.3.3 Physical properties associated with linear susceptibilities

Certain properties can be ascribed to the susceptibilities, χ_1, χ_2, χ_3 as shown in table 1.1. χ_1 is responsible for the conventional index of refraction and absorption. χ_4 and above tend to be neglected[16].

Currently, no third order devices are being produced and all commercial applications use second order non-linear optics[17].

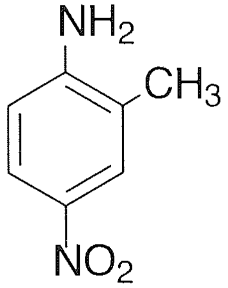
Table 1.1 Electric susceptibility functions χ_2 and χ_3 for various types of Interacting field components, Terminology, and Applications[15]

Susceptibility	Effect	Application
$\chi_2(0;\omega,\omega)$	Optical rectification	Hybrid bistable device
$\chi_2(-\omega;\omega,0)$	Electrooptic (Pockels) effect[18]	Modulators, Variable phase retarders
$\chi_2(-2\omega;\omega,\omega)$	Frequency doubling	Harmonic generation
$\chi_2(-\omega_o;\omega_a,\omega_b)$	Frequency mixing	Parametric amplifiers, IR up conversion
$\chi_3(0;0,-\omega,\omega)$	Second order optical rectification	
$\chi_3(-\omega;\omega,0,0)$	Quadratic electro-optic effect	Variable phase retardation, Liquid-crystal displays
$\chi_3(-\omega_o;\omega_a,\omega_b,-\omega_b)$	AC electrooptic effect AC Kerr effect Raman scattering	High speed optical gates
$\chi_3(-\omega;\omega,\omega,-\omega)$	Self focusing, degenerate four wave mixing, optical kerr effect	Optical bistability, phase conjugatiion, optical transistors, image processing
$\chi_3(-3\omega;\omega,\omega,\omega)$	Frequency tripling	Deep-UV conversion

1.3.4 Differences between second and third order materials

From equation 1.2, it is clear that χ^3 which contains the term EEE, will require three components of electric field and will therefore require higher optical intensities than χ^2 which will require only two components of electric field[19]. For this reason more progress has been made in the research of second order materials, even though a requirement for their use is that they must be non-centrosymmetric (the material must not be symmetric about a point close to the centre). Pugh/Eaton[20,21] confirmed that in a medium which is centrosymmetric all even number susceptibilities are zero and the properties of the material would depend only on the odd numbered terms. Third order effects are therefore symmetry independent.

Another difference between second and third order effects is that materials optimized for second order effects must possess a large internal dipole moment, while those optimized for third order effects must be highly polarizable, e.g. polyacetylene. This means that organic second order materials are typically conjugated donor- acceptor compounds such as 2-methyl-4-nitroaniline (MNA)[5,19,22]



It was recognised by Franken et. al.[23]; Kurtz and Perry[24] that many organic molecules exhibit large hyperpolarizabilities due to the delocalisation of their π-electronic clouds.

1.3.5 Advantages of inorganic crystals

Large NLO activities are observed which do not decay over a matter of months,
e.g. $LiNbO_3$ has a low loss of approximately 0.1dB/cm.

1.3.6 Advantages of polymers/organic compounds over inorganic crystals.

The requirements for organic/polymeric materials to be utilised for nlo applications are:-

a) high nlo activity (large susceptibilities) and low loss

b) stability,

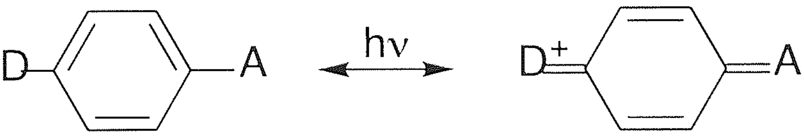
c) refractive index uniformity,

d) high laser damage threshold,

e) faster response times, and

f) relatively inexpensive.

Materials for second order non-linear optics are typically conjugated compounds[5,25] such as



which are characterised by an intense intramolecular charge transfer resonance. The presence of a polarizable conjugated system is not mandatory for SHG activity but the features are often found in the most efficient materials.[7] The optical non-linearities are relatively fast in these systems because the effects are derived almost exclusively from the movement of electrons, as opposed to large contributions from vibrational excitations, as in lithium niobate.

1.3.7 Materials examined for non-linear optical properties

Many organic materials have been investigated for second order properties and examples of these are shown in figure 1.1.

Singer et al.[27] studied azo dye disperse red 1 in polymethylmethacrylate, using a dopant molecule number density of $2.74 \times 10^{20} cm^{-3}$ and this showed a linear behaviour of χ_2 with poling field; the measured value agrees well with the predicted value. A theoretical value of 3×10^{-6} e.s.u. was obtained for χ_2 using a poling field of $0.6 \times 10^6 V/cm$. The second harmonic coefficient was also shown to rise in proportion to the guest concentration shown in figure 1.2[29], confirming that the non-linear optical properties of the film are the sum of the properties of the component species[10].

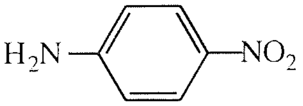
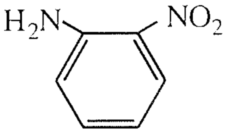
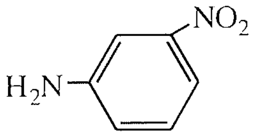
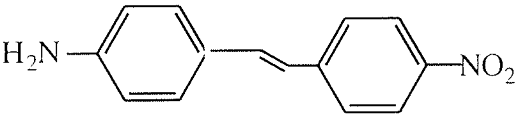
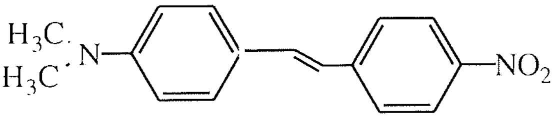
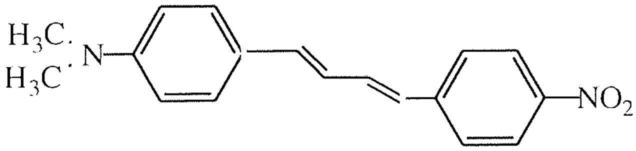
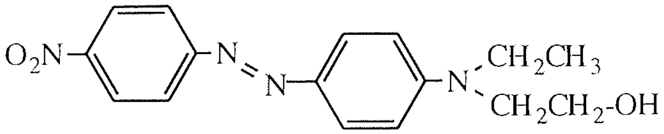
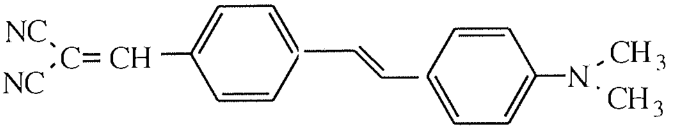
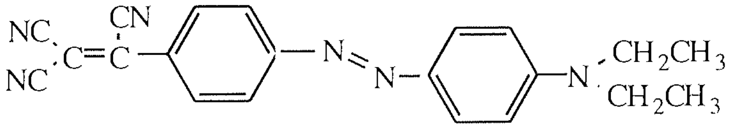
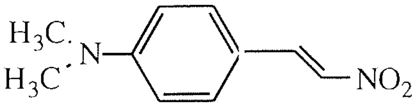
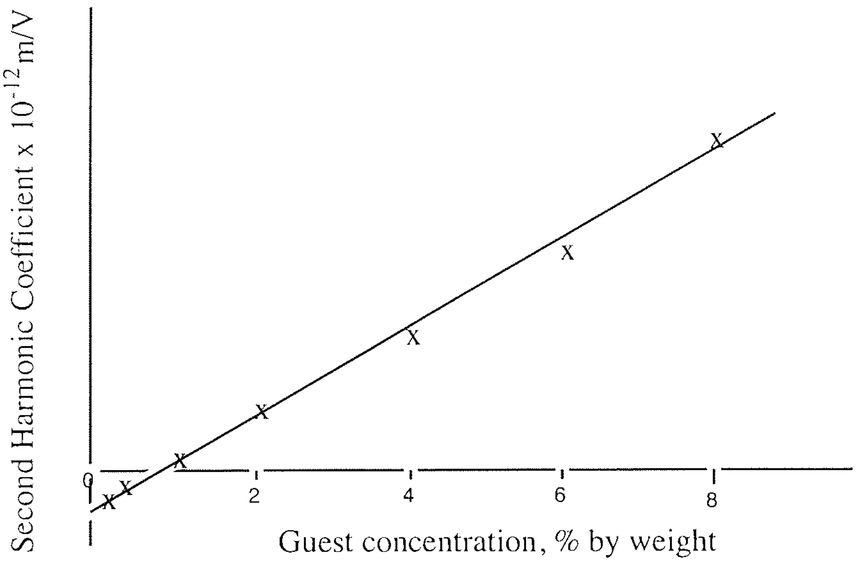
Molecule	β_{exp} (10^{-30}esu)	
	16.2 - 34.5	paranitroaniline (pNA)
	10.2	orthonitroaniline
	6	metanitroaniline (mNA)
	225 - 295	aminonitrostilbene
	450	(DANS)
	470 - 790	
	125	Disperse red 1
	323	
	390	
	180 - 260	
$LiNbO_3$	0.6	

Figure 1.1 Second hyperpolarizability values of organic materials for nlo applications[8,15,26,27,28]



Dependence of Second Harmonic Coefficient against concentration of guest

Figure 1.2

1.3.8 Disadvantages of inorganic crystals

It is not supposed that poled polymers and organic molecules will supercede the inorganic materials currently used, but more likely that they will compete well in terms of cost for new applications[30]. The major disadvantages of inorganic crystals are:-

a) slow response times,

b) high absorption,

c) degradative photorefractive effects, and

d) expense, it is very expensive to grow crystals of good optical quality,and not very suitable for large scale production.

1.4 SECOND HARMONIC GENERATION (SHG)

Second harmonic generation has been of practical interest ever since it was demonstrated that efficient conversion from fundamental to second harmonic frequencies could be obtained at reasonable fundamental power levels. This possibility has made available powerful sources of coherent radiation at hitherto unattainable wavelengths. This phenomenon is already widely used for doubling fundamental wavelengths from the infra red into the ultra violet, for producing radiation of wavelengths for pumping dyes and the analysis of short pulses.

Second harmonic generation represents a special case of the more general process of sum - frequency generation, in which two frequencies are added to form the sum. Second harmonic generation in a medium arises from the second order polarization, P_2 induced in a medium by an applied electric field E, given by

$$P_2 = \chi_2 EE \qquad \text{Equation 1.6}$$

χ_2 = second order non-linear susceptibility

It follows that a laser field at frequency, ω

$$\text{i.e. } E = E_o \cos(\omega t+\phi) \qquad \text{Equation 1.7}$$

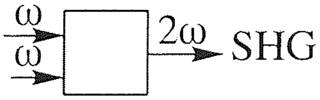
second order polarization depends on E^2 therefore

$$E.E = E_o E_o \cos^2(\omega t+\phi)$$

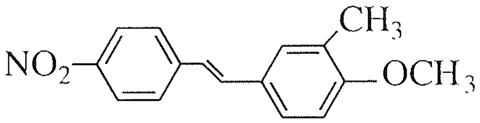
$$= E_o E_o 1/2(4\cos 2\omega t) \qquad \text{Equation 1.8}$$

hence will generate a second order polarization oscillating at frequency 2ω as shown in equation 1.8.

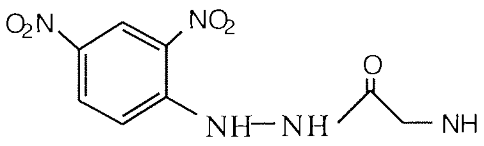
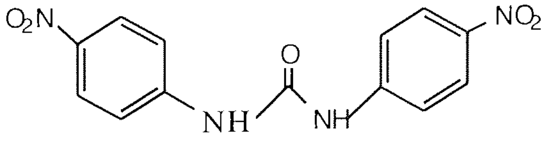
Peter A Franken et. al.[23,31] were the first to observe second harmonic generation experimentally in 1961. They focused a 3kw pulse of red (694.3nm) ruby laser light onto a quartz crystal, one part in 10^8 of this incident wave was converted to the 347.15nm ultraviolet second harmonic. For second harmonic generation, a major synthetic challenge is to construct necessarily non centrosymmetric molecular assemblies. For efficient SHG, the doubled frequency should lie in a region where the molecule is transparent to avoid optical losses.[27,32,33]



3-methyl-4-methoxy-4'nitrostilbene (MMONS) has the highest reported powder SHG value (1250xUrea) among simple stilbene derivatives. Eaton et. al.[16] have shown that the SHG value depends strongly on the solvent from which it is crystallised.



Tweig/Jain[7] carried out work in molecules that combined the favourable non centrosymmetric crystal properties of urea with the large nonlinearity of nitroaniline. They found that the materials shown below, whose properties were measured relative to urea, were most efficient.

	Powder Eff (wrt Urea)
	8.8
	8.8

There are three methods by which the non-linear optical chromophore may be incorporated into a polymer:-

1.4.1 a) Guest/host system

The non-linear optical chromophore may be added as a guest dopant to a transparent host polymer[10,34]. Meredith[27] was the first to explore doped poled polymers. Many host polymers have been examined, polystyrene by Hampsch[35], polyoxyethylene by Watanabe[36] and polymethylmethacrylate by Singer[37].

Polystyrene makes a good host because it has[38,39]:-

a) excellent transparency,

b) low dielectric constant,

c) relatively high T_g (to help stabilise chromophore alignment), and

d) amenability to varying levels of functionalization and processing.

The disadvantages are that only a limited quantity of guest may be dissolved in any host, which thereby limits the nlo activity. Over a period of time, the guest normally begins to deposit out of the host forming two distinct phases. The second harmonic intensity decreases over a period of time, as the polymer chains may have begun to relax and dopant molecules that were locked in alignment have greater freedom to rotate and decrease the second harmonic efficiency[30,40].

Lalama et. al.[15] using polymethylmethacrylate as a host for a very soluble, very compatible dye, disperse red b, were able to obtain films with $\chi_2 = 1.2x10^{-8}$esu, which was the largest reported value to date.

Using a crystalline copolymer of polyvinylidene fluoride and trifluoroethylene with an aminoazo compound, Pantelis et al.[30] were able to obtain a χ_2 value nearly identical to the disperse red system. The measured second harmonic coefficient of polymethylmethacrylate doped with the material shown in figure 1.3 dropped by 50% in only two weeks.

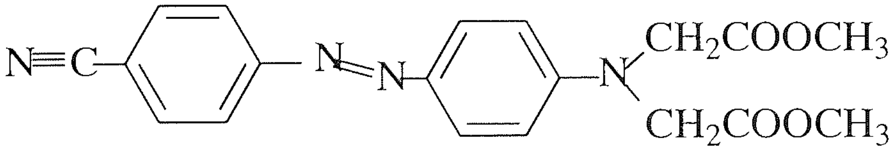
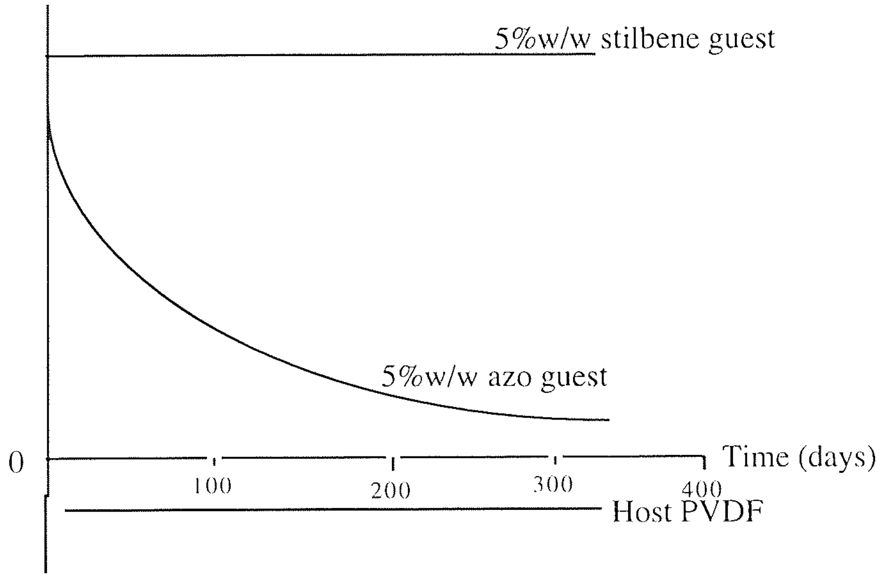


Figure 1.3 4-(4'-cyanophenylazo)-N,N-bis-(methoxycarbonylmethyl)-aniline

Polystyrene and polyoxyethylene have also been shown to be unstable with regards to relaxing of molecule orientation and therefore show a rapid decay in the non-linear coefficient.



Room temperature ageing of second harmonic coefficient

Figure 1.4

The precipitation of the guest can be prevented by appropriate selection of the guest. For example Hill[10] showed that in the cyanophenylazoaniline system, the guest precipitated out. However in the aminonitrostilbene system, the guest remained in solution and there was no change in the non-linear properties, figure 1.4.

1.4.2 b) Single component polymer systems

These may be obtained by either chemically binding an active non-linear group on to an existing polymer or by polymerisation of a monomer containing the non-linear species. In order to decouple the motion of the non-linear group from that of the polymer backbone it is usually distanced from the active group by a short flexible hydrocarbon chain (spacer)[4], shown in figure 1.5.

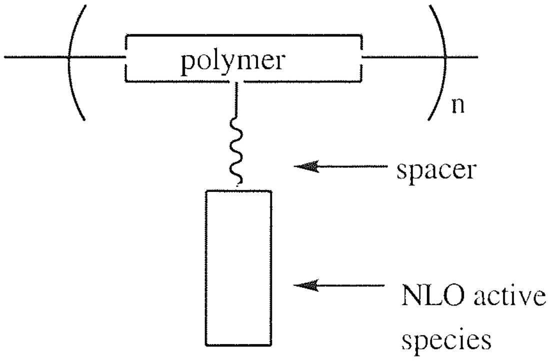


Figure 1.5[41,42] Single component polymer systems

In this way, nlo activity is not limited by the solubility of the active material which dissolved in the host polymer. Ye[43] showed that single component systems do not show phase separation at high chromophore densities or deleterious relaxation of poling - induced chromophore alignment[43]. This is due to the restricted chromophore mobility imparted by covalent linkage to the polymer backbone. Le Barny[44] showed that the spacer length affects certain physical properties of the final polymer,such as the glass transition temperature. The longer the spacer length, the lower is the observed Tg. The prime ageing mechanism will be the loss of poled order with time. Singer[45] and Ye[46] showed that the rate of thermal reorientation in side chain polymers is much lower than in similar guest /host systems, but there is still no proof that thermal relaxation can be reduced to a level consistent with long term device stability[47]. Polyesters and polystyrenes have also been examined as backbone polymers by Ye[48]/Demartino[49]. The poly(acrylate) system shown in figure 1.6 showed no significant degradation in second harmonic coefficient after two years.

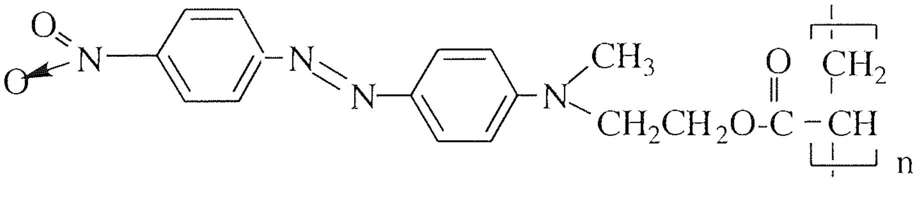


Figure 1.6 Poly(acrylate) disperse red 1 side chain polymer

1.4.3 c) Crosslinked polymer systems

The non-linear optical chromophore is covalently attached to a polymer and crosslinked during poling. The polymers maybe crossslinked by thermal means or photochemical means, shown in figure 1.7[50]. This greatly improves the stability over long periods of time and phase separation is no longer a problem.

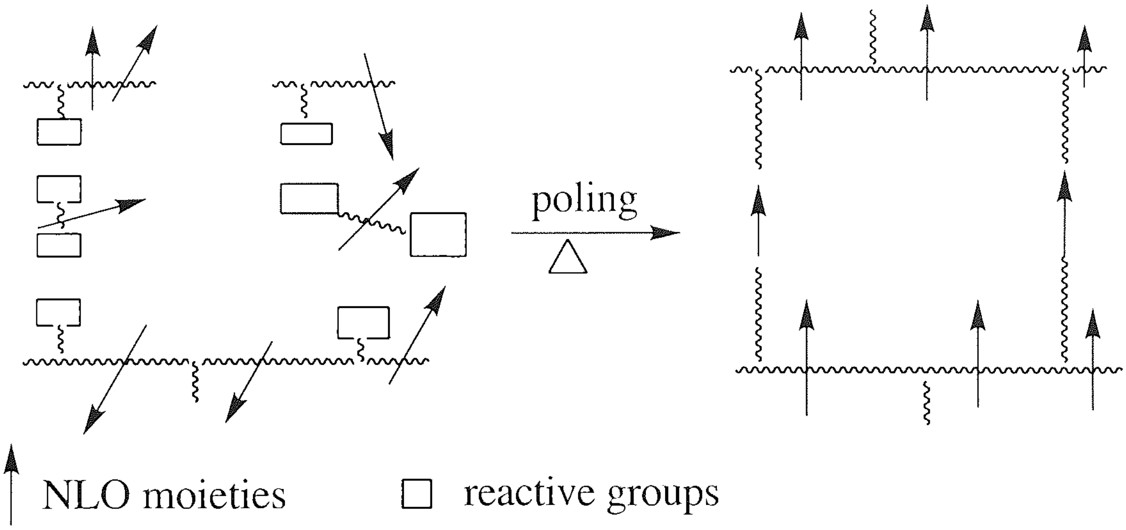


Figure 1.7 Crosslinked polymer systems

Jeng [51]showed that in a crosslinked polymer non-linear optical moieties are covalently bound, rigid and therefore they are less likely to relax. This was first reported by Eich et. al.[52]for the system shown in figure 1.8. These crosslinked epoxy polymers showed no detectable decay in second harmonic generation for over 500 hours under ambient conditions and no relaxation tendency even at 850°C.

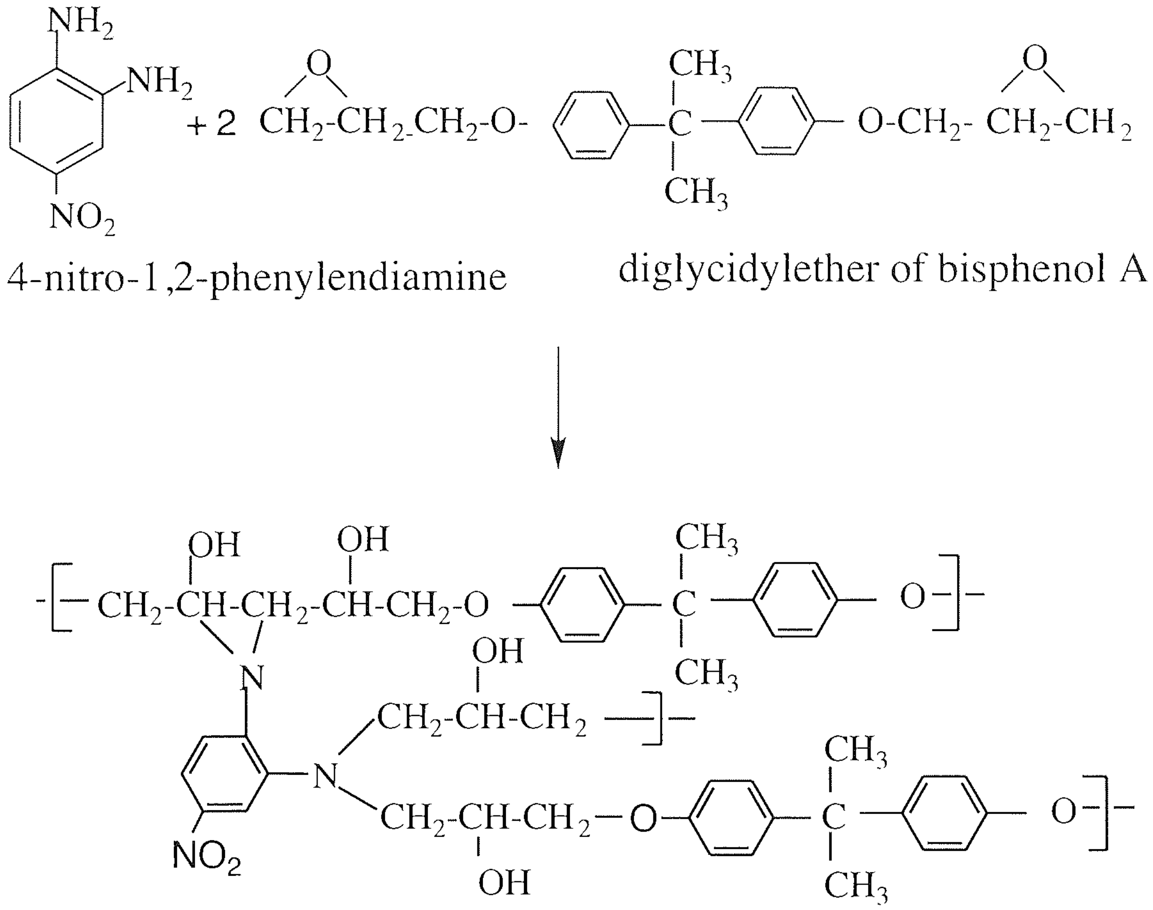
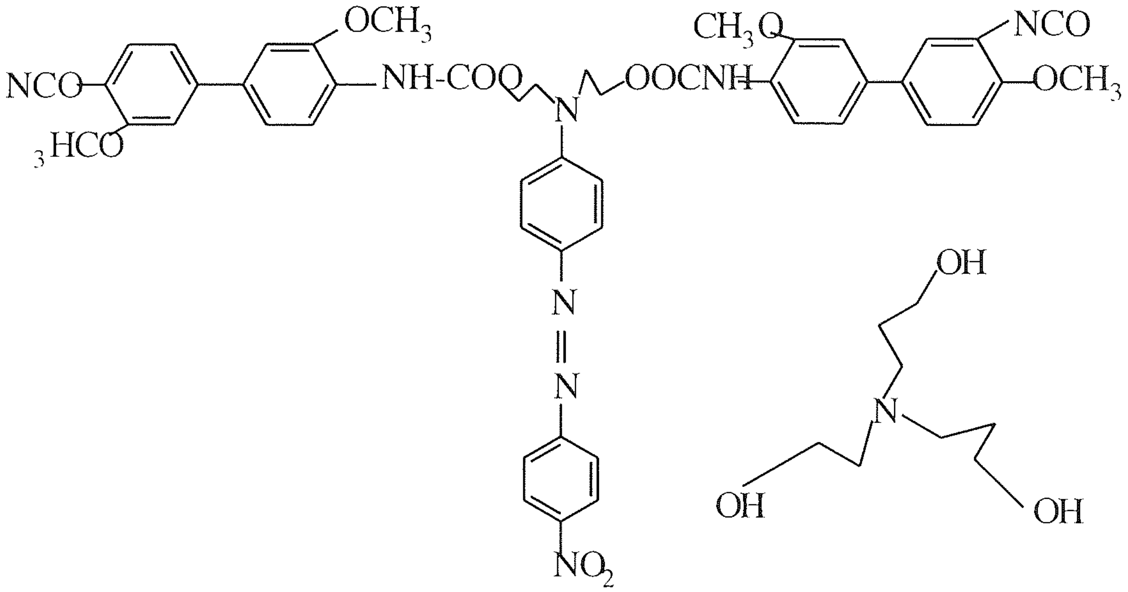


Figure 1.8 Crosslinked epoxypolymers

Dalton et al [47] have prepared the polymer shown in figure 1.9 that retains second order activity for periods exceeding 5000 hours.



Monomer a   Crosslinking agent b

Figure 1.9 Dalton's crosslinked polymer

Their approach was to prepare a precursor polymer based upon the self condensation of monomer a, crosslinking with b. Chen et. al.[38]also prepared a series of photochemically crosslinked polymers which combine very high chromophore densities with very large and stable second order nlo activities.

1.5 POLING OF POLYMERS

The mixture was heated above the glass transition temperature (T_g) whilst applying an external d.c. electric field. The non-linear optical material adopts its new orientation in the presence of the external field and when the sample is cooled in the presence of the external field the adopted orientation is maintained[53], as shown in figure 1.10.

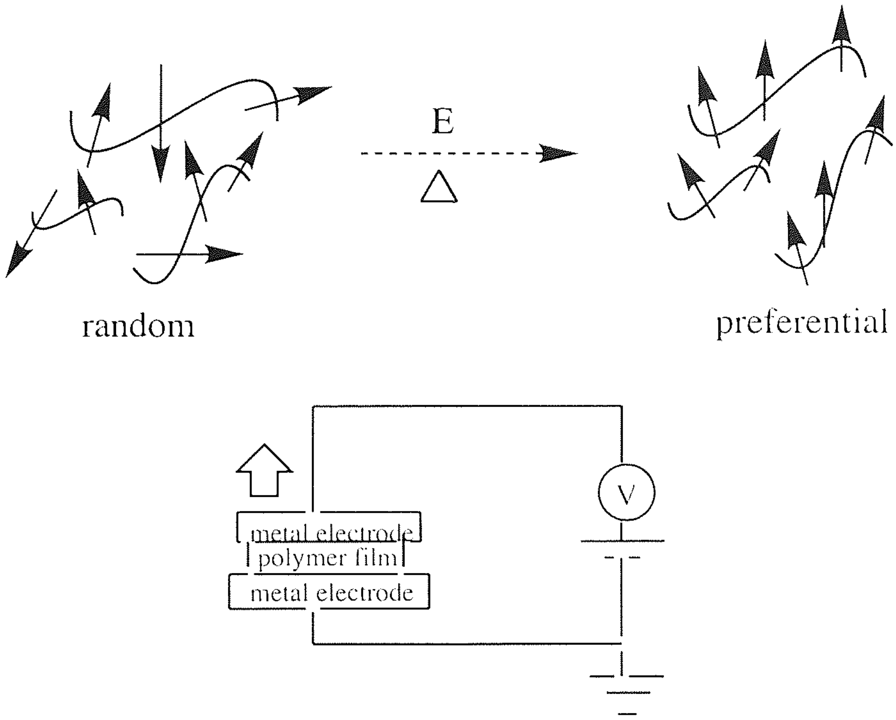


Figure 1.10 Poling of polymers[3]

1.6 REQUIREMENTS FOR NON-LINEAR OPTICAL APPLICATIONS.

Williams[27,54] stated that for uniquely useful applications, organic materials will require a χ_2 of 10^{-7}esu or greater; additionally a variety of additional application- dependent properties and attributes must be present in a material e.g.

- uniform birefringence
- minimized scattering losses
- transparency
- stability in ambient and operating environments
- thickness control, and
- processability.

Bailey et. al. [55] investigated a new technique to assess second order nlo coefficients. The material (1%) was compressed with KCl to produce a disk and the SHG measured relative to urea. The advantages of this method are it allows rapid determination of high nlo coefficients, only small quantities of materials are required, plus the disks may also be used for infrared techniques.

1.7 AIMS

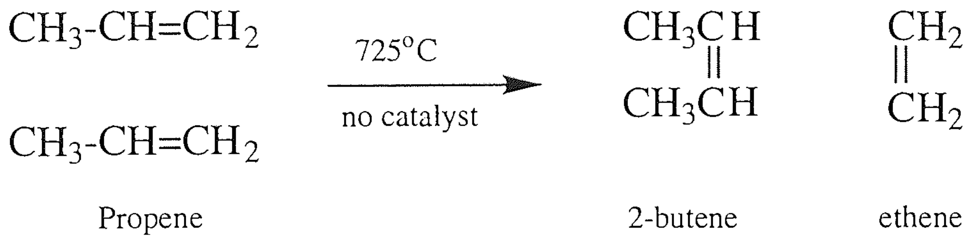
The aim of this research programme is to synthesise other new or novel polymers with non-linear optical properties, our main field of interest being polymers generated by the ring opening polymerisation of bicyclic monomers. All the polymers synthesised contained fluorine, as it was hoped that the presence of fluorine would assist with aligning the dipole moments. The polymers would also contain a bulky group which should also help with alignment. The NLO properties of certain fluorinated aromatics as guests in the synthesised host polymers were also investigated.

CHAPTER 2

METATHESIS

2.1 INTRODUCTION

Catalytically promoted olefin metathesis was first reported in 1964 by Banks and Bailey[56]. This was also confirmed by Mango et.al.[58] and Van der Lugt[59]. Prior to this report, Schneider and Frolisch[57] determined that higher hydrocarbons could be made from lower members at high temperatures shown below.

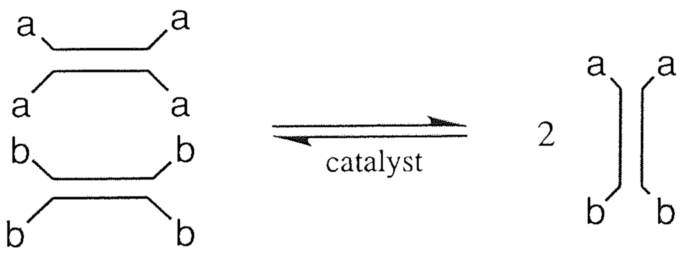


$$\begin{matrix} CH_3\text{-}CH{=}CH_2 \\ CH_3\text{-}CH{=}CH_2 \end{matrix} \xrightarrow[\text{no catalyst}]{725^\circ C} \begin{matrix} CH_3CH \\ \| \\ CH_3CH \end{matrix} \quad \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix}$$

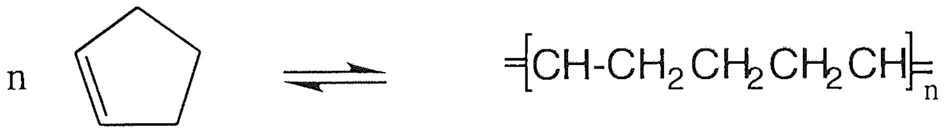
According to the Woodward-Hoffmann rules of orbital symmetry the thermal rearrangement reaction is symmetry forbidden and consequently requires a high reaction temperature.

Olefin metathesis involves the catalytically promoted interchange of carbon atoms between a pair of double bonds and can be divided into three categories

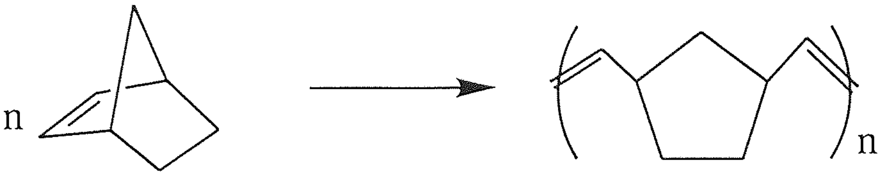
2.1.1 (a) olefin metathesis (exchange)



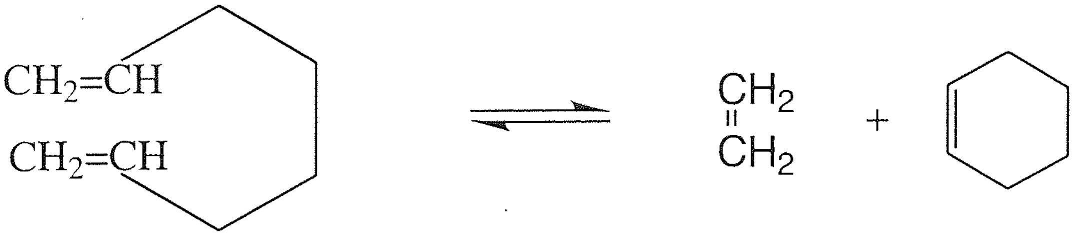
2.1.2 (b) ring opening metathesis polymerisation



The ring undergoes cleavage to produce an acyclic polymer. Bicyclic compounds, e.g. norbornene, undergo bond cleavage to produce a polymer with in-chain cyclopentyl rings.



2.1.3 (c) degradation metathesis



An α-, ω- linear diene undergoes an intramolecular reaction to produce an acyclic and a cyclic compound. This reaction is particularly effective when the ring formed is cyclohexene because cyclohexene is a completely strain-free ring.

2.2 CATALYST SYSTEM

Olefin metathesis requires the interaction of the olefinic substrate and a catalyst, as it is not a spontaneous reaction. The catalyst generally comprises a transition metal compound, a co-catalyst and sometimes a third component, a promoter. Catalyst systems for metathesis reactions fall into two categories,

a) homogeneous and

b) heterogeneous.

2.2.1 Homogeneous catalysts

Homogeneous catalysts are those catalysts which exist in the same physical phase as one or more of the reactants. The catalysts are usually soluble complexes of transition metals. The major attraction of homogeneous catalysis is selectivity, i.e. the ability to produce pure products in high yield. This is particularly useful for the pharmaceutical and polymer industries. Better selectivity is obtained with homogeneous catalysts than with heterogeneous because the temperatures of reaction and mixing are generally lower.

2.2.2 One component systems

The largest group of one component catalysts for olefin metathesis, are those with structures that are believed to be analogous to the structure of the intermediate involved in the metathesis reaction. e.g. Casey carbenes $(C_6H_5)_2C{=}W(CO)_5$ [60,61] and $[(Me)_3\text{-}C\text{-}]_3Ta{=}CH\text{-}C(Me)_3$ prepared by Schrock[62]. But these are not particularly efficient for the metathesis reaction. More recent examples include $RuCl_3$ (hydrate) and rhodium complexes. Some examples are shown in table 2.1.

Table 2.1 One component homogeneous catalyst systems

Catalyst	Substate	Ref
$Re(CO)_5Cl{:}EtAlCl_2$	Cyclopentene, Cyclohexene, cycloheptene, cyclooctene	63
$(CO)_5W{=}C(C_6H_5)_2$	Bicyclo[4.2.0]octa-7-ene, Cyclooctene	64
$(CO)_5W{=}C(C_6H_5)OCH_3$	Bicyclo[4.2.0]octa-7-ene, Norbornene	64
$RuCl_3$	Cyclobutene, methylcyclobutene	65

2.2.3 Bimetallic systems

In these cases a transition metal salt from groups VI or VII and a cocatalyst are used to initiate the metathesis reaction. A metal alkyl is usually added as the cocatalyst, which affects the reaction in two ways. The metal alkyl is a good reducing agent and also controls the Lewis acidity of the reaction medium. Grubbs has prepared a stable titanocyclobutane intermediate which was an efficient metathesis catalyst. The mechanism for the initiation of metathesis was obtained from Muetterties reaction of an olefin with WCl_6/Me_2Zn. In some cases a promoter may be added, usually an oxygen containing species, e.g. alcohols, hydroperoxides. Calderon's[66,67,68] system, $WCl_6/C_2H_5AlCl_2/EtOH$ is much more effective than the $WCl_6/C_2H_5AlCl_2$ system. Motz and Farona[69] modified $Mo(CO)_5Py/RAlCl_2$

($R=C_2H_5$ or CH_3) by adding $(C_4H_9)Cl$ as the cocatalyst which produces an effective catalyst for the metathesis of terminal olefins. Some examples are shown in table 2.2.

2.2.4 Heterogeneous catalysts

Heterogeneous catalysts are those catalysts which are in a different physical state from the reacting substrate. Heterogeneous catalysts are nearly always solid and the substrate is either in the liquid or gas phase. Generally, effective heterogeneous catalysts comprise transition metal compounds, with the majority belonging to molybdenum, tungsten and rhenium in the form of an oxide, carbonyl of sulphide. The advantages of heterogeneous catalysts over homogeneous catalysts are that after reaction, product separation and catalyst recovery are easier. Some examples are shown in table 2.3.

Table 2.2 Two component homogeneous catalyst systems

Catalyst	Co-catalyst	Substrate	ref
WCl_6	$(CH_3)_4Sn$	Cyclooctene, Norbornene	70
WCl_6	Al, $AlCl_3$	Cyclopentene	71
WCl_6	$(CH_3)_4Sn$	Bicyclo[4.2.0]octa-7-ene	64
WCl_6	$EtAlCl_2$	5-methylbicyclo[2.2.1] hept-2-ene	72
WCl_6	$EtAlCl_2$/ EtOH	Cyclooctene	73
WCl_6	$EtAlCl_2$/ EtOH	2-pentene	74
WCl_6	$EtAlCl_2$/ EtOH	1,5-cyclooctadiene/1,5-hexadiene	75
WCl_6	$(CH_3)_4Sn$	bicyclo[2.2.1]hepta-2,5-diene	76
WCl_6	$AlBr_3$	Cyclopentene	65
WCl_6	$AlBr_3$	Cyclopentadiene	65
WCl_6	$AlBr_3$	cis-cycloheptene	65
WCl_6	$AlBr_3$	cis-cyclooctene	65
WCl_6	$AlBr_3$	endo-dicyclopentadiene	65
WCl_6 or $MoCl_5$	$(CH_3)_4Sn$	5,6-bis(chloromethyl)bi cyclo[2.2.1]hept-2-ene	77
WCl_6 or $MoCl_5$	$(CH_3)_4Sn$	2-trifluoromethylbicyclo [2.2.1]hepta-2,5-diene	78
WCl_6 or $MoCl_5$	$Al(Et)_3$	Cyclopentene	79,80
Re_2O_7-Al_2O_3 or WCl_6	$(CH_3)_4Sn$	Ethylene/methyl oleate	81
$MoCl_5$	$(CH_3)_4Sn$	endo-5-trifluoromethylbi cyclo[2.2.1]hept-2-ene	82
$MoCl_5$	$(CH_3)_4Sn$	2,3-bis(trifluoromethyl) bicyclo[2.2.1]hepta-2,5-diene	83
$Mo(NO)_2Br_2(PPh_3)_2$	$EtAlCl_2$	2-pentene	74
$(CO)_5W=C(OEt)Ph$	$TiCl_4$ UV	1,5-cyclooctadiene	75
$(CO)_4(PPh_3)W=C(OMe)Ph$	$TiCl_4$	1,5-cyclooctadiene	75

Table 2.3 Heterogeneous catalyst systems

Catalysts	Co-catalysts	Substrate	ref
WCl_6		Cyclopentene	84,85,86
WCl_6		Bicyclo[2.2.1]hepta-1,4-diene	86
WCl_6	Ph_4Sn	5,5,6-trifluoro-6-trifluoro methylbicyclo[2.2.1]hepta-2-ene	87,88
WCl_6	Ph_4Sn	5,6-bis(trifluoromethyl) bicyclo[2.2.1]hepta-2-ene	87,88
WCl_6	Ph_4Sn	5-(trifluoromethyl)bi cyclo[2.2.1]hepta-2-ene	87,88
WCl_6	Ph_4Sn	5,6-dichloro-5,6-(trifluoro methyl)bicyclo[2.2.1]hepta-2-ene	87,88
WCl_6	Ph_4Sn	2-(trifluoromethyl) bicyclo[2.2.1]hepta-2,5-diene	87,88
WCl_6	Ph_4Sn	2,3-bis(trifluoromethyl) bicyclo[2.2.1]hepta-2,5-diene	87,88
WCl_6	Ph_4Sn	5-fluoro-5-pentafluoroethyl-6,6-bis(trifloromethyl)bicyclo[2.2.1] hept-2-ene	89
WCl_6	Ph_4Sn	5,6-difluoro-5-heptafluoro isopropyl-6-trifluoromethyl bicyclo[2.2.1]hept-2-ene	89
WCl_6	Ph_4Sn	2,3,3,4,4,5,5,6-octafluoro tricyclo[5.2.1.$0^{2,6}$]dec-8-ene	89
WCl_6	Ph_4Sn	2,3-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene	89
WCl_6	$(iC_4H_9)_3Al/ Na_2O_2$	2,3-bis(trifluoromethyl)bicyclo [2.2.1]hepta-2,-diene	83
WCl_6 or $MoCl_5$	Ph_4Sn	2,3-bis(trifluoromethyl)bicyclo [2.2.1]hepta-2,-diene	83
WCl_6 or $MoCl_5$		4,5-bis(trifluoromethyl)tricyclo [6.2.1.$0^{2,7}$]undeca-2,4,6,9-tetraene	90
WCl_6 or $MoCl_5$		3,4,5,6-tetrafluoro [6.2.1.$0^{2,7}$] undeca-2,4,6,9-tetraene	90
WCl_6 or $MoCl_5$		3,4,5,6-tetrafluoro-11-isopropylidene[6.2.1.$0^{2,7}$]undeca -2,4,6,9-tetraene	90
Re_2O_7-Al_2O_3	R_4Sn, R=Me or Et	$CH_2=CH(CH_2)_nCN$,n=2,3,4,5	91
$TiCl_3$-α	$Al(Et)_3$	Propene	92

The activity of heterogeneous catalysts depends to a great extent on the surface characteristics of the catalysts. The important physical characteristics are:-

a) surface area: the greater the surface area of the catalyst, the greater the activity of the catalyst. Catalysts are generally prepared with a specific area of over $100m^2g^{-1}$

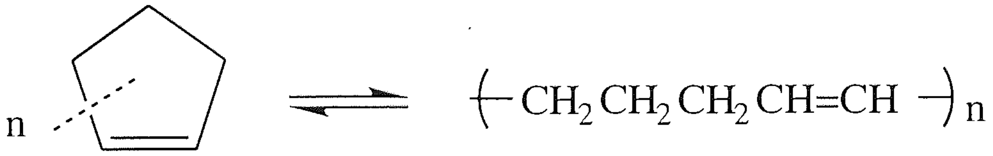
b) pore size: for high activity towards metathesis, the average diameter and total pore volume must be 5-20nm and below 1cm^3/g respectively.

c) particle size: generally, pellets from extrusion or grains of precipitate are used, depending on the carrier.

The activity of heterogeneous catalysts may be altered by external, physical or chemical factors. The catalysts are active within a specific temperature and pressure range. If the temperature is too low, the catalyst may be rendered inactive and if too high, the surface structure may be altered to deactivate the catalyst. Total modification of the active centre could lead to the production of secondary products from side reactions. Heterogeneous catalysts may be destroyed by moisture, oxygen, acids, carbon dioxide and other compounds containing polar groups. If adsorbed onto the catalyst, they block the active centres, thus changing the activity of the catalyst. Since regeneration of the active catalyst is virtually impossible once poisoning has taken place, precautions should be taken to exclude these substances. This can be done by ensuring that all reagents and solvents are pure, dry and oxygen free.

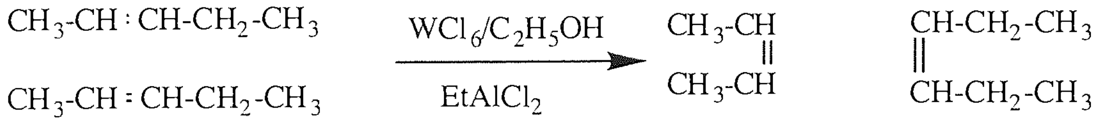
2.3 MECHANISTIC PATHWAYS

It had been suggested by Natta that metathesis involved cleavage of the carbon - carbon single bond, α to the double bond during polymerisation of cyclopentene.

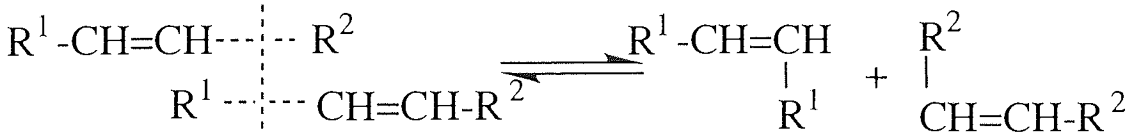


Although no evidence was offered to support this theory, it had been assumed that due to the fact that single bonds are generally weaker than double bonds, those would be easier to cleave.

Ring opening polymerisation was already known prior to the discovery of olefin metathesis. Cyclopentene was polymerised by Eleuterio[93], using alumina supported molybdenum trioxide and cyclobutene was polymerised homogeneously by Natta et. al[94]. In 1964 Banks and Bailey[95,96] disclosed a catalytic disproportionation reaction in which unsymmetrical, linear olefins of 3 to 8 carbon atoms produced a mixture of shorter and longer chain olefins under the influence of a heterogeneous catalyst. Calderon[97] was the first to realise that acyclic olefin metathesis and ring opening polymerisation of cycloolefins were the same reaction. 2-Pentene was converted using, WCl_6, C_2H_5OH and $EtAlCl_2$[98] shown below.

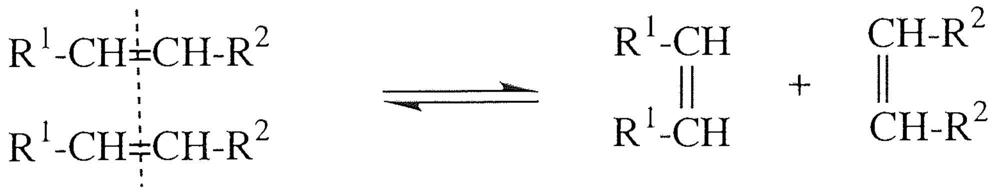


In attempts to establish the mechanism of metathesis two routes were considered to be plausible, transalkylation and transalkylidenation. Transalkylation involves the exchange of alkyl groups via cleavage of a carbon - carbon single bond, similar to the scheme proposed by Natta, and shown in scheme 2.1.



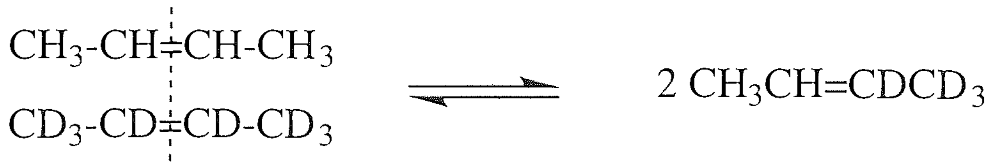
Scheme 2.1
Transalkylation mechanism

Transalkylidenation involves the interchange of alkylidene groups by cleavage of carbon - carbon double bonds, as shown in scheme 2.2.



Scheme 2.2
Transalkylidenation mechanism

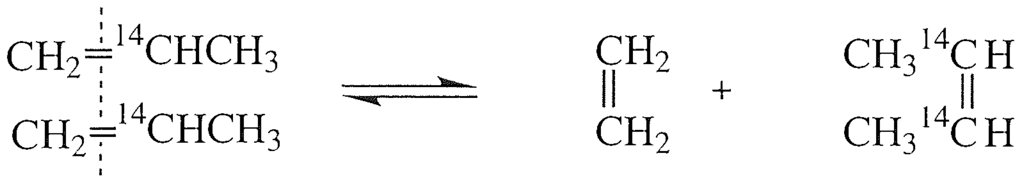
Calderon et. al. studied the metathesis of 2-butene and perdeutero-2-butene using $WCl_6/C_2H_5AlCl_2/EtOH$. Only one new product was observed, 1,1,1,2-tetradeuterobut-2-ene, consistent with the transalkylidenation route, shown in scheme 2.3.



$$\begin{matrix} CH_3\text{-}CH{=}CH\text{-}CH_3 \\ CD_3\text{-}CD{=}CD\text{-}CD_3 \end{matrix} \rightleftharpoons 2\ CH_3CH{=}CDCD_3$$

Scheme 2.3
Confirmation of transalkylidenation mechanism using perdeutero-2-butene

This mechanism was further confirmed by Mol et.al.[99] who studied the metathesis of propene labelled with ^{14}C. It was found that 2-^{14}C-propene produced radioactive 2-butene and non radioactive ethene, shown in scheme 2.4.



$$\begin{matrix} CH_2{=}^{14}CHCH_3 \\ CH_2{=}^{14}CHCH_3 \end{matrix} \rightleftharpoons \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + \begin{matrix} CH_3{}^{14}CH \\ \| \\ CH_3{}^{14}CH \end{matrix}$$

Scheme 2.4
Confirmation of transalkylidenation mechanism using radioactive 2-butene

1-^{14}C-propene and 3-^{14}C-propene were also studied which produced radioactive ethene and 2-butene respectively, consistent with transalkylidenation.

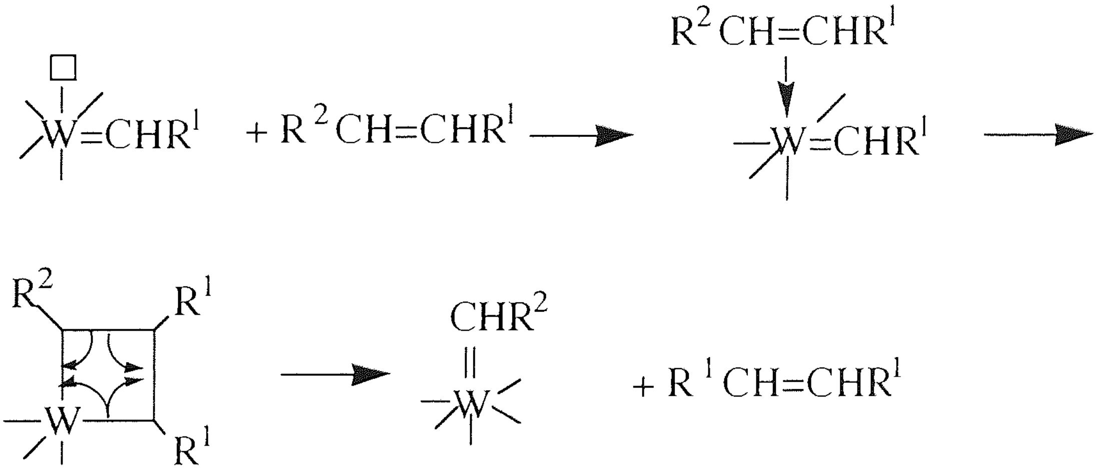
A great deal of work has been carried out to determine the mechanism of the reaction since the discovery of the reaction by Banks and Bailey.

2.4 PAIRWISE MECHANISM

The pairwise mechanism involved the simultaneous exchange of alkylidene groups. Bradshaw et. al.[100] suggested that two olefin molecules bonded to the transition metal atom, rearranged to form a quasicyclobutane intermediate, which then dissociated to yield two product olefins. Calderon[66,67] proposed a mechanism in which the catalyst and cocatalyst reacted together to form an active centre, as the transition metal was thought to possess vacant co-ordination sites or labile ligands, to which reacting olefins could co-ordinate. If this were true, then it would be reasonable to expect cyclobutane, even in small quantities, but none has ever been detected. It has been demonstrated that cyclobutanes are unreactive under usual metathesis conditions. As a result of this, Lewandos and Pettit[101], Grubbs[102] have suggested other mechanisms.

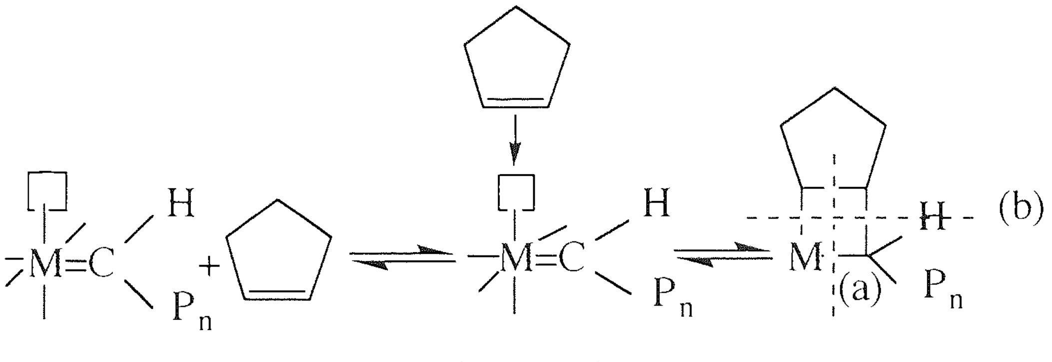
2.5 THE CARBENE MECHANISM

The pairwise mechanism could explain the direct exchange of alkylidene units, but it still left unexplained many features of the metathesis reaction. It was found that metathesis of ethene led to the formation of cyclopropane and methylcyclopropane, this could not be explained using the pairwise mechanism. The currently accepted mechanism of reaction is that proposed by Chauvin and Herisson[103] shown in scheme 2.5. It was suggested that the active centre in the reaction was a transition metal carbene which possessed a labile ligand or a vacant co-ordination site at which the olefin can complex. The reaction proceeds by formation of an intermediate metallocyclobutane, which could either revert to the original olefin or produce another metal carbene and a product olefin.



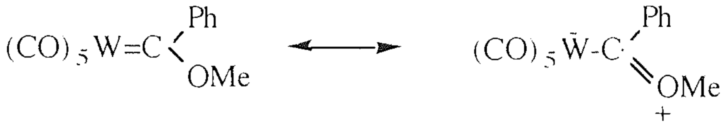
Scheme 2.5
The carbene mechanism

The mechanism can also be used to explain the polymerisation of cycloolefins as shown in scheme 2.6 if cleavage of the metallocyclobutane takes place along (a).



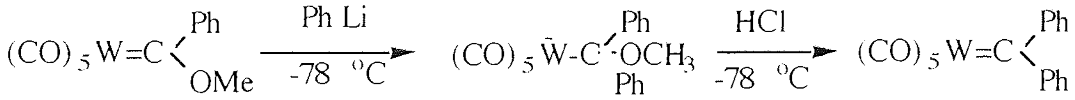
Scheme 2.6
The polymerisation of cycloolefins via carbene mechanism

Fischer[104] prepared a stable metal carbene complex shown in scheme 2.7.



Scheme 2.7
Fischer carbene complex

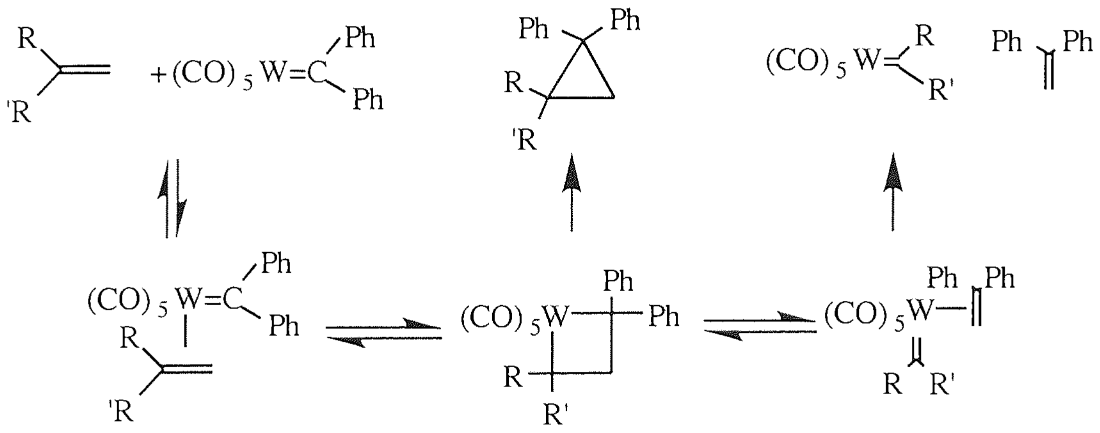
This carbene complex stabilised by electron donation of the heteroatom was found to be too stable for metathesis reactions. Casey[60,105] prepared a stable, but more reactive heteroatom free metal carbene complex shown in scheme 2.8.



Scheme 2.8
Casey carbene complex

In this case stability was associated with conjugation of the phenyl rings to the tungsten-carbon double bond.

The cyclopropanation and alkene scission reactions can then be explained by the mechanism shown below.



This mechanism includes formation of a metallocyclobutane intermediate which can undergo a reductive elimination to give a cyclopropane or can undergo cleavage to give a metal complex and a new carbene ligand.

Shrock[106] isolated a stable neopentylidene complex of tantalum shown in scheme 2.9.

$$2Li\text{-}CH_2C(CH_3) + Ta[CH_2C(CH_3)_3]_3Cl_2$$

$$\Big\downarrow \begin{array}{l}\text{pentane}\\ \text{room temp}\end{array}$$

$$2LiCl + [(CH_3)_3\text{-}C\text{-}]_3Ta{=}CH\text{-}C(CH_3)_3$$

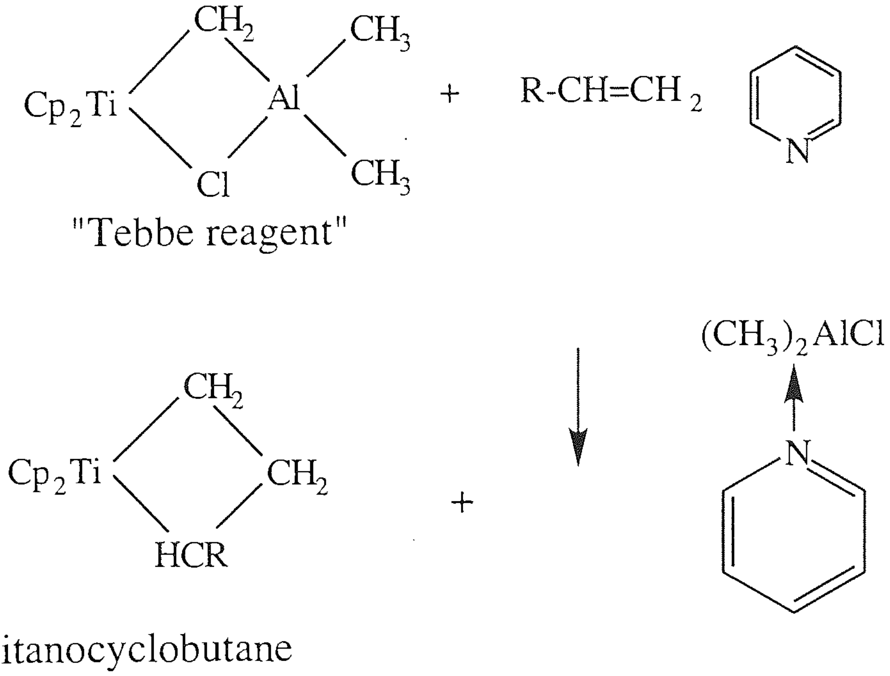
Scheme 2.9

Tantalum neopentylidene complex

This complex was also too stable in regard to metathesis reactions[107], and when the metathesis reaction did proceed a large proportion of side products were also formed.

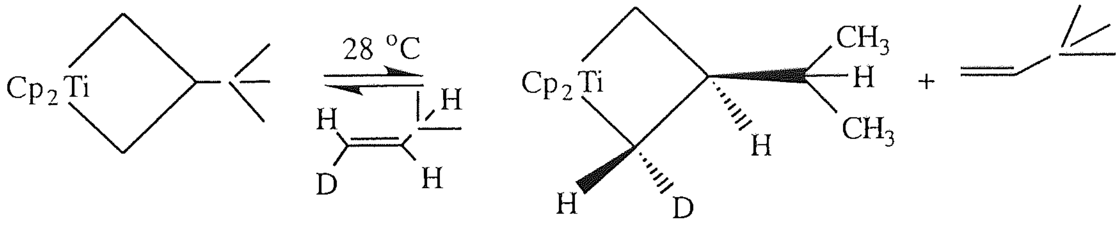
Grubbs[108,109] has managed to isolate a titanocyclobutane using the "Tebbe" catalyst[110] shown in scheme 2.10. Although such structures are ordinarily highly reactive this has been shown to be an active and efficient metathesis catalyst[111,112].

$$Cp_2TiCl_2 + 2AlMe_3 \longrightarrow CH_4 + \underset{\text{Tebbe catalyst}}{Cp_2TiCH_2AlClMe_2} + AlMe_2Cl$$



Scheme 2.10
Tebbe complex

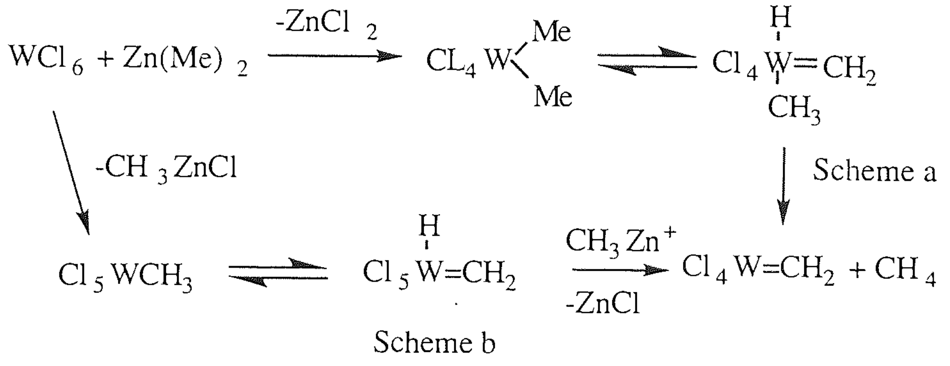
A titanocyclobutane intermediate has been shown to be active in the metathesis of 3,3-dimethylbut-1-ene, see scheme 2.11.



Scheme 2.11
Metathesis of 3,3-dimethylbut-1-ene

Muetterites[113] proposed an explanation of the production of the metallocarbene from the catalyst system. He suggested that the metal alkyl interacted with the WCl_6 followed by elimination of the C-H group, to produce the metallocarbene, shown in scheme 2.12. Evidence comes from the use of tetramethyltin as a cocatalyst, analysis in the initial stages shows the presence of methane.

The reaction product from WCl_6 and $Zn(Me)_2$ in deuterated solvents produced methane free from deuterium, indicating α-hydrogen elimination from a tungsten methyl moiety[113,114].



Scheme 2.12
The metallocarbene mechanism

More recently Schrock[115] has synthesised stable carbenes which are efficient initiators. Such compounds are shown as

$W(CH\text{-}t\text{-}Bu)\text{-}(NAr)(OR)_2$

Ar= 2,6-diisopropylphenyl

OR= O-t-Bu, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, $OC(CF_3)_2(CF_2CF_2CF_3)$

$$WCl_6 \xrightarrow[CH_2Cl_2]{MeOSiMe_3} W(O)Cl_4 \xrightarrow[Octane]{ArNCO} \underset{\text{83\% from } WCl_6}{W(NAr)Cl_4} \xrightarrow[THF/Ether]{2LiO\text{-}t\text{-}Bu}$$

$$\underset{85\%}{W(NAr)(O\text{-}t\text{-}Bu)_2Cl_2(THF)} \xrightarrow{2(t\text{-}BuCH_2)MgCl} \underset{88\%}{W(NAr)(O\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2}$$

$$\xrightarrow[\text{dimethoxyethane}]{PCl_5} \underset{90\%}{W(CH\text{-}t\text{-}Bu)(NAr)(dme)Cl_2} \xrightarrow[-2MgCl_2\ -dme]{2t\text{-}BuCH_2MgCl}$$

$W(CH\text{-}t\text{-}Bu)(NAr)(CH_2\text{-}t\text{-}Bu)_2$

Osborn[116] synthesised $W(CH\text{-}t\text{-}Bu)(OCH\text{-}t\text{-}Bu)_2Br_2$ which was active in the metathesis of cis MeCH=CHEt in the presence of AlX_3 (X=Cl,Br).

2.6 STEREOCHEMISTRY

The reaction conditions and catalyst systems employed during metathesis reactions of acyclic olefins and ring opening polymerisation of cycloolefins affect the stereochemistry of the products produced. This is related to the fact that the metallocarbene intermediate may coordinate monomer with equal facility in orientation leading to either a cis or trans configuration. This was demonstrated by Wang and Menapace[117] who showed that using WCl_6/BuLi as the catalyst, the percentage conversion of trans-2-pentene was much lower than that of the cis isomer. This was confirmed by Basset et.al.[118] and Katz et.al.[119]. The reason for this was thought to be due to steric hinderance that occurred when the trans isomer co-ordinated to the tungsten atom. The reaction is complicated by secondary metathesis of the new olefins produced.

2.6.1 Stereochemistry of olefins in ring opening metathesis polymerisation.

Polymerisation leads to an in chain carbon-carbon double bond and the configuration around this double bond can be either cis (Z) or trans (E). In contrast to acyclic olefins, bicyclic olefins do not undergo secondary metathesis as the carbon-carbon double bonds are sterically hindered by the cyclopentyl rings, and unable to react. Tacticity in a polymer chain is a form of isomerism which arises when the monomer unit contains an asymmetric carbon atom. When two consecutive asymmetric carbons have the same configuration, this is referred to as a meso (m) dyad and if they have opposite configurations, a racemic (r) dyad. There are two types of completely stereoregular polymers that can exist; an isotactic polymer is one which is comprised exclusively of meso dyads and a syndiotactic polymer is comprised exclusively of racemic dyads. Polymers which do not conform to either of these extremes are called atactic. When two asymmetric chiral centres exist per repeat unit and a vinylene unit, which can adopt either cis or trans stereochemistry, this can lead to four distinct regular homopolymers shown in figure 2.1.

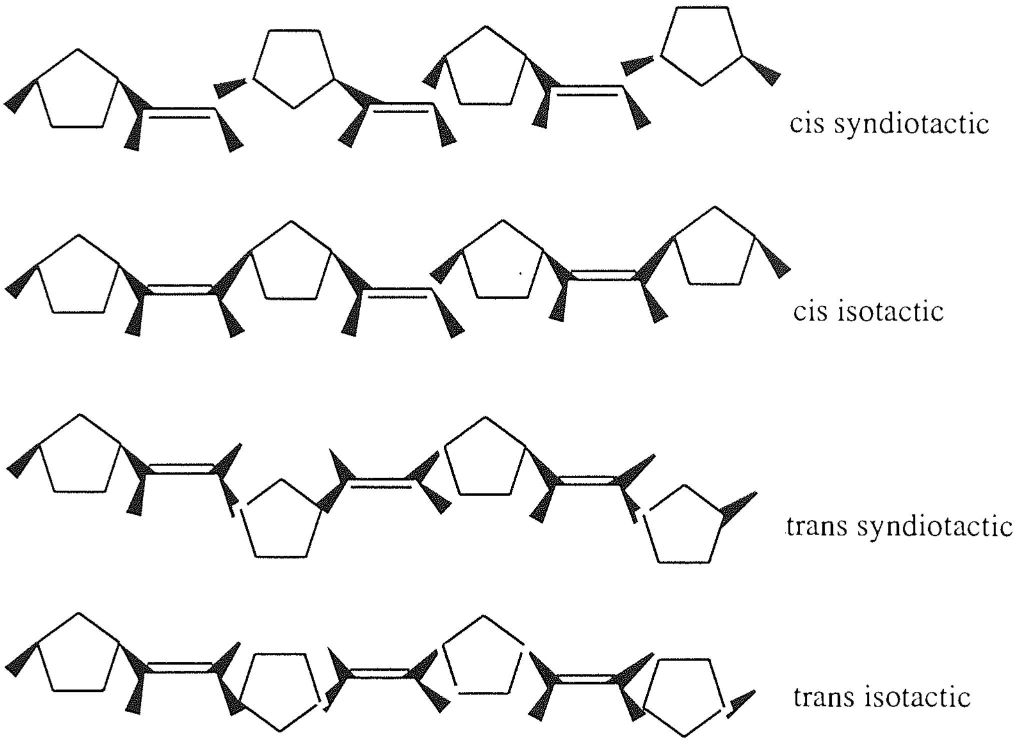


Figure 2.1 Stereochemistry of olefins in ring opening metathesis polymerisation

Ivin/Rooney[120,121] confirmed that a polymer containing only meso dyads leads to a isotactic ring sequence shown in figure 2.2.

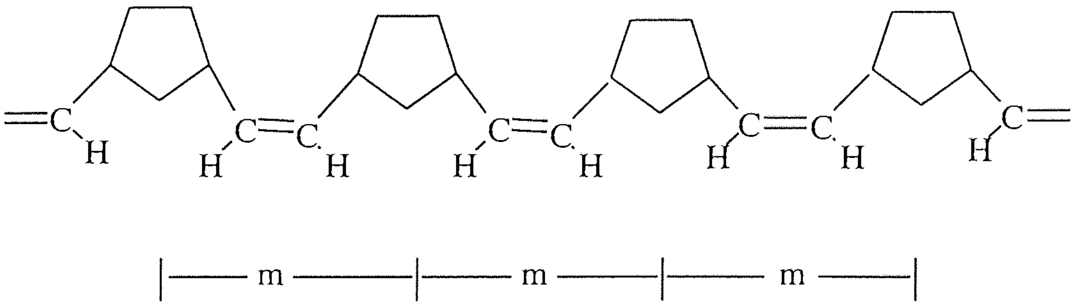


Figure 2.2 Meso dyads in isotactic ring sequence

Whereas a polymer containing only racemic dyads leads to a syndiotactic ring sequence shown in figure 2.3.

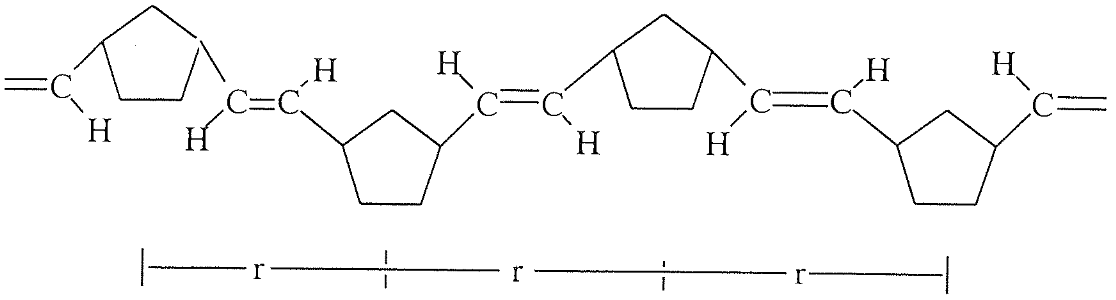


Figure 2.3 Racemic dyads in syndiotactic ring sequence

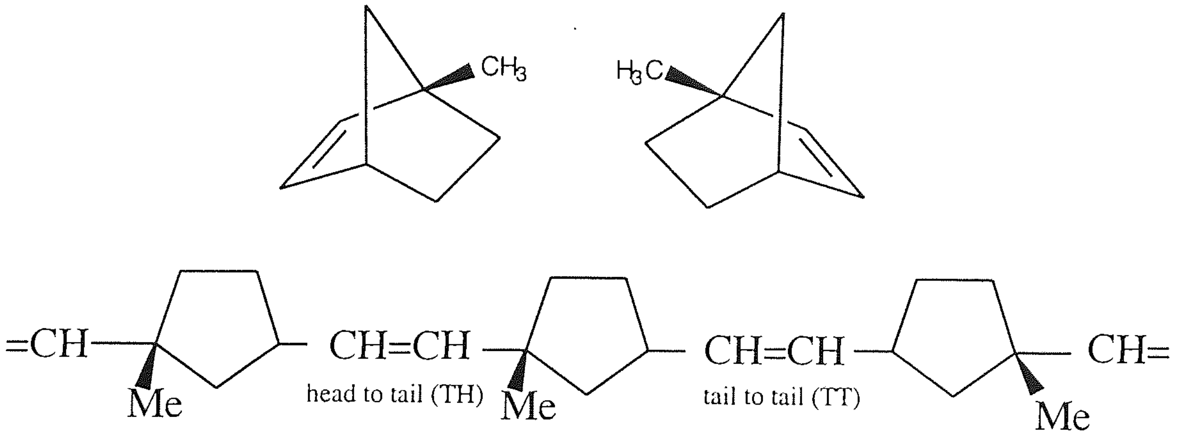
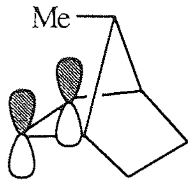
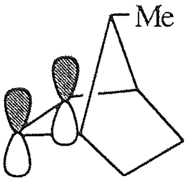


Figure 2.4 Head-tail isomerism in the polymerisation of 4-methylnorbornene

There can be further distinction between the different kinds of polymer when the cyclopentyl rings are substituted as shown below. If the monomer is unsymmetrically substituted it exists in two enantiomeric forms and there is the possibility of head-head (HH), tail-tail (TT) and head-tail (HT) isomerism in the polymerisation of 4-methylnorbornene shown in figure 2.4.

Feast[122] has shown that in general the proportion of cis/trans vinylene units depends on the nature of the transition metal in the catalyst, although substituents on the carbon bridgehead can also affect the outcome, due to possible steric hinderance of any substituent with the lone pair of electrons available for polymerisation as shown below.





2.7 FLUORINATED BICYCLICS

Feast[73] also investigated the effect of halogen substituents on the reactivity of bicyclic monomers. It has been shown that if a halogen atom is directly bonded to the carbon- carbon double bond or if a fluorine atom is bonded to the ring containing the unsaturated carbon atoms, the monomer will not polymerise: this was confirmed by Overberger[72,123].

Feast [87,88] polymerised the monomers shown below via ring opening metathesis.

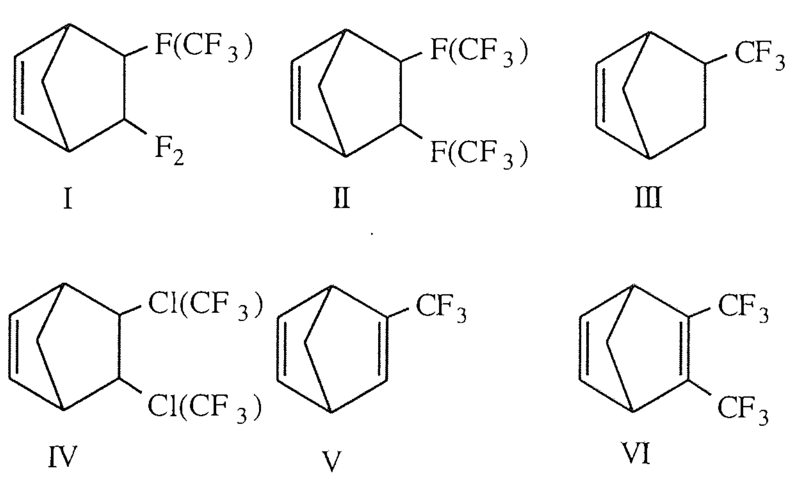


Figure 2.5 Monomers for ring opening metathesis polymerisation

Table 2.4 Fluorinated monomers for ring opening polymerisation

Adduct	Dienophile	Reaction Time/hr	Temperature/ºC	Reference
I	$CF_3CF=CF_2$	72	160	124
II	$CF_3CF=CFCF_3$	24	100	122,125
III	$CF_3CH=CH_2$	72	160	126,127
VI	$CF_3\,CCF_3$	24	100	125,127
	$CF_3CH=CF_2$	72	160	

As monomer VI was the easiest to produce, requiring less drastic reaction conditions than the production of the other monomers, the majority of literature reports refer to the polymerisation of this monomer using various catalysts.

Table 2.5[83] Catalysts for ring opening polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene

Catalyst	Co-catalyst	Molar ratio Cat:Cocat:M	Solvent/ml	Temp/ ºC	Time/hr	Yield(%)
WCl_6	none	1:200	C 1.1	50	48	4
WCl_6	$(C_6H_5)_4Sn$	1:2:150	T 10	RT	1	80
WCl_6	$(nC_4H_9)Sn$	1:2:60	T 10	RT	1	75
$MoCl_5$	none	1:200	neat	80	48	2
$MoCl_5$	$(C_6H_5))_4Sn$	1:2:60	T 10	RT	18	75
$MoCl_5$	$(CH_3)_4Sn$	1:2:200	C 1	50	2min	25
$RuCl_3$	$(CH_3)_4Sn$	1:2:200	CE 1.5	40	2.5	74

M: 2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene

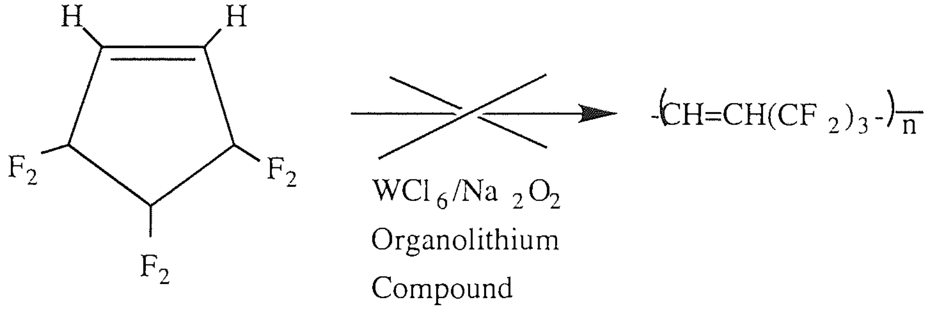
CE: 1:1 (v/v) mixture of Chlorobenzene/Ethanol

C: Chlorobenzene

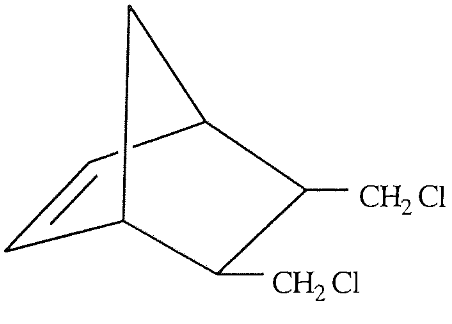
RT: Room Temperature

2.7.1 Reactivity of monomers

The production of the monomers shown in figure 2.5 was a result of the failed polymerisation attempt of 1H,2H-hexafluoropentane shown below, which Feast et. al.[87] hoped would yield a polymer with good elastomeric properties, low Tg and thermal stability.



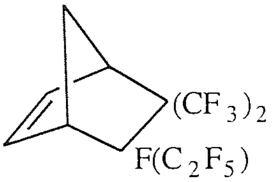
It was proposed that failure of this polymerisation was due to high number of electronegative substituents, which may reduce the π-donor capacity of the double bond to a point where co-ordination to the transition metal is inhibited. But as expected on addition of the catalyst and co-catalyst the colour is seen to change, suggesting that fluorinated cyclopentene does in fact interact with the transition metal.



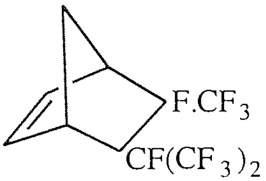
Feast[77] reported the successful polymerisation of the monomer shown above. There have been a few reported successes of polymerisation chlorinated monomers by ring opening metathesis polymerisation. This polymerisation was carried out using $WCl_6/(CH_3)_4Sn$ and $MoCl_5/(CH_3)_4Sn$.

WCl_6 based polymerisation produced a polymer which contained predominantly cis vinylene bonds in an atactic polymer. The polymerisation carried out using $MoCl_5$ produced a polymer which contained predominantly trans vinylene bonds in an atactic polymer.

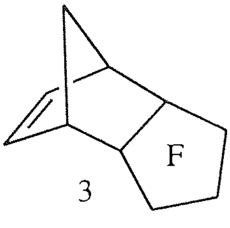
Seehof/Risse[89] produced various monomers for ring opening metathesis polymerisation, these are shown below.



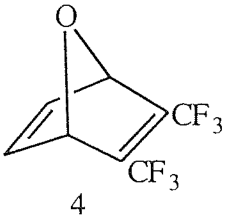
1



2

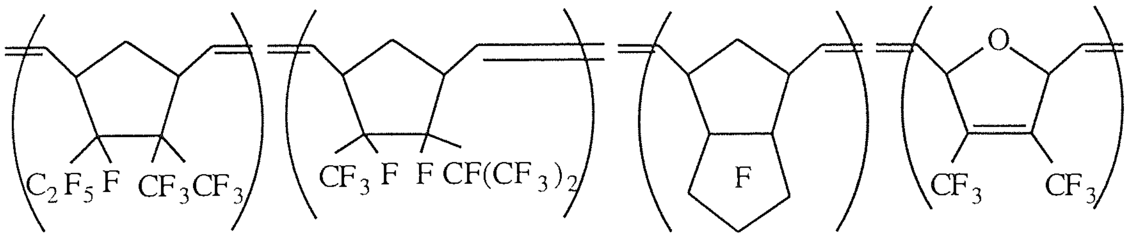


3



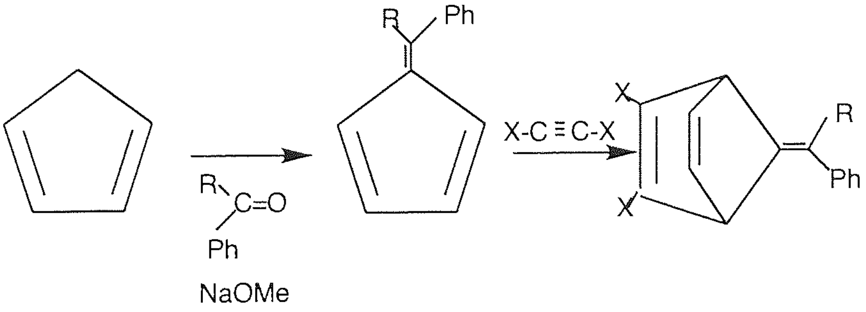
4

All could be polymerised using $WCl_6/(Ph)_4Sn$, although 4 was polymerised using $RuCl_3$ hydrate to yield polymers shown below.



The polymers were found to be amorphous, no melting endotherms were detected by DSC analyses.

As an attempt to extend the range of monomers for ring opening metathesis polymerisation, Feast[128] carried out the production of some aryl substituted bicyclofulvene derivatives shown in figure 2.6.



	R	X
Ia	CH_3	CF_3
Ib	C_6H_5	CF_3
Ic	CH_3	CO_2CH_3
Id	C_6H_5	CO_2CH_3

Figure 2.6 Aryl substituted bicyclofulvene derivatives

Polymerisations were carried out using $MoCl_5/(CH_3)_4Sn$ as tungsten based catalysts were not active.

CHAPTER 3

EXPERIMENTAL

3.1 GENERAL TECHNIQUES

The catalysts employed for olefin metathesis are very sensitive to air and moisture, and so the majority of the work was carried out using high vacuum techniques.

3.1.1 The high vacuum line

The vacuum line shown in figure 3.1 was constructed of glass and consisted of a manifold which was evacuated by an Edwards rotary pump assisted by a mercury diffusion pump that could produce pressures approaching 10^{-3} Torr. Liquid nitrogen cooled cold traps were used to prevent organic and mercury vapours escaping and to prevent fouling of the pump oil. Apparatus could be attached to the vacuum line by the use of four ground glass joints which could be isolated from the manifold by polytetrafluoroethylene taps.

3.1.2 Freeze-thaw degassing

In order to carry out distillations under vacuum the liquids, whether solvent, monomer, must have all dissolved gases had to be removed. A flask containing the liquid to be degassed was attached to the vacuum line and this was then frozen by immersing in a dewar of liquid nitrogen. When frozen, the flask was evacuated by opening the maintap to the vacuum line, when a high vacuum was obtained the tap to the vacuum line was closed. The frozen 'liquid' was allowed to warm up slowly, and trapped gas was released and equilibrated in the atmosphere above the liquid. The procedure was generally carried out three or four times to ensure that all the dissolved gases were removed. The flask was then removed from the vacuum line and stored until required.

3.1.3 Trap to trap distillation

A flask containing the degassed liquid was attached to the manifold of the vacuum line. A receiving flask was also attached to the manifold, evacuated and then cooled by immersing in liquid nitrogen. The main tap was closed and the taps attaching the flasks to the manifold were opened, to allow the liquid to distil into the receiver flask.

3.2 THE SPINNING BAND COLUMN

Fractional distillation is a process which can be used to isolate large quantities of materials, producing very pure samples. The spinning band column shown in figure 3.2 is a special type of fractional distillation. The column contains a band supported on an inner rod that is rotated. This rod may be spun at speeds up to 7200rpm. The advantages of the spinning band column are:-

a) low hold up volume,

b) low pressure drop and

c) high efficiency (capable of separating liquids with a difference of 0.5°C in boiling points).

Figure 3.2 The spinning band column

3.3 APPARATUS

Glassware was cleaned prior to use by soaking with a solution of sodium hydroxide, thoroughly rinsed with distilled water and then dried in an oven at 120 °C for at least 24 hours. With glassware that was difficult to clean a solution of chromic acid was prepared from sodium/potassium dichromate, water and concentrated sulphuric acid[129].

The glassware was left to soak in chromic acid and then thoroughly rinsed with distilled water.

3.4 MONOMER SYNTHESIS

Some organic/polymeric materials have shown very large nlo responses which has been attributed, in part, to the delocalization in the π electron system. These potential advantages are usually counterbalanced by other less attractive properties;
e.g. polyacetylene is insoluble and infusible.
We are attempting to synthesise fluorinated polymers which possess properties similar to those of typical fluoropolymers (e.g. polytetrafluoroethylene), such as high thermal stability, chemical inertness and low water absorptivity, but are easier to handle. Fluorinated polymers often have high internal fields (e.g. polyvinylidenefluoride), which improves alignment of nlo materials in them. It is hoped that this will also aid compatibility between guest and host.

3.4.1 The synthesis and polymerisation of 2,3-bis(trifluoromethyl) bicyclo[2,2,1] hepta-2,5-diene.

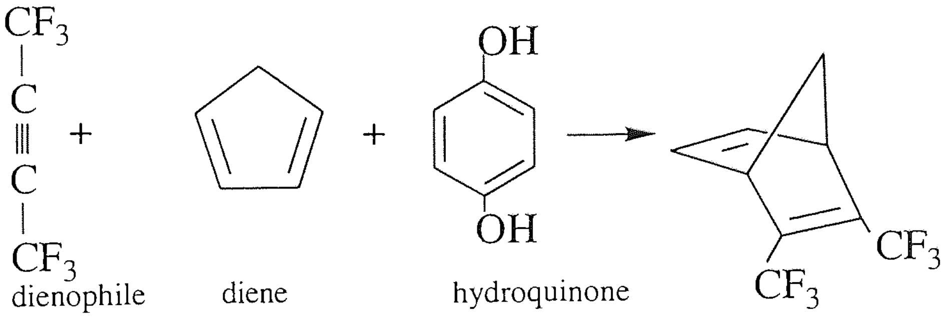
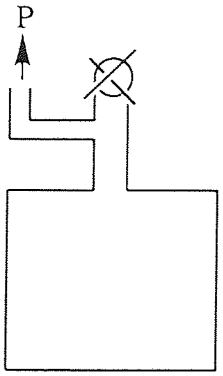


Figure 3.3 The synthesis of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene

The reaction used for the synthesis of this monomer is shown in figure 3.3. The reaction invloved a Diels-Alder reaction between cyclopentadiene and hexafluorobutyne at room temperature. The latter is a gas at STP and hence the reaction was carried out in a steel container. The canister in which the hexafluoro-2-butyne was supplied was found to be convenient for this purpose and is shown below.



The canister was fitted with a removable pressure gauge.

3.4.1.1 Preparation of 2,3-bis(trifluoromethyl) bicyclo[2,2,1] hepta-2,5-diene.

Dicyclopentadiene was placed in a round bottomed flask containing sand and heated to approximately 170 °C. The vapour generated passed thorough a Vigreux column and was collected in a receiving flask placed in an ice bath. The collected cyclopentadiene was analysed by Gas Liquid Chromatography and then degassed on a vacuum line. This was carried out immediately as approximately 20% of cyclopentadiene dimerised to dicyclopentadiene when left standing at room temperature for a few hours.

Hydroquinone (0.03g) was placed in reaction vessel and the degassed cyclopentadiene (10.2g) was then distilled into it. The flask containing the cyclopentadiene/ hydroquinone mixture was then connected by nylon tubing to the cannister which contained hexafluoro-2-butyne (25g). The canister was cooled in a methanol/cardice bath to approximately -80°C, to liquify hexafluoro-2-butyne. The taps on the cannister and reaction vessel were then opened and the cyclopentadiene/ hydroquinone mixture was admitted and then all the taps were closed. The canister was then removed from the methanol/cardice bath and placed behind a safety screen in a fume cupboard and left at room temperature for at least 24 hours. After this period the canister was opened and the liquid product inside collected was transferred to a round bottomed flask. To obtain a pure sample of 2,3-bis(trifluoromethyl) bicyclo[2,2,1] hepta-2,5-diene, the liquid collected was fractionally distilled using a spinning band column (10mmHg at 30°C). The colourless liquid was stored over calcium hydride in a fridge until required. The

2,3-bis(trifluoromethyl)bicyclo[2,2,1]hepta-2,5-diene must be over 90% pure prior to polymerisation as even a trace of dicyclopentadiene can lead to a highly crosslinked and insoluble polymer. The product was collected as the second fraction, purity (96.3%) was determined by GLC.

3.4.1.2 NMR

All NMR spectra were obtained using tetramethylsilane (TMS) as internal standard, for spectra see appendix A4.

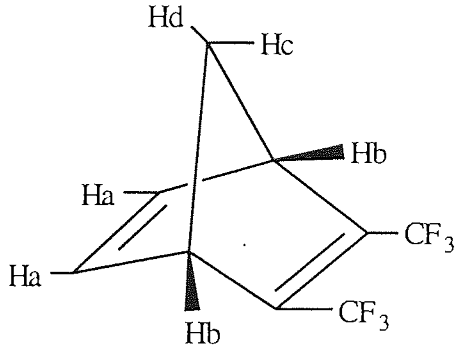


Table 3.2 ^{1}H NMR of 2,3-bis(trifluoromethyl)bicyclo[2.2.1] hepta-2,5-diene.

Hydrogen	ppm	Area	Multiplicity
d	2.1	60.0	triplet
c	2.3	59.9	triplet
b	7.0	118.2	singlet
a	4.0	118.6	singlet

Table 3.3 ^{13}C NMR of 2,3-bis(trifluoromethyl) bicyclo[2.2.1]hepta-2,5-diene.

Peak	ppm
singlet	53.6
singlet	74.5
quartet	123
singlet	143.2
doublet	149.8

3.4.2 Synthesis of 5-(2-bromotetrafluoroethyl) bicyclo[2,2,1]hepta-2-ene

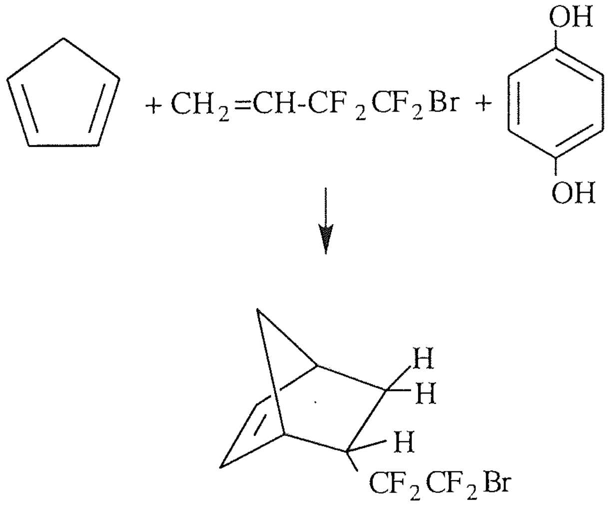


Figure 3.4 The synthesis of 5-(2-bromotetrafluoroethyl)bicyclo[2.2.1]hepta-2-ene

The method used for the synthesis of 5-(2-bromotetrafluoroethyl) bicyclo[2,2,1]hepta-2-ene, shown in figure 3.4, was as described in section 3.4.1.1. Reaction was carried out at 45°C for 18 hours. The product was obtained by fractional distillation and analysed by GLC (purity 22%) and NMR. Distillation failed to produce a pure enough product for polymerisation as complete removal of dicyclopentadiene proved impossible. The NMR spectra obtained were very complicated due to the presence of side products.

3.4.3 The synthesis of 5,5-difluoro-6-trifluoromethyl bicyclo[2,2,1]hepta-2-ene

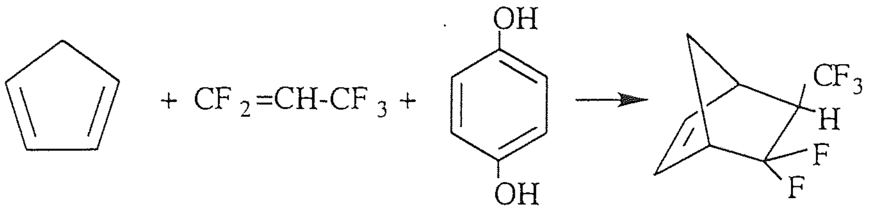
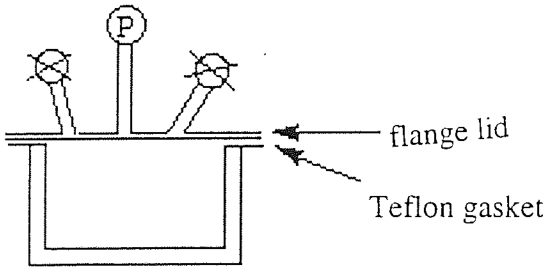


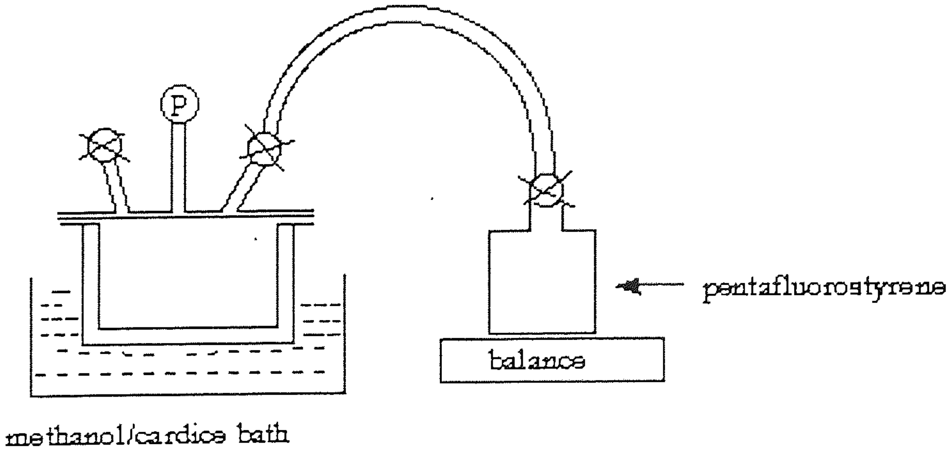
Figure 3.5 The synthesis of 5,5-difluoro-6-trifluoromethylbicyclo[2.2.1]hepta-2-ene

3.4.3.1 Preparation of 5,5-difluoro-6-trifluoromethyl bicyclo [2,2,1]hepta-2-ene

A modification was made to the synthetic procedure for the synthesis of this monomer shown in figure 3.5. This synthesis was carried out in a constructed flanged stainless steel reactor fitted with a pressure gauge shown below.



A canister containing cooled pentafluoropropene was connected by nylon tube to the vessel which was placed in a methanol/cardice bath as shown below. The taps were opened and pentafluoropropene was condensed into the vessel.



When the required amount of pentafluoropropene had been added, the cyclopentadiene was added. Whilst the reactor was still in the cardice/methanol bath at -80°C, all the taps were closed and the vessel removed from the methanol/cardice bath and allowed to warm to room temperature. The vessel was then placed in a silicon oil bath at 160°C for 3 days. As soon as the reactor was placed in the oil bath, the pressure rose to a previously calculated value and during the reaction the pressure steadily fell to a previously calculated final value. The reactor was removed from the oil bath and left to cool to room temperature. The liquid product was removed, fractionally distilled using a spinning band column, and analysed using GLC (purity 21.6%). Distillation failed to remove the majority of the dicyclopentadiene produced even after repeated attempts.

3.4.4 Experimental procedure for the synthesis of 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hepta-2-ene

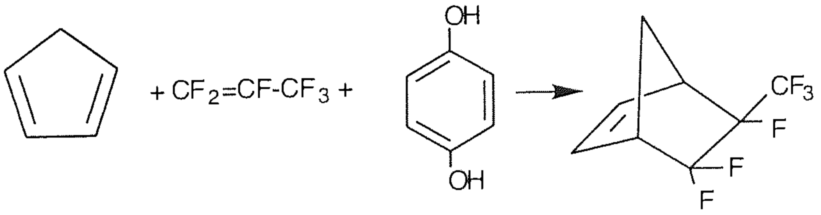


Figure 3.6 The synthesis of 5,5,6-trifluoro-6-trifluoromethylbicyclo[2.2.1]hepta-2-ene

3.5.4.1 Preparation of 5,5,6-trifluoro-6-trifluoromethylbicyclo [2,2,1] hepta-2-ene

This reaction shown in figure 3.6 was carried out using a method similar to that described in section 3.4.3.1. After charging with the reactants the reactor vessel was placed in an oil bath at 160°C for 3 days. The product was recovered by fractional distillation using a spinning band column and analysed using GLC (purity 40.5%). Distillation failed to remove significant amounts of dicyclopentadiene.

3.4.5 Experimental procedure for the synthesis of 5,6-bis(trifluoromethyl)-5,6-difluorobicyclo[2,2,1]hepta-2-ene

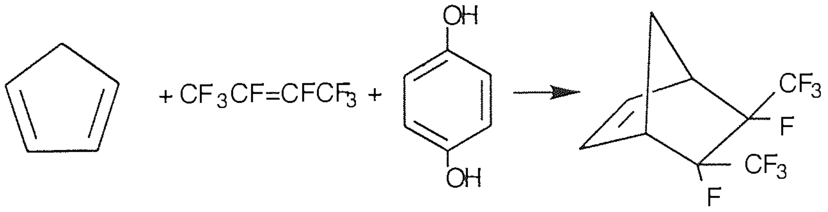


Figure 3.7 The synthesis of 5,6-bis(trifluoromethyl)-5,6-difluorobicyclo[2.2.1]hepta-2-ene

3.4.5.1 Preparation of 5,6-bis(trifluoromethyl)-5,6-difluorobicyclo [2,2,1]hepta-2-ene

This reaction shown in figure 3.7 was carried out using a similar method to the previous reaction except that instead of hexafluoropropene, perfluorobutene was used. The reactor was placed in a silicon oil bath at 120°C for 24 hours. The product was recovered by fractional distillation using a spinning band column and analysed by GLC (purity 60.3%). Even after repeated distillations the product could not be separated from the dicyclopentadiene, thereby making polymerisation impossible.

3.5 FUTURE WORK

Great difficulty was experienced separating the product from the side products (mainly dicyclopentadiene). Several repeated fractional distillations using a spinning band column did not appear to separate the product. A more efficient method of separation needs to be found. NMR's were not very clear as dicyclopentadiene has a very complex spectrum and this tended to overshadow the peaks of the product.

3.6 POLYMERISATIONS

3.6.1 The preparation of tungsten hexachloride in chlorobenzene

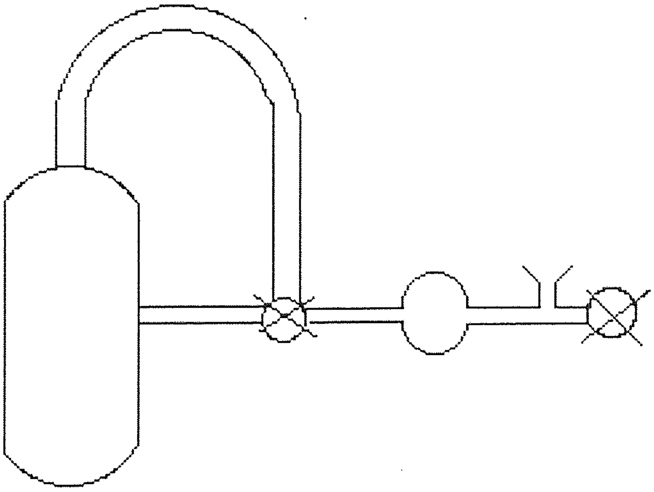
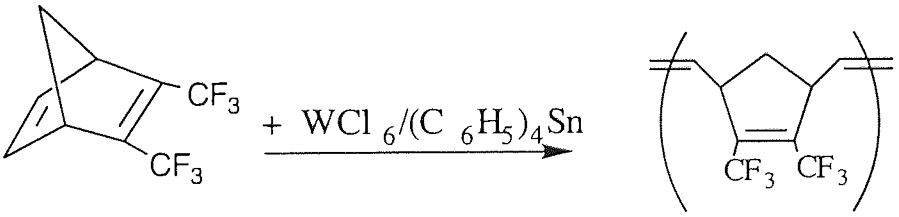


Figure 3.8 Catalyst flask

Tungsten hexachloride (0.85g) was placed into a catalyst flask shown in figure 3.8. The vessel was evacuated and chlorobenzene(11.45g) was distilled into it. A deep blue/black solution was produced(0.22mol dm^{-3}).

3.6.2 Experimental procedure for the synthesis of poly-{2,3-bis (trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene} using tungsten-tin catalyst



3.6.2.1 The synthesis of poly-{2,3-bis(trifluoromethyl)bicyclo [2.2.1] hepta -2,5-diene} using tungsten hexachloride

Tetraphenyltin (0.25g) was placed into a clean, dry vessel which, was then evacuated. Tungsten hexachloride solution (0.74cm^3) was injected through a subaseal into the reaction vessel and the vessel shaken for approximately 10 minutes until the colour of the solution changed from blue/black to a red/brown colour, a red /brown indicating that the catalyst mixture is active. Chlorobenzene (15.4g) was distilled into the vessel and then the dried and degassed monomer (10g). The vessel was left at room temperature for approximately 30 minutes, during which time polymerisation took place. A very dense gel like material was produced which was insoluble in virtually all common organic solvents. Several polymerisations using this catalyst system were carried out and the variation of molecular weights observed is shown in table 3.4.

Table 3.4 GPC results of the polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten-tin complex.

Run	Mn	Mw	Polydispersity
1	500,000	900,000	1.8
2		120,000	broad
3	400,000	1,200,000	3.0

Reproducible materials were not obtained even under identical conditions, this was due to impurities in the monomer.

3.6.2.2 ^{13}-C NMR

All NMR spectra were obtained using tetramethylsilane (TMS) as internal standard, for spectra see appendix A4.

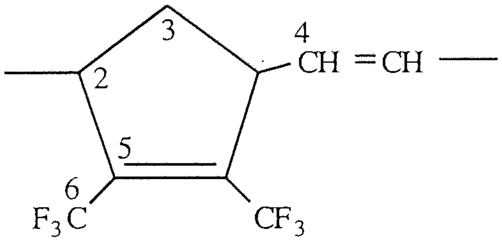


Table 3.5 ^{13}C NMR of poly-2,3-bis(trifluoromethyl)bicyclo [2.2.1] hepta-2,5-diene via tungsten/tin complex.

Carbon atom	Multiplicity	Chemical Shift

3		
cc/tc/tt	triplet	37
2		
trans	singlet	49
cis	singlet	44
6	quartet	116-127
4		
t/c (trans further downfield)	doublet	132
5	singlet	139

3.6.3 The synthesis of poly-2,3-bis (trifluoromethyl)bicyclo[2,2,1] hepta-2,5-diene using molybdenum pentachloride.

Tetraphenyltin (0.125g) and molybdenum pentachloride (0.04g) were placed into a clean, dry reaction vessel. Chlorobenzene (2g) was distilled into the reaction vessel and the mixture shaken until a red/brown colour was observed. 2,3-Bis (trifluoromethyl)bicyclo [2,2,1]hepta-2,5-diene (3g) was distilled into the reaction vessel which was then left for 1/2 hours. A black polymer was produced, which when washed with acetone, subsequently turned paler, due to the removal of some of the catalyst residue. The polymer was then dried in a vacuum oven.

Table 3.6 ^{13}C-NMR of poly-2,3-bis(trifluoromethyl)bicyclo [2.2.1] hepta-2,5-diene via molybdenum/tin complex.

Carbon atom	Multiplicity	ppm
3 cc/tc/tt	triplet	37
2		
trans	singlet	48
cis	singlet	43
6	quartet	116-127
4 t/c	doublet	131
5	singlet	139

Different intensities for cis/trans ratios were observed in the tungsten based polymers compared with the molybdenum based polymers, which had a greater proportion of trans-double bonds. The molybdenum based polymer also contained significant quantities of catalyst residue: a more effective method of removal needs to be found.

3.7 ESTIMATION OF NONLINEAR OPTICAL PROPERTIES BY LASER TECHNIQUES.

Ideally adding a known nlo active material to an nlo active host should enhance the nlo properties of the system as a whole. The effect of the compatibility of paranitroaniline may be examined by comparison of its nlo properties as a pure material to its nlo properties as a guest in a guest/host system.

2-Nitro-5-aminobenzotrifluoride, 2-amino-5-nitrobenzotrifluoride and paranitroaniline were tested as guests in poly-{2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene}, prepared using both tungsten and molybdenum catalysts. Films were produced with varying concentrations of additives dissolved in the polymer. The films were also examined under a microscope to observe the homogeneity of the additive in the polymer. The films were then placed in the path of a Nd/YAG laser and the second harmonic intensity was measured relative to quartz. Some films were poled prior to laser testing to check what effect, if any, this process had on the polymers and/or additives.

3.7.1 Experimental procedure.

A sample of each polymer (0.5g) was dissolved in acetone (5ml) in a small vial along with the appropriate quantity of each additive to be tested. The solutions were left to evaporate in a fumecupboard overnight and the polymer films recovered from the bottom of the sample vials.

All results were obtained after placing polymer film samples in the path of the laser, two measurements were taken relative to quartz. Ideally a trace similar to figure 3.9a should be obtained, but this is rare and usually a trace similar to figure 3.9b is obtained.

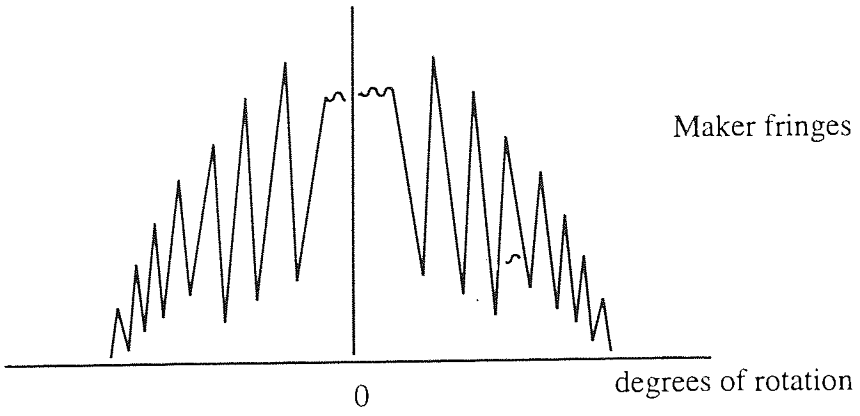


Figure 3.9a Maker fringes

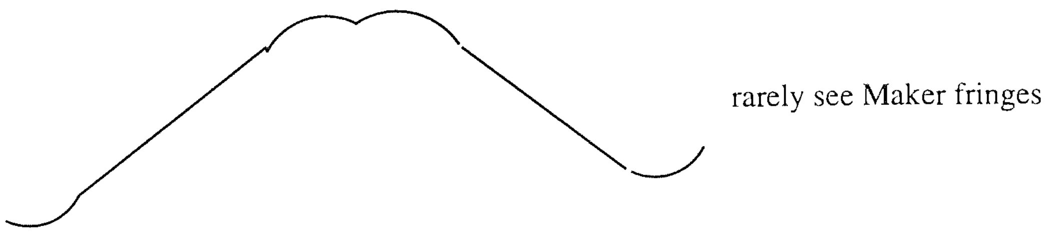


Figure 3.9b Experimentally observed chromatogram

The peak measurement is taken from each side of the curve, then the average value is then calculated.

3.7.2 Laser results for poly-{2,3-bis(trifluoromethyl)bicyclo[2.2.1] hepta-2,5-diene} prepared using tungsten

Polymer1- Poly2,3-bis(trifluoromethyl)bicyclo[2.21]hepta-2,5-diene via $WCl_6/Sn(Ph)_4$.

Polymer2- Poly2,3-bis(trifluoromethyl)bicyclo[2.21]hepta-2,5-diene via $MoCl_5/Sn(Ph)_4$.

Additive1- Paranitroaniline

Additive2- 5-Nitro-2-aminobenzotrifluoride

Additive3- 2-Nitro-5-aminobenzotrifluoride

Table 3.7 NLO intensity for poly-2,3-bis(trifluoromethyl) bicyclo[2.2.1] hepta-2,5-diene via tungsten/tin complex.

Polymer	Additive	%	Poled	NLO intensity relative to quartz
1	none	-	no	0.2135×10^{-2}
1	none	-	no	0.1265×10^{-2}
1	none	-	yes	0.3665×10^{-2}
1	none	-	yes, left a few days	0.557×10^{-2}

Prior to poling, slight nlo properties, which were increased by poling, but not much change after a few days.

Table 3.8 NLO intensity for poly-2,3-bis(trifluoromethyl)bicyclo [2.2.1] hepta-2,5-diene via tungsten/tin complex doped with 5% paranitroaniline.

Polymer	Additive	%	Poled	NLO intensity relative to quartz	Homogeneity
1	1	5	no	0.72	
1	1	5	no	0.6335	
1	1	5	yes	0.7035	
1	1	5	yes	0.803	
1	1	5	yes, left a few days	0.867	homogeneous

NLO properties before poling better than without additive, but after poling there does not appear to be much difference.

Table 3.9 NLO intensity for poly-2,3-bis(trifluoromethyl)bicyclo [2.2.1] hepta-2,5-diene via tungsten/tin complex doped with 10% paranitroaniline.

Polymer	Additive	%	Poled	NLO intensity relative to quartz	Homogeneity
1	1	10	no	0.34×10^{-2}	
1	1	10	no	0.2235×10^{-2}	
1	1	10	yes	1.5535×10^{-2}	
1	1	10	yes	2.44×10^{-2}	
1	1	10	yes, a few days later	0.8785	additive mostly round edges in small patches

Adding 10% paranitroaniline slightly increased nlo properties compared to the same polymer without additive. Poling greatly increased the nlo properties of this polymer.

Table 3.10 NLO intensity for poly-2,3-bis(trifluoromethyl)bicyclo [2.2.1]hepta-2,5-diene via tungsten/tin complex doped with 5-nitro-2-aminobenzotrifluoride.

Polymer	Additive	%	Poled	NLO intensity relative to quartz	Homogeneity
1	2	5	no	0.2235×10^{-2}	
1	2	5	no	0.77×10^{-2}	
1	2	5	yes	0.9235×10^{-2}	
1	2	5	yes	0.3535×10^{-2}	
1	2	5	yes, left a few days	0.493×10^{-2}	additive mostly around edges in small patches
1	2	10	no	0.7385×10^{-2}	
1	2	10	no	1.7065×10^{-2}	
1	2	10	yes	0.7865×10^{-2}	
1	2	10	yes	0.8265×10^{-2}	two definite phases observed

Slight nlo properties before poling but not much difference after poling.

Table 3.11 NLO intensity for poly-2,3-bis(trifluoromethyl)bicyclo [2.2.1]hepta-2,5-diene via tungsten/tin complex doped with 2-nitro-5-aminobenzotrifluoride.

Polymer	Additive	%	Poled	NLO intensity relative to quartz	Homogeneity
1	3	5	no	0.187×10^{-2}	
1	3	5	yes	0.703×10^{-2}	
1	3	5	yes	0.6965×10^{-2}	
1	3	5	yes, left a few days	0.34×10^{-2}	small crystalline patches
1	3	10	no		
1	3	10	yes	0.3265×10^{-2}	homogeneous

Polymer1 + 5% additive 3 slight nlo properties, which increase after poling, but decays after a few days. Polymer1 + 10% additive 3 showed very little nlo properties, before and after poling.

Table 3.12 NLO intensity of poly-2,3-bis(trifluoromethyl) bicyclo[2.2.1] hepta-2,5-diene via molybdenum/tin complex.

Polymer	Additive	%	Poled	NLO intensity relative to quartz
2	none	-	no	0.41×10^{-2}
2	none	-	no	0.4535×10^{-2}
2	1	10	no	0.8935×10^{-2}
2	1	10	no	1.56×10^{-2}

Slight nlo properties prior to poling. Adding paranitroaniline increased nlo properties.

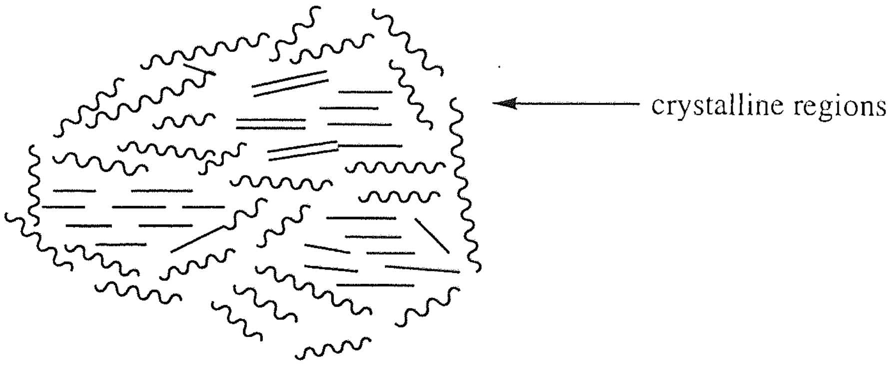
There are no measurements for samples of polymer 2 after poling because all these films were destroyed when poling was attempted. This was due to the fact that the Tg's of these polymers were much lower than expected. Low Tg's mean that poling the polymers will not affect the second harmonic intensity, as alignment of the additive is not maintained during cool down.

3.7.3 Second Harmonic Generation

KBr discs of polyhexafluorobutylmethacrylate and polypentafluorostyrene were tested at a fundamental of 830nm for second harmonic generation relative to urea. However they did not show any SHG properties relative to urea. This could mean that the powdered polymers are isotropic and have no ordering at all, and that poled polymer films would show second order nonlinear optical properties, but it is more likely that the polymers are anisotropic as the other laser tests show that they do not show much with regard to second order nonlinear optical properties.

3.8 Homogeneity of Polymer Films.

All the doped polymer films were examined under a microscope to check the homogeneity of the films.



As can be seen above most of the doped polymer films showed some degree of phase separation and crystallinity. This leads to results dependent on which area of film the laser beam strikes, not a measurement representative of the film as a whole. Adding dopant reduces Tg and as DSC was not effective in determining the Tg of the polymers, possibly DMA would be a better method.

3.9 Conclusions and future work

The unsymmetrical curves observed for our films are possibly due to the films not being completely flat. No significant nlo properties were observed for any of these films. It would be advantageous to synthesise other functional polymers to investigate if they would demonstrate any larger nlo activity.

CHAPTER 4

THE RING OPENING POLYMERISATION OF HETEROCYCLIC MONOMERS.

4.1 INTRODUCTION

The fluorinated polymers produced via ring opening metathesis polymerisation showed no significant non-linear properties. Therefore other methods of synthesis of polymers that could be functionalised with groups that show non-linear effects were investigated. The monomers producing these polymers would be constructed as to possess functionality already or be readily functionalised. The cationic ring opening polymerisation of bicyclic monomers was to be investigated because it was felt that the aromatic ring in such monomers could be functionalised. Historically, ring opening polymerisation of cyclic ethers is one of the oldest examples of the formation of macromolecules. Ionic ring opening polymerizations are divided into three types, namely cationic, anionic and co-ordinate anionic polymerisation.

The main chemical factors affecting the free energy of polymerization in approximate order of decreasing importance are:-

a) the size and nature of the ring in the monomer and hence the steric strain

b) substituents in the monomer, and hence the polymer,

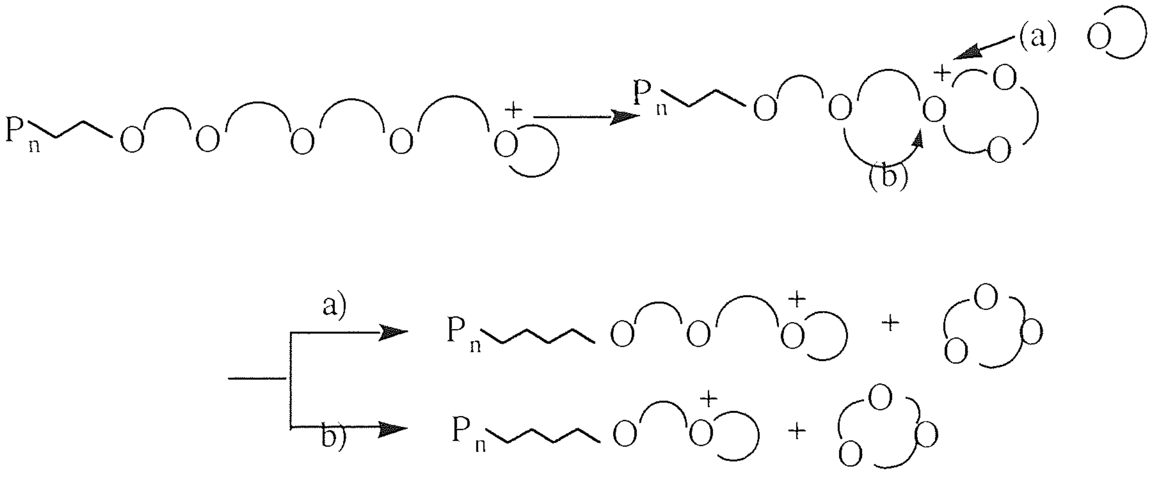
c) geometric isomerism in the polymer, cis/trans,

d) configurational isomerism in the polymer, tacticity.

When cyclic compounds are polymerised by ring opening it is frequently found that in addition to linear high polymer, a series of cyclic oligomers is formed. It is likely that these oligomers are formed by 'backbiting' or 'tailbiting' reactions of the growing polymer chain, which in the case of cationic polymerisation involves a propagating oxonium ion.[130] shown in figure 4.1.

4.2 METHODS OF INITIATION

Several types of compound are described as initiators for the cationic polymerisation of oxacyclics. They are not equally well suited for all monomers and the effectiveness of these initiators depends very much on the conditions employed. Lewis and protonic acids are the classic initiators for the cationic polymerisations of heterocyclics.



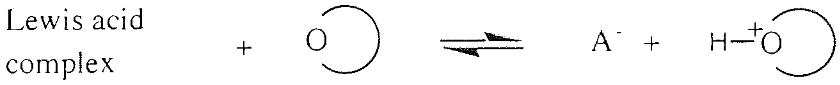
mechanism of tailbiting

Figure 4.1

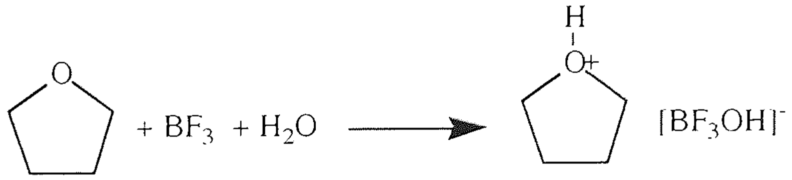
4.2.1 Lewis acids

A Lewis acid can be defined as a species which enters into a reaction by employing an empty orbital or is electron deficient.[131] $AlCl_3$, BF_3, BF_3-complexes, $SnCl_4$ and $TiCl_4$, are the most commonly used Lewis acid initiators. Some strong Lewis acids initiate polymerisation directly, however a cocatalyst which will provide either a proton or an alkyl group is usually required. The ability of Lewis acids to initiate polymerisation without a cocatalyst depends on both the ring strain and the nucleophilicity of monomer as well as the strength of the Lewis acid.

The initiation step can be represented as shown below.



However the reaction is much more complicated and may involve a number of equilibria. Complexation occurs between the Lewis acid and the nucleophilic oxacyclic compound.



4.2.2 Protonic acids

Perchloric, fluorosulphonic, trifluoroacetic and trifluoromethane sulphonic acids are the acids most commonly used for initiation of cationic polymerisation. Most undiluted pure protonic acids, from the very weak carboxylic acids to the very strong perchloric and trifluoromethanesulphonic acids, display a covalent structure with little self-dissociation into ions, but often considerable association into dimers or higher aggregates through hydrogen bonding.

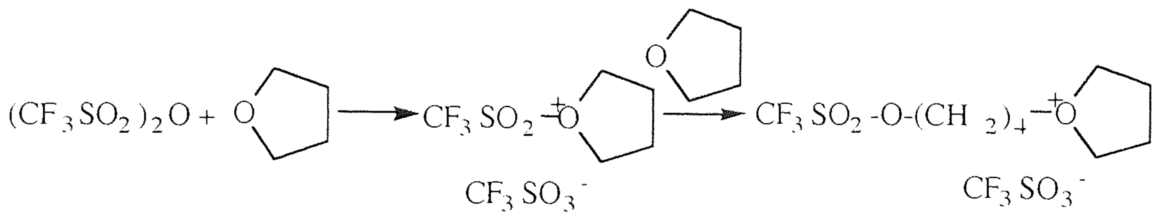
$$\mathrm{HA} \overset{\mathrm{HA}}{\rightleftharpoons} \mathrm{H_2A^+A^-}$$

The minimal strength of protonic acid required for polymerisation is dependent on the nucleophilicity of a monomer. Trifluoromethanesulphonic acid is an efficient initiator for the polymerisation of nearly all heterocyclic monomers. However other factors affecting the choice of acid initiator include the solubility of the acid in the common solvents used, its inertness towards them and the relative stability of the ions formed in the protonation reaction against their collapse to the corresponding ester etc. All these factors can play a major role in determining the real qualities of possible initiators.

4.2.2.1 Trifluoromethanesulphonic acid

Trifluoromethanesulphonic acid (triflic acid)[132] has often been acclaimed as the strongest of all known monoprotic organic acids. It does not provide a source of fluoride ions even in the presence of strong nucleophiles. Hazeldine and Kidd were the first to report a synthesis of trifluoromethanesulphonic acid in 1954. Pure trifluoromethanesulphonic acid is a clear, colourless liquid which boils at 162°C (760Torr) and fumes in moist air until it is converted to a stable monohydrate which is a solid at room temperature (MP 34°C).

Triflic anhydride can be a bifunctional initiator for polymerisation[133]



propagation may occur through both the oxonium (as above) and ester function.

$(CF_3SO_2)_2O$ is a far superior initiator for cationic polymerisation than BF_3 or its complexes, which stems from the higher stability of the anions. BF_4^-, BF_3OR^- anions are known to break easily and give highly nucleophilic F^- or OR^- anions which then cause termination.

4.2.2.2 Protonic acids with complex anions

Combination of e.g. HF with BF_3 or SbF_5 in a polar solvent should formally result in the formation of the corresponding protonic acid as shown below.

$$HX + MtX \rightleftharpoons HX.MtX_n \rightleftharpoons H^+(MtX_{n+1})^-$$

Mt = metal

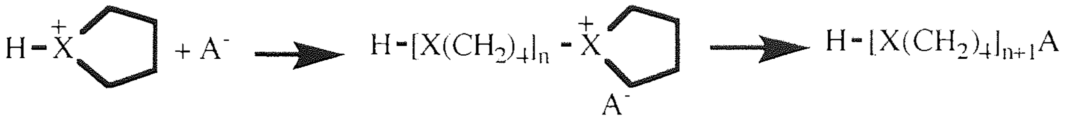
The stability of the complex anion depends on the nature of both Mt and X and decreases in the following order.

$$SbF_6^- \sim AsF_6^- > PF_6^- > SbCl_6^- > BF_4^- > AlCl_4^-$$

In general this stability depends on geometric (crowding of halogen atoms) and electronic features (electronic structure of the central atom and its ability to stabilise the negative charge).

4.2.2.3 Protonic acids with non-complex anions

If the gegenion A^- denotes a non-complex anion, e.g. Cl^-, $CF_3SO_3^-$, then the competition between the recombination of counterions and propagation has to be considered because such anions may recombine with growing macrocations to give covalent bonds. This is the major difference between non-complex anions and complex anions, the latter being unable to form such chemical bonds except by dissociation. Thus in the polymerisation with non-complex anions, recombination after a certain number of propagation steps can be expected.



Thus a given anion may be unable to sustain the polymerisation of a monomer of low nucleophilicity whereas the same anion can recombine only after thousands of propagation steps of a more nucleophilic monomer. The chloride anion can be used as an example: this anion cannot give rise to the polymerisation of cyclic acetals or ethers because simple addition of the initiator (e.g. HCl) to the first monomer molecule would take place. On the other hand, highly nucleophilic N-substituted cyclic amines can be successfully polymerised to high polymerisation degrees with Cl^- anions.

4.2.2.4 Other cationic initiators

There are many initiators for cationic polymerisation[134], these include:-

a) carbenium ions such as triphenylmethylium salts $(C_6H_5)_3C^+A^-$ initiate olefins by direct addition, although steric hindrance is an important factor.

b) Oxocarbenium ions such as

$$R\text{-}C\equiv O^+A^-$$

where $A^- = BF_4^-, PF_6^-$ etc.

c) Onium ions such as $R_3O^+A^-$ have been shown to be initiators for all classes of heterocycles.

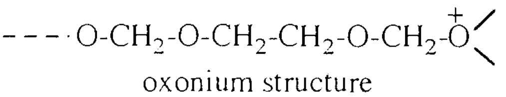
d) Most stable commercial trityl cations initiate by hydride abstraction. Cations generated in situ (benzhydryl type) are efficient in most cases.

The role of the initiator, whichever is used, is therefore predominantly seen as generating a hydroxonium or alkyloxonium species such as

$---\ O\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{+}{C}H_2$

alkoxycarbenium structure

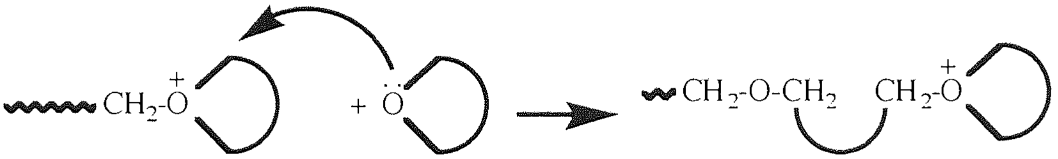
or



oxonium structure

4.3 PROPAGATION

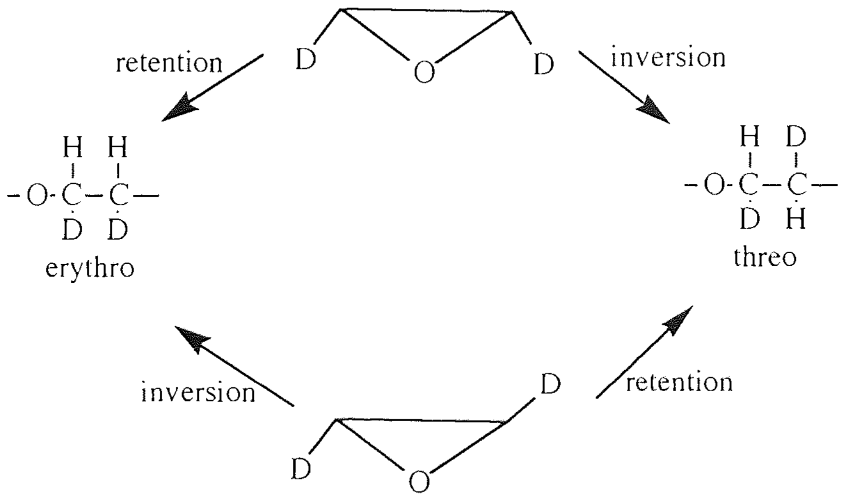
Propagation involves attack of monomer at the a carbon atom of such oxonium species:-



The polymerisation of cyclic ethers proceeds with inversion of configuration[203]. Cis and trans di-deuterated monomers such as shown below have been used to demonstrate this fact.

cis $\xrightarrow{+\text{ inversion}}$ threo

trans $\xrightarrow{+\text{ inversion}}$ erythro

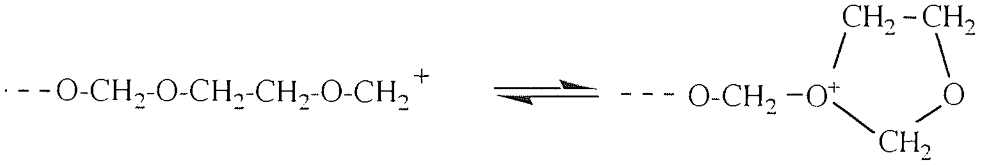


A 70/30 mixture of cis/trans ethylene oxide produced a 70/30 mixture of threo- and erythro- diads.

In the cationic polymerisation of heterocyclic monomers an increase of reactivity of monomers is accompanied by a decrease in the reactivity of the propagating active centres. The rate constants of propagation follow the reactivity of active centres and very large differences between different classes of monomers may be found. By comparison, in the polymerisation of alkenes, an increase of reactivity of carbocations is nearly compensated for by the decrease in reactivities of monomers, and similar rate constants of propagation are found for a wide range of monomers.

Oxonium ions are much more stable than carbocations and thus much more discriminating in their reactions. The much higher stability of oxonium ions, compared to that of the majority of carbocations, reflects the fact that oxonium ions can be considered to be carbocations bonded to and therefore stabilised by electron donating groups.

In the polymerisation of 1,3-dioxolane, the carbenium ion is stabilised by an a-oxygen[130] shown below.



Such stabilisation systems reduce the frequency of transfer and termination which have a significantly greater activation energy in these systems than in the polymerisation of alkenes where the intermediate is a carbenium ion.

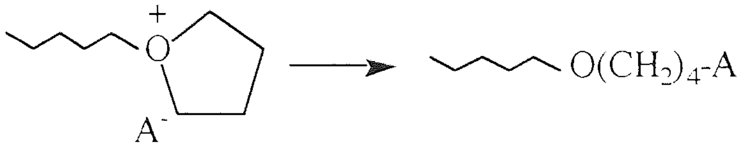
$$-O-CH_2-O-CH_2-CH_2-\overset{+}{O}=CH_2 \rightleftharpoons -O-CH_2-O-CH_2-CH_2-O-\overset{+}{C}H_2$$

This equilibrium is also feasible, the ring strain of the system should determine the position of equilibrium.

The rate of polymerisation increases for a given group of heterocycles with increasing ring strain and with decreasing degree of substitution. Ring strain facilitates breaking of the bond between a carbon atom and heteroatom in the intermediate onium ion while increasing substitution hampers the approach of a new monomer molecule. For approximately the same ring strain, the rate of polymerisation for homopolymerisation changes in the order:

acetals > ethers >sulfides >amines.

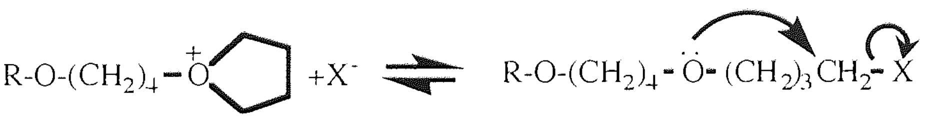
In dealing with propagation reactions the nature of the gegenion (A^-) has also to be considered. The more stable the counterion (A^-), i.e. the stronger the acid from which it is derived, the less likely it is to be involved in termination reactions with the propagating cation, such as



4.4 TERMINATION AND TRANSFER

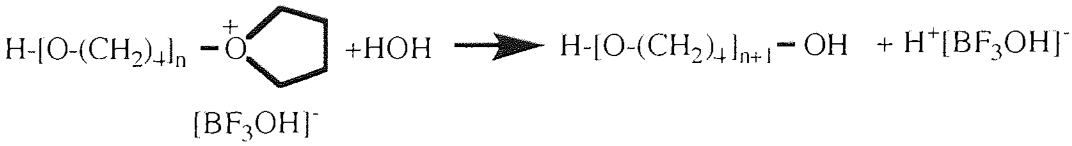
Termination is the least understood step of the polymerisation of cyclic compounds. Chain transfer and termination reactions leave their imprint primarily on the resulting structure of the end groups. The borderline between transfer and termination is not very sharp and the following distinctions for transfer are used: every act of transfer forms one 'dead' macromolecule but regenerates an active centre. Termination forms one dead macromolecule and annihilates one active species.

Reversible termination may occur by recombination of the growing macrocation with an anion.



$X^- =$ halide ion, ClO_4^-, $CF_3SO_3^-$ etc.

Transfer may be illustrated by transfer to traces of water.



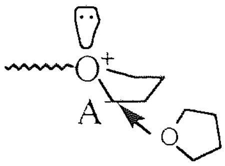
The possibility always exists for reinitiation by the terminated species, although in this case the product of transfer reinitiates without involving the dead polymer molecule. Cyclic amines, sulfides, esters, ethers and acetals were demonstrated to polymerise without signifcant amounts of transfer or termination. The degree of polymerisation is also affected by the temperature of polymerisation. As increasing the temperature also increases kinetically the likelihood of transfer and termination reactions.

4.5 SOLVENTS

Since the solvents used for cationic polymerizations must sustain the existence of cations, they must be protophobic or neutral. Any tendency of the medium to interact with the electrophilic initiator would jeopardize the chances of building up a reasonable concentration of active species. Even with formally acceptable solvents, care must be taken to ensure that no specific chemical interaction occurs, particularly when using strong acids as initiators.

Apart from the generalised solvating power of the medium, there exist more specific interactions between solvent and other components of a polymerisation system which must sometimes be taken into account. For example, the solvent may play a cocatalytic role. Another factor affecting choice of solvent is the ease of purification of a given solvent. Some solvents are considerably more difficult to purify than others. e.g. nitrobenzene. It is for this reason, and because they are generally non-specific and possess an acceptable degree of polarity, that methylene chloride and ethylene chloride are by far the most frequently employed solvents in cationic polymerisation.

Most solvents, not only ethers but also halogenated solvents, have a stronger tendency to solvate cations than anions. In anionic systems, the solvation is directed not towards growing centres but towards counterions. Therefore there is a tremendous difference between dissociated anions which are really 'free' non-solvated ions and ion pairs that become strongly solvated. On the the other hand, the difference between propagating dissociated cations and ion pairs in cationic systems is very small because both species are strongly solvated. This is less important for the ring opening polymerisation, where the pyramidal (non flat) structure of the oxonium ions, shown below decreases chances of the steric hindrance from counterion[135].



Generally the solvent is present to encourage:-

a) dissociation of ion pairs and

b)"donicity"- complexation with ions particularly cations.

4.6 MONOMERS

The basic requirements for suitability of monomers for cationic polymerisation are:

a) a site for attack by positively a charged centre, e.g. C=C or heteroatom,

b) a decrease of the free energy by converting a monomer into polymer and

c) a balance between monomer reactivity and stability of propagating active centres. The latter may be defined as a chemoselectivity of propagation versus undesired transfer and termination reactions.

4.6.1 Factors affecting reactivity of monomer in ring opening polymerisation

The three main factors which affect the reactivity of the monomer are;

a) the nature of the heteroatom, its electronegativity and bond strength with the carbon atom,

b) the size of the ring and associated free energy of polymerisation and

c) steric factors.

Nucleophilicity reflects the ability of the species to combine with an electrophilic substrate, determined by the kinetically controlled conditions, whereas basicity is measured under thermodynamically controlled conditions. Among factors affecting the basicity of the monomer are;

a) inductive effects: increasing the positive inductive effect tends to increase the donor ability e.g. compare 2,5-dimethyltetrahydrofuran with tetrahydrofuran,

b) conjugation: because a lone pair of electrons on a heteroatom can interact with an adjacent p- orbital, conjugation diminishes the ability of the heteroatom to co-ordinate with an acceptor molecule,

c) steric affects: the presence of bulky groups close to the heteroatom or on the acceptor molecule may inhibit the interaction of a monomer with a cation,

d) the ring size: ring strain causes a decrease in the bond angle involving a heteroatom, which results in less steric hindrance to interaction; changes in its valence angle result in a variation of the electron density on the heteroatom.

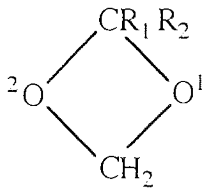
As the thermodynamic driving force in the polymerisation of heterocyclics is a release of the ring strain, polymerisation usually goes to completion for rings which are either smaller or larger than five and six membered. Unsubstituted five membered cyclic ethers and acetals polymerise above an equilibrium monomer concentration, which is temperature dependent. Monosubstituted rings polymerise much less readily and disubstituted rings usually do not polymerise at all, but such factors depend on the position of the substitution relative to the heteroatom.

The reactivity of monomers generally decreases in the order of their basicities and nucleophilicities. On the other hand the most nucleophilic monomers produce the most stable and least reactive onium ions. Because rate constants of propagation follow the order of reactivities of growing species, the highest propagation rates are observed in polymerisation of the least nucleophilic monomers, i.e. orthoesters and acetals and the lowest rates in polymerisation of sulphides and amines.

4.7 ACETALS

There exists a class of heterocyclic monomers which contain more than one oxygen atom and are known as cyclic acetals. The simplest of these is 1,3-dioxolane which has been polymerised cationically using several initiators.[136]

The ring opening polymerisation of cyclic acetal monomers always proceeds through cleavage of the acetal linkage (i.e. O-C bond of the formal group.

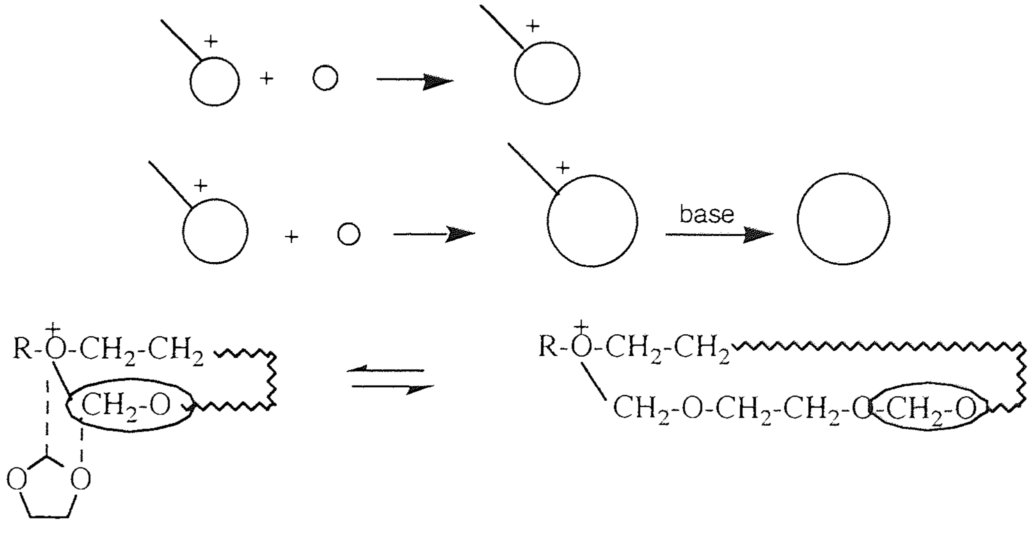


R_1,R_2= H, alkyl

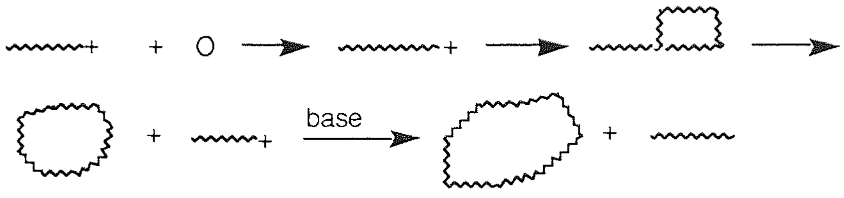
In the case of symmetrical cycloacetals it is impossible to distinguish between the bonds O^1-CH_2 and CH_2-O^2. In the case of unsymmetrical cycloacetal monomers, the repeating unit in the polymers can occur either in the 'head-to-tail' fashion or in the 'head-to-head' 'tail-to-tail' fashion.

4.7.1 Propagation of cyclic acetals

There have been two major controversies in the polymerisation of cyclic acetals. The first concerns the structure of the polymers, and the second the way the macromolecules grow. The first assumption by Plesch[137] was that the structure of the end groups should be related to the initiators and/or to transfer reactions. When these end groups were not found he then assumed that growth proceeded by ring expansion, i.e. cationated rings added cyclic monomer, these rings produced larger cationated rings and the process continued leading to entirely cyclic macromolecules.



However Jaacks[136] suggested that polyacetals were mostly linear, and that various proportions of cyclic oligomers and/or polymers were formed by a back-biting reaction. Alkoxy end groups may be converted into the corresponding alcohols, which were analysed by GC or IR.



Semlyen[138] also proposed a back-biting mechanism, which was in good agreement with theory derived for random back-biting.

In order to find the true mechanism, the influence of water was studied. Plesch concluded that under 'dry conditions', a ring expansion mechanism operates, whereas in the presence of water, linear macromolecules are formed. Penczek et. al.[139] concluded that the higher the concentration of polymer at equilibrium, the highest is in bulk, the lower the proportion of cyclics.

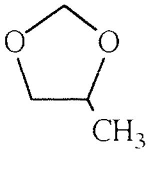
Hill and Carothers established that seven or eight membered and even higher cyclic acetals will polymerise but not the six membered ring. 1,3-Dioxolane was polymerised by Gresham and Muetterites who obtained a solid polymer using phosphorous pentafluoride catalyst. Free energy changes of these polymerisations are rather small in all cases, and substituents on the rings generally decrease these values.

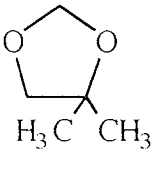
Okada et. al.[140] also investigated the polymerisation of 5-7 membered cyclic compounds. The polymerisation of 2-methyl-1,3-dioxepane in dichloromethane using $BF_3.Et_2O$ was studied. The decrease in free energy was generally quite small so that some of these monomers do not polymerise at all under ordinary conditions and when polymerisation does take place, the conversion is incomplete.

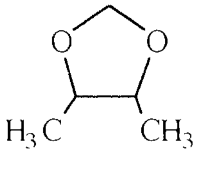
In the case of seven membered 1,3-dioxepane, methyl substitution at the C-2 atom lowers its tendency to form polymers, e.g. 2,2 dimethyl forms only a cyclic dimer.

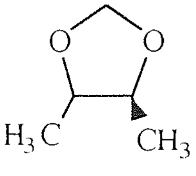
Okada et. al.[141] reported that many 5-membered cyclic systems have a large number of minimum energy conformations which lie somewhere in between the 'envelope' and 'half chair' forms.

Substitution at the C-2 atom of 1,3-dioxolane prevents its polymerisation, whereas its C-4 substitution results in lower rates and degrees of polymerisation. 4-Phenyl-1,3-dioxolane has been polymerised and the thermodynamics of the polymerisation of 4-methyl-1,3-dioxolane have also been studied Okada et.al.[142]





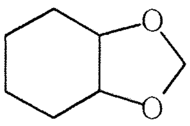


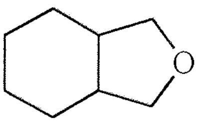


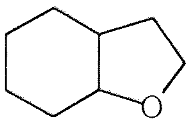
Polymerisations were carried out using $BF_3O(Et)_2$/perchloric acid-acetic anhydride binary system as initiator. Their results showed that even adding one methyl group slows the reaction considerably compared to unsubstituted 1,3-dioxolane, as the polymerisation is depressed by both enthalpy and entropy effects. The products when recrystallised using dichloromethane produced different M_w fractions.

4.7.2 Bicyclic monomers

Kops et. al.[143] investigated the polymerisation behaviour of bicyclic ethers with attached cyclohexane rings.

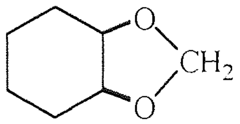




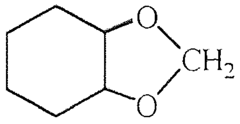


These can generally be polymerised quite easily whereas usually disubstituted 1,3-dioxolanes cannot.

Kops and Spangaard[144] also investigated the polymerisation of the monomers shown below using PF_5 catalyst. They reported that the cis isomer produced a dimer upon polymerisation, whereas polymerisation of the trans isomer produced high molecular weight material.

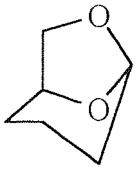


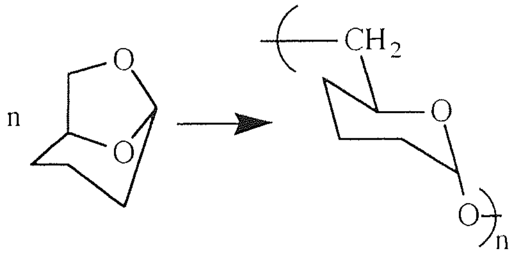
cis



trans

The bicyclic acetal 6,8-dioxabicyclo[3.2.1]octane, which can be considered as a 2,4-disubstituted 1,3-dioxolane ring has also been polymerised.



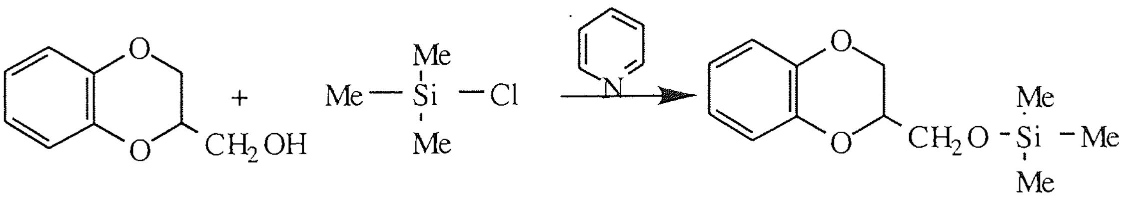


Several of these compounds have been shown to readily undergo polymerisation when the strain is sufficient, in contrast to the simple disubstituted five membered ring compounds which are normally inactive.

CHAPTER 5 THE SYNTHESIS OF OTHER FUNCTIONAL MONOMERS

5.1.THE SILYLATION OF 2-HYDROXYMETHYL-1,4-BENZODIOXANE USING TRIMETHYLSILYLCHLORIDE

2-Hydroxymethyl-1,4-benzodioxane is available commercially and it was thought that this would lead to suitable substrates for ionic polymerisation. However hydroxyl groups act as inhibitors and terminating agents in cationic polymerisation and therefore these hydroxyl groups had to be protected prior to polymerisation. The protecting group should be readily removable after polymerisation and the trimethylsilyloxy group was suitable for this purpose.



5.1.1 Experimental procedure

2-Hydroxymethyl-1,4-benzodioxane (0.06moles; 10g) was placed in a 100cm^3 round bottomed flask. Pyridine (50ml) and trimethylsilylchloride (0.06moles; 6.5g) were added and the mixture was stirred. Pyridine was distilled, which left a white solid with a melting point of 87^{o}C. Recrystallisation was attempted using cold pyridine, but the product was not particularly soluble, so dichloromethane was also added. The pyridine and dichloromethane were removed by distillation using a rotary evaporator and the product (yield 6g), was dried in a vacuum oven.

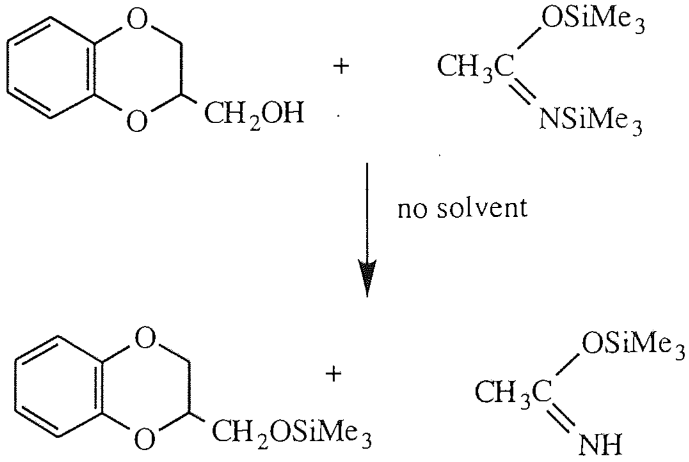
Infra-red	Si-O	1110-1000cm^{-1}	
		900-600cm^{-1}	
	Si-Me$_n$	1275-1260(s) cm^{-1}	n = 1 approx. 765cm^{-1}
		880-760cm^{-1}	n = 2 approx. 855cm^{-1}
			n = 3 approx. 840cm^{-1}

Infra-red analysis showed that bands characteristic of Si-O and Si-$(CH_3)_n$ groups were absent from this material. It is unlikely that any reaction took place in this instance because the melting point of 2-hydroxy-1,4-benzodioxane is 87°C, close to that of the product.

5.2 THE SILYLATION OF 2-HYDROXYMETHYL-1,4-BENZODIOXANE USING BIS(TRIMETHYLSILYL) ACETAMIDE (BSA)

Trimethylsilylchloride was found to be an unsuitable silylating agent for 2-hydroxymethyl-1,4-benzodioxane and therefore protection to form the trimethylsilylether using BSA was carried out. Because of the sensitivity of BSA to moisture, this synthetic route was carried out in apparatus assembled in a glove box to minimise side reactions.

5.2.1 Experimental procedure

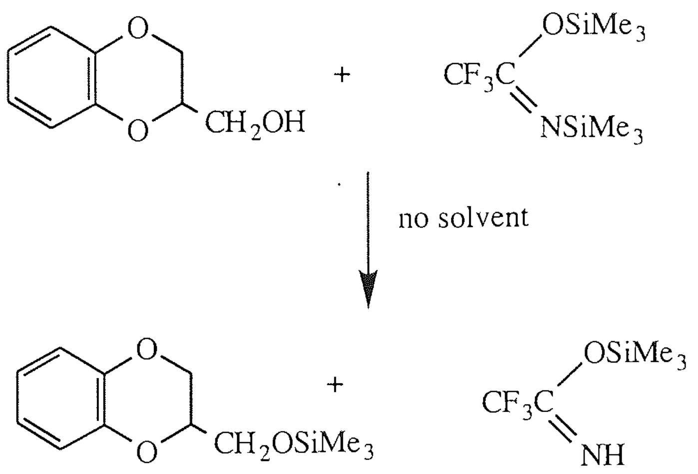


2-Hydroxymethyl-1,4-benzodioxane (0.06moles; 10g) was placed in a 100cm^3 round bottomed flask, which was placed in a glove box. BSA (0.06moles; 14.8cm^3) was added and the mixture was stirred. After 30 minutes all the benzodioxane had dissappeared and a gel like substance remained. The reaction flask was removed from the glove box and fitted with an air condenser. The monoacetamide by-product was then removed by distillation at reduced pressure. The liquid product (yield 7.5g) was the trimethylsilyl ether of 2-hydroxymethyl-1,4-benzodioxane.

Analysis: purity 95% by GPC, Infra-red 1020cm^{-1} (Si-O), 840cm^{-1} (Si-Me_3).

5.3 THE SILYLATION OF 2-HYDROXYMETHYL-1,4-BENZODIOXANE USING BIS(TRIMETHYLSILYL) TRIFLUOROACETAMIDE (BSTFA)

5.3.1 Experimental procedure



2-Hydroxymethyl-1,4-benzodioxane (0.15moles; 25g) was placed in a $100cm^3$ round bottomed flask,which was placed in a glove box. BSTFA (0.15moles; $40cm^3$) was added and the mixture was stirred. After 30 minutes all the benzodioxane had dissappeared and a gel like substance remained. The reaction flask was removed from the glove box and fitted with an air condenser. The monoacetamide by-product was then removed by distillation at reduced pressure. The liquid product (yield 23.1g) was trimethylsilyl ether of 2-hydroxymethyl-1,4-benzodioxane.

Analysis: purity 92% by GPC, Infra-red $1025cm^{-1}$ (Si-O), $842cm^{-1}$ (Si-Me_3).

5.4 CATIONIC POLYMERISATION USING BORONTRIFLUORIDE ETHERATE/ETHANOL

5.4.1.Experimental procedure for the polymerisation of the 2-trimethylsiloxymethyl-1,4-benzodioxane (TMSBD)

Monomer (TMSBD) (0.024moles; 5.6g) was placed in bulb B of the reaction vessel, shown in figure 5.1. Borontrifluoride etherate (0.4mol dm^{-3}; $1.18cm^3$) and ethanol (0.4mol dm^{-3}; $1.18cm^3$) were added in a glove box to section A, the side arm of the reaction vessel, and then mixed with the monomer. The vessel was then left at room temperature for 8 hours, after which time no polymerisation appeared to have taken place. No heat was evolved and the viscosity of the solution had not increased. The failure of this polymerisation could be due to several factors:-

a) the monomer was too stable compared to the polymer,

b) the initiator was not a strong enough acid,

c) the incomplete protection of the hydroxyl group and

d) the presence of impurities.

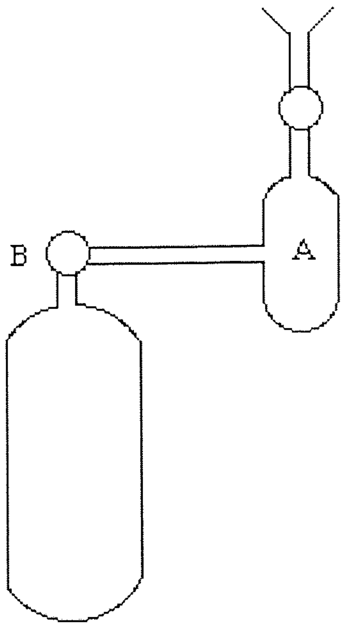


Figure 5.1 Reaction vessel

5.4.2 Experimental procedure for the copolymerisation of oxetane/ 2-trimethylsiloxymethyl-1,4-benzodioxane

The previous section has shown that TMSBD was not polymerised by $BF_3OEt_2/EtOH$. However it is possible in some cases to copolymerise monomers of low reactivity with other monomers of very high reactivity. Work has shown for example that THF, which is not polymerised alone by this same initiator system, may be copolymerised with oxetane.[145] It was thought therefore that such studies might be fruitful in this case.

Monomer(TMSBD) (0.042moles; 10g), oxetane (4.2×10^{-3}moles; 0.244g) and dichloromethane ($25cm^3$) were placed into a clean, dry reaction vessel, so that the monomer: initiator molar ratio was 50:1. After several hours no polymerisation had taken place as the monomer was recovered when the dichloromethane and oxetane were removed by distillation.

5.4.3 Experimental procedure for the polymerisation of oxetane

Due to the unsuccessful polymerisations of TMSBD and copolymerisations of oxetane and TMSBD using the BF_3OEt_2/EtOH initiator system, the reactivity of the system was investigated using oxetane, which is known to polymerise rapidly using this system.

Oxetane (0.1moles; 6g) was distilled into a clean dry reaction vessel. Using a glove box borontrifluoride etherate (0.4moldm^{-3}; 5cm^3) and ethanol (0.4moldm^{-3}; 5cm^3) were injected. Polymerisation was instantaneous and very exothermic. The monomer became very viscous, thus confirming the activity of the initiator solutions and suitability of the solvent. The confirmed activity of the initiator solutions shows that even if the oxonium ion is formed from the reaction of TMSBD, it is too stable and therefore not susceptible to polymerisation. Due to the fact that the monomer possessed a saturated ring fused to a benzene ring it was thought likely to have sufficient ring strain to lead to polymerisation. There are several possible reasons therefore for the failure of these polymerisations.

a) Insufficient ring strain in the saturated ring, which may be compared to strain in cyclohexene (which has a negligible tendency to polymerisation).

b) The initiators may not be suitable for this type of polymerisation. For example THF does not homopolymerise using these initiators, but does with stronger acids.

c) Incomplete protection of the hydroxyl group.

d) The presence of impurities.

5.4.4 Experimental procedure for the polymerisation of 1,2-methylenedioxybenzene

In order to distinguish between c) and d) above the polymerisations of unsubstituted monomers 1,2-methylenedioxybenzene and 1,4-benzodioxane were attempted. The reaction vessel shown in figure 5.1 was dried, transferred to the glove box and the required volume of 1,2-methylenedioxybenzene was added to section A. Dichloromethane was then distilled into the vessel. The required quantities of borontrifluoride etherate and ethanol solutions were injected into section B through a subaseal. Tap B was opened and the initiator components mixed with the monomer. The mixture was then left at room temperature for 24 hours, after which time the solution did not appear to become viscous and no heat was evolved. GPC confirmed that monomer was recovered after distillation of the initiator components and dichloromethane. The reaction was repeated in the absence of solvent. No signs of polymerisation were observed.

5.4.5 The polymerisation of 1,2-methylenedioxybenzene using U.V.

The above experiments failed to show any signs of polymerisation. However further studies were carried out on this system to ascertain whether any monomer was converted under the above conditions.

A solution of 1,2-methylenedioxybenzene (5x10-5moldm^{-3}) was made up in a volumetric flask, using tetrahydrofuran as solvent, as it has a cutoff value of 220nm. A U.V. spectrum was obtained of this solution.
λ_{max}=272nm
1,2-Methylenedioxybenzene (0.08moles; 10.29g) was placed in a reaction vessel, along with a quantity of dichloromethane. Reaction was carried out using a [M]:[I] ratio of 50:1, and therefore the required volumes of initiators were added. A sample of the polymerisation mixture was placed in a U.V. cell, and U.V. spectra obtained at regular intervals. The U.V. spectra of the reaction mixture compared to that of monomer showed no changes over a long period indicating that no polymerisation or other reaction took place.

5.4.6 The polymerisation of 1,4-benzodioxane

The same procedure as described in section 5.4.5 was carried out. No reaction was observed using BF_3OEt_2:EtOH as initiator .

5.5.CATIONIC POLYMERISATION USING TRIFLUOROMETHANESULFONIC ACID

Borontrifluoride etherate/ethanol system was unsuccessful in polymerising 1,2-methylenedioxybenzene or 1,4-benzodioxane, whether in bulk or in solution. As

$BF_3O(Et)_2$ is a Lewis acid it was thought that it would be useful to investigate what reaction, if any, occurred using a stronger acid to initiate polymerisation, e.g. a protonic (Brønsted) acid, such as trifluoromethanesulfonic acid.

5.5.1 The polymerisation of 1,2-methylendioxybenzene

1,2-Methylenedioxybenzene (0.08moles; 10.29g) was placed into a clean, dry reaction vessel, which was placed in a glove box. Trifluoromethanesulfonic acid solution (0.55×10^{-3}moldm^{-3}; 2.96cm^3) was then injected into the vessel, [M]:[I] ratio of 50:1, which was left at room temperature. The monomer immediately turned pale red and after 24 hours a purple solid was produced. The polymer was washed with dichloromethane which produced a solution with insoluble particles, which were filtered to dryness. The filtrate was evaporated and the solid produced was dried in a vacuum oven overnight (yield 5.23g).
Mw 550 by GPC.

5.5.2 [M]:[I] ratio 50:1, 0°C

To study the effect of temperature on yield and molecular weight of the polymer the reactions were repeated varying first the temperature and/or the molar monmer:initiator ratio. The same procedure as described in section 5.5.1 was repeated, but the reaction vessel was placed in an ice bath overnight. The solution again turned pale red on addition of the initiator and dark purple on standing. The polymer was washed with dichloromethane, filtered and dried in a vacuum oven (yield 5.7g). The molecular weight obtained by GPC is shown in table 5.1.

Table 5.1 GPC results[M]:[I] ratio 50:1 at 0°C

Sample	Molecular Weight
before filtration	600, 200, 150
solid after filtration	870, 300
filtrate	14,000(small peak), 300, 100

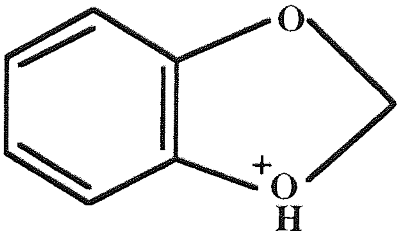
5.5.3 [M]:[I] ratio 50:1, 60°C

The reaction as described in section 5.5.1 was repeated but the flask was placed in a water bath at 60°C for 8 hours. The polymer was again recovered after washing with dichloromethane and dried in a vacuum oven (yield 3.7g). Mw 430 by GPC.

The molecular weight within large experimental error decreases with increasing temperature, which suggests a larger number of propagating centres. However given the low degree of polymerisation no absolute values could be determined from the GPC results obtained. The following reactions were carried out in an attempt to examine the effect of monomer:initiator ratio on molecular weight and yield of the polymers produced.

5.5.4 [M]:[I] ratio 100:1, room temperature

A low [M]:[I] ratio leads to a high concentration of the species shown which therefore yields low molecular weight polymers. Increasing the monomer:initiator ratio should increase the molecular weight of the polymers produced.



The same procedure as described in section 5.5.1 was repeated, but the [M]:[I] ratio was increased to 100:1. The polymer was dried in a vacuum oven (yield 5.1g). Molecular weight was determined by GPC and the results are shown in table 5.2.

Table 5.2 GPC results [M]:[I] ratio 100:1 at room temperature

Sample	Molecular Weight
before filtration	600, 750
solid after filtration	700
filtrate	11,500(small peak), 350

5.5.5 [M]:[I] ratio 100:1, 40°C

The same procedure as described in section 5.5.1 was repeated but the flask was placed in a water at 40°C for 8 hours and the [M]:[I] ratio was increased to 100:1. The GPC results of the dried polymer (yield 4.1g) are shown in table 5.3.

Table 5.3 GPC results [M]:[I] ratio 100:1 at 40°C

Sample	Molecular Weight
before filtration	500, 200, 150
solid after filtration	700, 300, 100

5.5.6 The monitored polymerisation of 1,2-methylenedioxy benzene

In order to determine how the polymerisation progressed, (e.g. whether polymer built up gradually) a polymerisation was carried out removing samples at various intervals. The same procedure as described in section 5.5.1 was used, but a [M]:[I] ratio of 100:1 was used. The aliquots of the solution were removed at hourly intervals and diluted in dichloromethane then analysed by GPC. The results are shown in table 5.4.

Table 5.4 GPC results [M]:[I] ratio 100:1 monitored reaction at room temperature

Time/hr	Molecular Weight
1	100
2	200
2.5	200, 150
3	200, 150
4	300, 200
5	400, 300, 200
24	700, 400, 200, 100

This experiment suggested that the polymer in fact built up gradually to a maximum of approximately 5-8 units in each polymer chain.

5.5.7. The polymerisation of 1,4-benzodioxane

Due to the success of the polymerisation of a five membered ring using trifluoromethanesulfonic acid, the effect of this initiator on a six membered ring was investigated. 1,4-Benzodioxane (0.03moles) was placed into a clean, dry reaction vessel. Trifluoromethanesulfonic acid solution in dichloromethane (0.55×10^{-3}mol dm^{-3}; 1cm^3) was then injected. The mixture was left for 24 hours after which time there appeared to be no sign of reaction, the mixture was no more viscous and no heat had been evolved.

5.5.8 The copolymerisation of 1,2-methylenedioxybenzene/1,4-benzodioxane at room temperature.

After the failure of the homopolymerisation of 1,4-benzodioxane, it was thought that copolymerisation with 1,2-methylenedioxybenzene may be possible.

1,2-Methylenedioxybenzene (0.05moles; 6g) and 1,4-benzodioxane (0.047moles; 7.4g) were placed into a clean dry reaction vessel. Trifluoromethanesulfonic acid solution (2.02×10^{-3}moles; 3.67cm^3) was also injected, [M]:[I] ratio of 50:1. After mixing a pale red colour was observed, and after 24 hours the mixture was deeper red/purple and slightly more viscous, but not as viscous as the homopolymerisation of 1,2-methylenedioxybenzene. The polymer was recovered from distillation of dichloromethane. Mw=310 by GPC.

5.6 CATIONIC POLYMERISATION OF 1,2-METHYLENEDIOXYBENZENE USING TRIFLUOROMETHANESULFONIC ANHYDRIDE.

TFMSA was investigated as a method of initiation in an attempt to increase the molecular weight of the polymers produced.

5.6.1 [M]:[I] ratio 150:1, room temperature.

The same procedure as described in section 5.5.1 was repeated using a monomer : initiator ratio of 150:1. The polymer produced was dried in a vacuum oven (yield 3.2g). Mw=610, 730,(polymerisation quenched with base) by GPC.

5.6.2 [M]:[I] ratio 200:1, room temperature.

The same procedure as described in section 5.5.1 was repeated using a monomer : initiator ratio of 200:1. The polymer produced was dried in a vacuum oven (yield 2.2g). Mw=530 by GPC

Table 5.5 Summary of reactions

Monomer	Initiator	Solvent	[M]:[I]	Temp °C	polymerisation
1,2-MDB	TFMS	No	50:1	room	Yes
1,4-BD	TFMS	No	50:1	room	No
MDB/BD	TFMS	No	50:1	room	Yes a
1,2-MDB	TFMS	No	50:1	0	Yes b
1,2-MDB	TFMS	No	50:1	60	Yes
1,2-MDB	TFMS	No	100:1	room	Yes
1,2-MDB	TFMS	No	100:1	0	Yes c
1,2-MDB	TFMS	No	500:1	0	No
1,2-MDB	TFMS	No	200:1	room	No
1,2-MDB	TFMS	No	150:1	room	No
1,2-MDB	TFMSA	No	100:1	room	Yes
1,2-MDB	TFMSA	No	150:1	room	Yes
1,2-MDB	TFMSA	No	200:1	room	Yes
1,2-MDB	TFMSA	CH_2Cl_2	100:1	room	Yes
1,2-MDB	TFMSA	CH_2Cl_2	100:1	-78	No
1,2-MDB	HBF_4	No	100:1	room	slight
1,2-MDB	HBF_4	CH_2Cl_2	100:1	-78	No
1,2-MDB	SbF_5	No		room	No
1,4-BD	SbF_5	No		room	No

1,2-MDB- 1,2-methylenedioxybenzene

1,4-BD- 1,4-benzodioxane

a- Polymerisation not as viscous as homopolymerisation of 1,2-methylenedioxybenzene b- A lower temperature could not be obtained without a solvent

c- Polymerisation did not go to completion

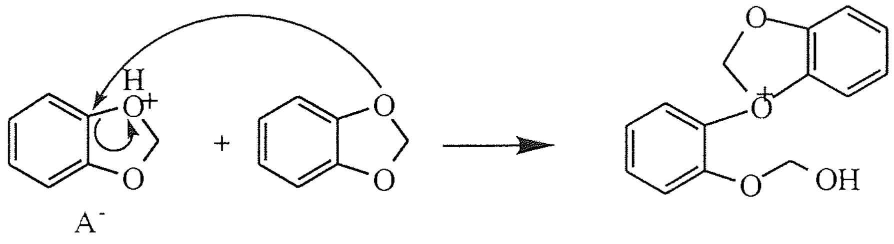
TFMS- Trifluoromethanesulphonic Acid

TFMSA- Trifluoromethanesulphonic Anhydride

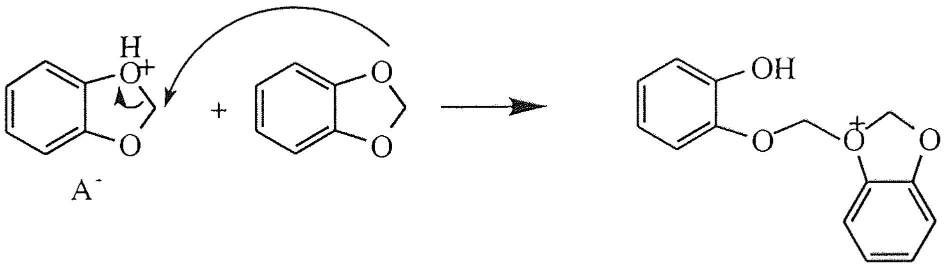
HBF_4- Tetrafluoroboric Acid (solution in ether)

The reactions using SbF_5 were carried out using a 5KW U.V. lamp

There are two possible mechanisms by which propagation could proceed.



mechanism a



mechanism b

Propagation is more likely to proceed via mechanism a) as it is easier to stabilise the positive charge via this mechanism. Analysis of the environment surrounding the hydroxyl group should confirm the mechanism.

Although trifluoromethanesulfonic acid was successful in polymerising 1,2-methylenedioxybenzene the molecular weights of the polymers produced were quite low. GPC showed that approximately 5-8 monomer units were linked together. Previous work has shown that trifluoromethanesulfonic acid yields only low molecular weight polymers. However trifluoromethanesulfonic acid was not successful in polymerising 1,4-benzodioxane. The inability to polymerise 1,4-benzodioxane, even when using a strong acid, suggests that there is insufficient ring strain in the heterocycle to lead to polymerisation. It would be advantageous to investigate the effects on polymerisation of using a weaker Protic acid or stronger Lewis acid.

5.7 CATIONIC POLYMERISATION USING TETRAFLUOROBORIC ACID

5.7.1 1,2-methylenedioxybenzene

The reaction as described in section 5.5.4 was repeated using tetrafluoroboric acid as initiator. The vessel was left at room temperature for 8 hours, after which time, no colour change was observed, no heat was evolved and no increase in viscosity appeared visible. The reaction was repeated but the vessel was placed in a bath at -78°C. After 8 hours there were still no signs of polymerisation. The reactions were repeated using 1,4-benzodioxane, which also failed to show any signs of polymerisation.

HBF_4 was unsuccessful in polymerising 1,2-methylenedioxybenzene or 1,4-benzodioxane. This is probably due to the fact that it is not a strong enough acid to initiate polymerisation.

5.8 PENTAFLUOROSTYRENE

Other fluorinated polymers were to be examined for nonlinear optical properties.

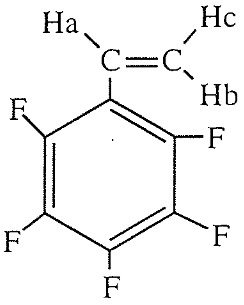


Table 5.6 ^{1}H NMR of pentafluorostyrene

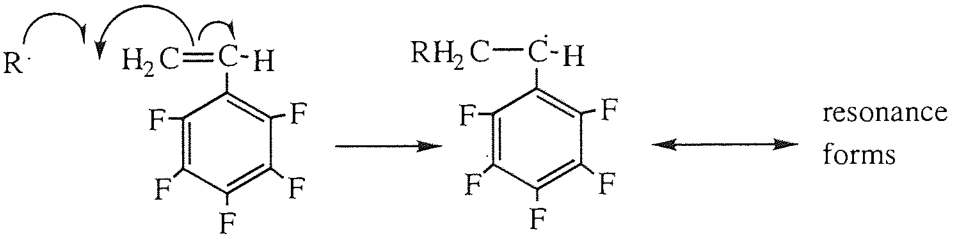
Chemical shift	Area	Multiplicity	
5.7	107.2	doublet	Hc
6.0	103.5	doublet	Hb
6.6	105.3	quartet	Ha

5.8.1 The free radical polymerisation of pentafluorostyrene

As fluorinated polymers have been shown to be nlo active, would simple polymers such as polypentafluorostyrene also show such properties.

5.8.1.1. The polymerisation of pentafluorostyrene using AZBN

Styrene may be polymerised via cationic, free radical and anionic mechanisms, so any difference between the reactivity of pentafluorostyrene and styrene may be assumed to be due to the presence of the fluorine atoms around the aromatic ring. In the first instance a free radical technique was used for polymerisation.

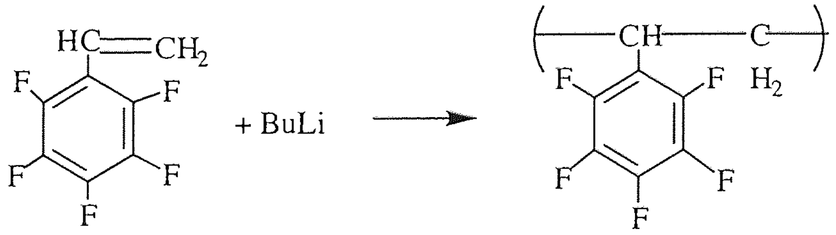


5.8.1.2 Experimental procedure

AZBN (0.085g) was placed in a clean, dry reaction vessel. THF (50g) and pentafluorostyrene (10g) were distilled into the vessel. The vessel was placed in a water bath at 60°C overnight, during which time the colourless solution turned clear yellow and more viscous. The polymer (yield 7.87g) was then obtained by precipitatation of the solution in methanol. The polymer was resdissolved in toluene/THF, reprecipitated using methanol and then centrifuged. The recovered polymer was then dried in a vacuum oven overnight. The molecular weight distribution of the polymer was determined by GPC and Mn and Mw calculated from the chromatogram. Mw=307,450, Mn=254,620, Polydispersity=1.2 by GPC.

5.8.2 The anionic polymerisation of pentafluorostyrene

5.8.2.1 Experimental procedure for the polymerisation of pentafluorostyrene using butyllithium



Pentafluorostyrene (5g) and THF (10cm^3) were distilled into a clean, dry reaction vessel. Butyllithium (0.13cm^3;2M) was injected into the monomer solution through a subaseal. The vessel was left for 8 hours at 60°C during which time the pale yellow solution became orange/brown in colour and slightly viscous. The polymer (yield 3.25g) was precipitated from methanol. Mw= 419,030, Mn= 279,680, Polydispersity= 1.49 by GPC.

The free radical and anionic polymerisations of pentafluorostyrene led to fairly high molecular weight poymers. Films of the polymer prepared using butyllithium were cast and examined for nlo activity, the results of these experiments are shown in tables 5.7 and 5.8.

Second harmonic intensity of polypentafluorostyrene

Table 5.7 NLO intensity of polypentafluorostyrene via Buli.

Additive	%	Poled	NLO intensity relative to quartz
none	-	no	0.21×10^{-2}
none	-	yes	SH intensity increased

Very slight nlo properties prior to poling, which increase after poling.

Table 5.8 NLO intensity of polypentafluorostyrene doped with paranitroaniline.

Additive	%	Poled	NLO intensity relative to quartz	Homogeneity
1	10	no	2.57×10^{-2}	
1	10	no	2.32×10^{-2}	
1	10	yes	1.353×10^{-2}	
1	10	yes	0.4185	
1	10	yes, left a few days	0.6565	highly crystalline

Polypentafluorostyrene + 10% paranitroaniline nlo properties better than undoped polymer film, although poling did not increase nlo propeties.

Polypentafluorostyrene+ 10% 5-nitro-2-aminobenzotrifluoride not really much nlo activity either prior to or after poling. Two distinct phases were observed.

5.9.Solubility of polypentafluorostyrene

A major hinderance in the analysis of the polymers produced has been their insolubility in most common organic solvents, shown in table 5.9.

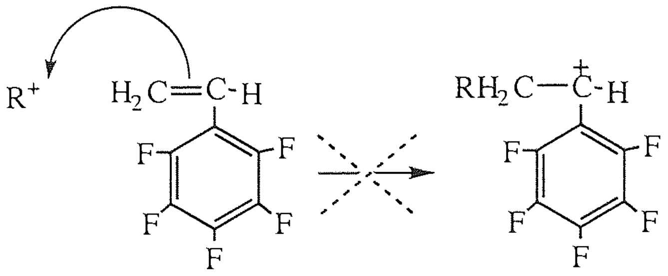
Table 5.9 Solvents for polypentafluorostyrene.

nonsolvent	Solvent
Chloroform	Acetone
Dimethylformaldehyde	Dimethylsulfoxide (slightly)
Toluene	THF
Water	
Methanol	
1,4-Dioxane	
Carbon tetrachloride	
Ethanol	

This limits the type of analyses that can be performed as they have to be performed in either THF or acetone.

5.10 Experimental procedure for the cationic polymerisation of pentafluorostyrene using borontrifluoride etherate

Pentafluorostyrene (7g), dichloromethane (5ml), tertiarybutyl chloride (0.0108moles) and borontrifluoride etherate (0.0108moles) were placed into a clean, dry reaction vessel. The vessel was then placed in an ice bath in a fume cupboard. Polymerisation did not appear to be taking place so more borontrifluoride etherate (1ml) and tertiarybutylchloride (1ml) were added. The vessel was then placed in a waterbath at 45°C and left for 8 hours. After evaporation of the solvent, no polymer was produced.



resonance forms
are not possible

The fluorine atoms around the phenyl ring influence the polymerisation a great deal, as they are such good electron withdrawing groups, they will stabilise a build up of negative charge and hence encourage anionic and free radical mechanisms, but they also destabilise a build up of positive charge and therefore hinder cationic polymerisation.

5.11 Conclusions and future work

Polypentafluorostyrene showed no significant nlo activity relative to quartz. It may be advantageous to study a polymer with a lower degree of fluorination to examine the effect, if any, this has on the nlo activity. This may also lead to improved solubility of the polymer in common organic solvents.

REFERENCES

1) Chen,M., Yu.L., Dalton,L.R., Shi,Y., Steier,W.H., New polymers with large and stable second order nonlinear optical effects, Macromolecules, 24, 5421-5428, 1991.

2) Bergman, J.G., McFee, J.H., Crane, G.R., Pyroelectricity and optical second harmonic generation in polyvinylidene fluoride films, Applied Physics Letters, vol 18, No.5, March 1971.

3) Journal of Macromolecular Science- Reviews in Macromolecular Chemistry and Physics, Vol.C31, No.4, 342-501, 1991.

4) Meredith,G.R., Van Dusen,J.G., Williams,D.J., Optical and nonlinear optical characterisation of molecularly doped thermotropic liquid crystalline polymers, Macromolecules, 15, 1385-1389, 1982.

5) Flytzanis,C., Optical nonlinearities and photo induced solitons in conjugated polymer crystals, American Chemical Society Symposium Series 233, Non-linear Optical properties of Organic and Polymer Materials, 167-185, 1983.

6) M^{c}graw Hill- Encyclopaedia of Science and Technology, Vol.9, 194, 1982.

7) Tweig,R.J., Jain,K., Organic materials for optical second harmonic generation, SPIE-International Society of Optical Engineering, 400, 183-6, 1983.

8) Williams, D.J., Organic polymeric and non-polymeric materials with optical nonlinearities, Angewandte Chemie International Edition, 23, 690-703, 1984.

9) Thakur, M., Tripathy,S., Electrooptical applications, Vol. 5, 756-771.

10) Hill,J.R., Pantelis,P., Davies,G.J., Non-linear optical and electro optical properties of polymer thin films for non-linear optical applications, Institute Physics Conference Series, No. 103, Materials for non-linear and electro optics, Cambridge, 215, July 1989.

11) Prasad,P.N., Polymeric mateials for non-linear optics and photonics, Polymer, Vol.32, No.10, 1991.

12) Oudar,J.L., Zyss,J., Structural dependence of nonlinear optical properties of methyl-(2,4-dinitrophenyl)-aminopropanoate crystals, Physical Reviews A, 26 2016, 1982.

13) Zyss,J., Nicoud,J.F. and Coquillay,M., Chirality and hydrogen bonding in molecular crystals for phase matched second harmonic generation: N-(4-nitrophenyl)-(L)-prolinol (NPP), Journal of Chemical Physics, 81, 4160, 1984.

14) Williams, D.J., Non-linear optical properties of organic molecules and crystals, Vol.1, Chemla,D.S., Zyss,J., American Chemical Society Symposium Series Washington DC, Quantum electronics- Principles and applications. Chapter II-7, Non-linear optical properties of guest-host polymer structures, 1983.

15) Willand, C.S., Williams, D.J., Non-linear optical properties of polymeric materials, Ber. Bunsenges. Physical Chemistry, 91, 1304-1310, 1987.

16) Eaton,D.F., Recent developments in nonlinear optical materials, Chemtech, 308-316, May 1992.

17) Allen, S., Materials with a bent for light, New Scientist, 1 July 1989.

18) Nayar,B.K., Booth,R.C., An introduction to integrated optics, British Telecom Technological Journal, Vol.4, No.4, 5, October 1986.

19) Schwerzel, R.E., Kurmer, J.P., Organic materials for nonlinear optics, Centre for photochemical sciences, The Spectrum , Vol.3, Issue 1,ISSN 1044-5536, Spring 1990.

20) Pugh,D., Sherwood, J.N., Organic crystals for nonlinear optics, Chemistry in Britain, 544-548, June 1988.

21) Eaton, D.F., Anderson, A.G., Tam,W., Mahler,W., Wang,Y., Guest-host molecular ensembles for nonlinear optics, Molecular Crystals: Liquid Crystals, Vol.211, 125-133, 1983.

22) Garito, A.F., Singer, K.D., Organic crystals and polymers- A new class of nonlinear optical materials, Laser Focus, 18.2, 59-62, and 64, Feb. 1982.

23) Franken,P.A., Hill, A.E., Peters,C.W., Weinrich,G., Generation of optical harmonics, Physical Review Letters, vol.7, No.4, 118-119, Aug. 1961.

24) Kurtz,S.K., Perry,T.T., A powder technique for the evaluation of nonlinear optical materials, J. of Applied Physics, vol.39, No.8, 3798,July 1968.

25) Mandal,B.K., Takahashi,T., Maeda,M., Kumar,S., Blumstein,A., Tripathy,S., Thin film processing of non-linear optical materials, Comb like polymers containing nonlinear optical active pendant groups, Makromolekulare Chemie: 192, 1009-1016, 1991.

26) Morrell,J.A., Albrecht,A.C., Second order hyperpolarisability of π-nitroaniline calculated from perturbation theory based expression using CNDO/S generated electronic states, Chemical Physics Letters, Vol.64, No.1, 46, June 1979.

27) Williams, D., American Chemical Society Symposium Series, Kansa City, Mo. Sept 12-17, 1982. Polymers in nonlinear optics, Electronic and photonic applications of polymers, Chapter 6.

28) Pugh, D., Sherwood, J.N., Organic crystals for nonlinear optics, Chemistry in Britain, 544-548, June 1988.

29) Meredith,G.R., Non-linear optics with polymers, Journal of Materials Education 9,(6),720-751,1988.

30) Jones,C., Polymers for Non-linear optical devices, Chemistry and Industry, 600-608, 1 October 1990.

31) Prasad,P.N., Williams,D.J., Introduction to non-linear optical effects in molecules and polymers, Wiley-Interscience, 1990.

32) Dirk,C.W., Tweig,R.J., Wagniere,G., The contributiion of π-electrons to second harmonic generation in organic molecules, Journal of the American Chemical Society, 108, 5387-5395, 1986.

33) Garito,A.F., Teng,C.C., Wong,K.Y., Khamiri,O.Z., Molecular Optics: Nonlinear optical processes in organic and polymer crystals, Molecular Crystal: Liquid Crystals, Vol.106, 219-258, 1984.

34) Tripathy, S., Cavicchi, E., Kumar,J., Kumar, R.S., Nonlinear optics and organic materials, Chemtech, 747-752, Dec. 1989.

35) Hampsch,H.L., Yang,J., Wong,G.K., Torkelson,J.M., Orientation and second harmonic generation in doped polystyrene and poly(methylmethacrylate) films, Macromolecules, 21, 526, 1988.

36) Watanabe,T., Yoshinaga,K., Fichou,D., Miyata,S., Large second harmonic generation in electrically ordered p-nitroaniline-poly(oxyethylene) 'guest-host' systems, Journal of the Chemical Society: Chemical Communications, 250, 1988.

37) Singer, K.D., Sohn, J.E., Lalama, S.J., Second harmonic generation in poled polymer films, Applied Physics Letters, 49 (5), 4 Aug 1986.

38) Chen,M., Yu,L., Dalton,L.R., Shi,Y., Steier,W.H., New polymers with large and stable second order non-linear optical effects, Macromolecules, 24, 5421-5428, 1991.

38) Khanarian,G., Tonelli,A.E., American Chemical Society Symposium Series, 233, Nonlinear electro optic and dielectric properties of flexible polymers, 235-244, 1983.

39) Kaul,S.N., Fernandez,J.E., Synthesis of molecular arrays with non-liner optical properties. Second harmonic generation by covalently functionalised glassy polymers, Macromolecules, 20, 2322-2324, 1987.

40) Hassanein,M., Ford,W.T., Orientation and second harmonic generation in doped polystyrene and polymethylmethacrylate films, Macromolecules, 21, 526-528, 1988.

41) Finkelmann, H., Ringsdorf, H., Wendorff, J.H., Model considerations and examples of enantiotropic liquid crystalline polymers, Makromolekulare Chemie, 179,273-276, 1978.

42) Prasad,P.N., Ulrich,D.R., Non-linear optical and electroactive polymers, Proceedings of an ACS symposium on electroactive polymers, ISBN 0-306-42768-0, Denver, Colorado, U.S.A. 6-10 April 1987.

43) Duran,R., Ballauff,M., Wenzel,H., Wegher,G., Persistant, efficiency frequency doubling by poled annealed films of a chromophore-functionalised poly (p-hydroxystyrene), Macromolecules, 21, 2899-2901, 1988.

44) Le Barny,P., Thin Solid Films, 152, 99, 1987.

45) Singer,K.D., Kuzyk,M.G., Holland,W.R., Sohn,J.E., Lalama,S.J., Comizzoli,R.B., Katz,H.E., Schilling,M.L., Electro optic phase modulation and optical second harmonic

generation in corona poled polymer films. Applied Physics Letters, 53(19), 1800-1802, 7 Nov 1988.

46) Ye,C., Minami,N., Marks,T.J., Yang,J., Wong,G.K., Persistent, efficient frequency doubling by poled annealed films of a chromophore-functionalized poly(p-hydroxystyrene), Macromolecules, 21, 2899, 1988.

47) Dalton, L.R., Yu, L.P., Chen, M., Sapochak, L.S., Xu, C., Recent advances in the synthesis and characterization of nonlinear optical materials: second-order materials, Synthetic Metals, 54, 155-160, 1993.

48) Ye,C., Marks,T.J., Yang,J., Wong,G.K., Synthesis of molecular arrays with nonlinear optical peoperties. Second harmonic generation by covalently functionalized glassy polymers, Macromolecules, 20, 2322, 1987.

49) Demartino, Choe,E.W., Khanarian,G., Haas,D., Leslie,T., Nelson,G., Stamatoff,J., Stuetz,P., Teng,C.C., Yoon,H., 'Nonlinear optical and electroactive polymers' Editors Prasad,P.N.and Ulrich,D.R., NY: Plenum publishing corp. p169-187, 1988.

50) Jeng, R.J., Chen, Y.M., Chen, J.I., Kumar, J., Tripathy, S.K., Phenoxysilicon polymer with stable second order optical nonlinearity, Macromolecules, 26, 2530-2534, 1993.

51) Jeng, R.J., Chen, Y.M., Kumar, J., Tripathy, S.K., Novel crosslinked guest-host system with stable second order nonlinearity, Journal of Materials Science: Pure Applied Chemistry, A29 (12), 1115-1127, 1992.

52) Eich, M., Reck, B., Yoon, D.Y., Willson, C.G., Bjorkland, G.C., Novel scond order nonlinear optical polymers via chemical cross linking induced vitrification under electric field, J. of Applied Physics, 66 (7), 3241, 1989.

53) Ulrich, D.R., Nonlinear optical polymer systems and devices, Molecular crystals, Liquid Crystals, Vol.160, 1-31, 1988.

54) Williams, D.J., NLO properties of organic and polymeric materials, ACS symposium, Ser. No.233, Washington, 1983.

55) Bailey, R.T., Blaney,S., Cruickshank, F.R., Guthrie, S.M.G., Pugh, D., Sherwood, J.N., A new method of assessing the efficiency of second harmonic generation by small samples of organic crystals, Applied Physics, B47, 83-86, 1988.

56) Amass,A.J., Polymerisation of Norbornene, Canadian Journal of Chemistry, 6, 60, 1982.

57) Schneider,V., Frolich,P.K., Mechanism of formation of aromatics from lower paraffins, Industrial and Engineering Chemistry, 23, 1405, Dec. 1931.

58) Mango,F.D., Catalysis of symmetry-forbidden reactions- a valence bond description, Chemical Technology, 758, 1971.

59) Van der Lugt,W., Symmetry control and transition metal catalysed reactions, Tetrahedron Letters, 2281, 1970.

60) Casey,C.P., Burkhardt,T.J., Reactions of (diphenylcarbene)pentacarbonyltungsten(0) with alkenes. Role of metal-carbene complexes in cyclopropanation and olefin metathesis reactions, Journal of the American Chemical Society, 96, 9808-9809, Dec 1974.

61) Casey,C.P., Tuinstra,H.E., Saeman,M.C., Reactions of $(CO)_5WC(TOL)_2$ with alkenes. A model for structural selectivity in the olefin metathesis reaction, Journal of the American Chemical Society, 98, 608, 1976.

62) Novak,B.M., Grubbs,R.H., Catalytic organometallic chemistry in water: The aqueous ring opening metathesis polymerisation of 7-oxanorbornene derivatives, Journal of the American Chemical Society, 110, 7542-7543, 1988.

63) Tsonis,C., Farona,M.F., Ring retention in the homopolymerisation of cyclic olefins by rhenium olefin metathesis catalysts, Journal of Polymer Science: Polymer Chemistry, 17, 185-191, 1979.

64) Thu,C.T., Bastelberger,T., Hocker,H., On the polymerisation of Bicyclo[4.2.0]octa-7-ene by a metathesis catalyst and by tungsten carbenes, Makromolekulare Chemie: Rapid Communications, 2, 7-7, 1981.

65) Natta,G., Dall'asta,G., Porri,L., Polymerisation of cyclobutene and of 3-methylcyclobutene by $RuCl_3$ in polar protic solvents, Die Makromolekulare Chemie, 253, 81, 1965.

66) Calderon,N., Ofstead,E.A., Ward,J.P., Judy,W.A., Scott,K.W., Olefin metathesis:1. Acyclic vinylenic hydrocarbons, Journal of the American Chemical Society, 90, 4133, 1968.

67) Scott,K.W., Calderon,N., Ofstead,E.A.; Judy,W.A., Ward,J.P., Ring opening polymerisation of cycloolefins, Advances in Chemistry Series, 91, 399, 1969.

68) Graham,J.R., Slaugh,L.H., Alkylation behaviour of WCl_6, $MoCl_5$ and the metathesis cocatalyst system WCl_6-$C_2H_5AlCl_2$, Tetrahedron Letters, II, 787, 1971.

69) Motz,V.W., Farona,M.F., Olefin metathesis by pyridinepentacarbonyl molybdenum and related catalysts: reactions and mechanisms, Inorganic Chemistry, Vol.16, No.10, 2545, 1977.

70) Reif,L., Hocker,H., Kinetics and thermodynamics of the metathesis reaction of cycloolefins. 2. Molecular weight distribution, Macromolecules, 17, 952-956, 1984.

71) Gunther,V.P., Haas,F., Marwede,G., Nutzel,K., Oberkirch,W., Pampus,G., Schon,N., Witte,J., Ring opening polymerisation of cyclopentene, Die Angewandte Makromolekulare Chemie, 14, 87-109, 1970.

72) Ivin,K.J., Lam,L.M., Rooney,J.J., ^{13}C NMR Spectra of polymers made by ring opening polymerisation ofendo-5-methylbicyclo[2.2.1]hept-2-ene using metathesis catalysts, Makromolekulare Chemie, 182, 1847-1854, 1981.

73) Hocker,H., Reimann,W., Reif,L., Riebel,K., Kinetics and thermodynamic aspects of the metathesis reaction of cycloolefins considering particularly the molecular weight distribution of the products, Journal of Molecular Catalysis, 8, 191-202, 1980.

74) Leconte,M., Basset,J.M., Stereoselectivity of metathesis of various acyclic olefins with chromium-, molybdenum-, and tungsten based catalysts, Journal of the American Chemical Society, 7296-7302 Nov. 1979

75) Chauvin,Y., Commereuc,D., Zaborowski,G., Catalysis of olefin transformation by tungsten complexes,6., Makromolekulare Chemie, 179, 1285-1290, 1978.

76) Reif,L., Hocker,H., The two step polymerisation of Norbornadiene with metathesis catalysts, Makromolekulare Chemie: Rapid Communication, 2, 745-747, 1981.

77) Shahada,L.A., Feast,W.J., Metathesis ring opening polymerisation of 5,6-bis(chloromethyl)bicyclo[2.2.1]hepta-2-ene, European Polymer Journal, Vol.26, No.1, 25-27, 1990.

78) Blackmore, P.M., Feast, W.J., Taylor, P.C., Stereoregular Fluoropolymers: 5. The ring opening polymerisation of 2-Trifluoromethylbicyclo[2.2.1]hepta-2,5-diene, British Polymer Journal, 19, 205-209, 1987.

79) Dall'asta,G., Scaglione,P., All cis polypentamer: A potential new elastomer for low temperature applications, Rubber Chemistry Technology, 1235, 42, 1969.

80) Marshall,P.R., Ridgewell,B.J., A novel metal alkyl-free catalyst for the ring opening polymerisation of cyclo-olefins, European Polymer Journal, vol 5, 29-33, 1969.

81) Bosam,R.H.A., Van Den Aardweg,F., Mol,J.C., Cometathesis of methyl oleate and ethylene; a direct route to methyl dec-9-enoate, Journal of the Chemical Society: Chemical Communications, 1132-1133, 1981.

82) Feast, W.J., Blackmore, P.M., Stereoregular fluoropolymers: 3. The ring opening polymerisation of endo- and exo-5-trifluoromethylbicyclo[2.2.1] hepta-2-ene, Polymer, Vol.27, 1296-1303, 1986.

83) Alimunar,A.B., Blackmore,P.M., Edwards,J.H., Feast,W.J., Wilson,B., Stereoregular fluoropolymers: 1. The ring opening polymerisation of 2,3-bis (trifluoromethyl)bicyclo[2.2..1]hepta-2,5-diene, Polymer, Vol.27, 1281-1288, August 1986.

84) Amass,A.J., Lotfipour,M., Zurimendi,J.A., Tighe,B.J., Thompson,C., Studies in ring opening polymerisation. The kinetics of the reactions between tungsten hexachloride and cyclopentene: A study of the metathesis initiation reaction, Makromolekulare Chemie, 188, 2121-2139. 1987.

85) Amass,A.J., Lotfipour,M., Zurimendi,J.A., The kinetics of the metathesis polymerisation of cyclopentene, Journal of Molecular Catalysis, 8, 243-248, 1980..

86) Natta,G., Dall'asta,G., Mazzanti,G., Motroni,G., Stereospecific polymerisation of cyclobutene, Makromolekulare Chemie, vol 69, 163-7, 1963.

87) Feast,W.J., Wilson,B., Metathesis polymerisation of fluorinated bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]hepta-2,5-dienes, Journal of Molecular Catalysis, 8, 277-296, 1980.

88) Feast,W.J., Wilson,B., Ring opening polymerisation of fluorine substituted bicyclo[2.2.1]hept-2-enes and hepta-2,5-dienes, Polymer, vol 20 1182, October 1979.

89) Seehof,N., Risse,W., Ring opening olefin metathesis polymerisation of fluoroalkylsubstituted polycyclic olefins, Makromolekulare Chemie: Rapid Communications, 12, 107-112, 1991.

90) Feast,W.J., Shahada,L.A.H., Stereoregular Fluoropolymers:2. The ring opening polymerisation of some polyfluoroaryl polycyclic alkenes, Polymer, Vol.27, 1289-1295, August 1986.

91) Van Den Aardweg,G.C.N., Bosma,R.H.A., Mol,J.C., Heterogeneous metathesis of unsaturated nitriles, Journal of the Chemical Society: Chemical communications, 220, 262-263, 1983

92) Cossee,P., Stereoregularity in heterogeneous Ziegler-Natta catalysis, Trans Farad. Society II, 58, 1228, 1962.

93) Eleuterio,H.S., Improvements in and relating to the polymerisation of olefins, Patent No. 872,235, June 1957.

94) Natta,G., Dall'asta,G., Porri,L., Polymerisation of cyclobutene and of 3-methylcyclobutene by $RuCl_3$ in polar protic solvents, Die Makromolekulare Chemie, 253, 81, 1965.

95) Banks,R.L., Bailey,G.C., Four centre mechanism for olefin reactions, Journal of Catalysis, 14, 276, 1969.

96) Heckelsberg,L.F., Banks,R.L., Bailey,G.C., Diene disproportination reactions, Journal of Catalysis, 13, 99, 1969.

97) Scott,K.W., Calderon,N., Ofstead,E.A., Judy,W.A., Ward,J.P., Polymers from cycloolefins, Rubber Chemistry Technology, 44, 1341, 1971.

98) Verkuijlen,E., Boelhouwer,C., Metathesis of unsaturated acid esters and related compounds, Chemistry and Physics of Lipids, 305, 24, 1979.

99) Mol,J.C., Carbon-14 studies on the mechanism of disproportination of propene, Journal of the Chemical Society, Chemical Communications, 633,1968.

100) Bradshaw,C.P.C., Howman,E.J., Turner,L., Olefin dismutation: Reactions of olefins on cobalt oxide-molybdenum oxide-alumina, Journal of Catalysis, 7, 269, 1967.

101) Lewandos,G.S., Pettit,R., A proposed mechanism for the metal-catalysed disproportination reaction of olefins, Tetrahedron letters, No.11, 789, 1971.

102) Grubbs,R.H., Brunck,F.K., A possible intermediate in the tungsten-catalysed olefin metathesis reaxtion, Journal of the American Chemical Society, 94, 2538, 1972.

103) Herrison,J.L., Chauvin,Y., Catalyst for the transformation of olefins with tungsten complexes, Makromolekulare Chemie, 141, 161, 1970.

104) Fischer,E.O., Maasbol,A., On the existence of a tungsten carbonyl carbene complex, Angewandte Chemie. International Edition, 3, 580-581, 1964.

105) Casey,C.P., Albin,D.A., Burkhardt,T.J., Generation and reactions of (phenylmethylcarbene)pentacarbonyltungsten(0), Journal of the American Chemical Society, 2533, 99, 1977.

106) Schrock,R.R., An 'alkylcarbene' complex of tantalum by intramolecular α-hydrogen abstraction, Journal of the American Chemical Society, 96, 6796, 1974.

107) Grubbs,R.H., Burk,P.L., Carr,D.D., Consideration of the mechanism of the olefin metathesis reaction, Journal of the American Chemical Society, 97, 3265, 1975.

108) Ott,K.C., Lee,J.B., Grubbs,R.H., Stereochemical consequence of the interaction of alkylaluminiums with titanacyclobutanes and its relationship to the olefin metathesis reaction, Journal of the American Chemical Society, 104, 2942, 1982.

109) Cannizzo,L.F., Grubbs,R.H., In situ preparation of (μ-chloro)(μ-methylene)bis(cyclopentadienyl)(dimethylaluminium)titanium (tebbe reagent), Journal of Organic Chemistry, 50, 2386, 1985.

110) Tebbe,F.N., Parshall,G.W., Reddy,G.S., Olefin homologation with titanium methylene compounds, Journal of the American Chemical Society, 3611, May 1978.

111) Howard,T.R., Lee,J.B., Grubbs,R.H., Titanium metallacarbene-metallocyclobutene reactions: Stepwise metathesis, Journal of the American Chemical Society, 102, 6876-6878, 1980.

112) Lee,J.B., Ott,K.C., Grubbs,R.H., Kinetics and stereochemistry of the Titanacyclobutane-Titanamethylene interconversion. Investigation of a degenerate olefin metathesis reaction, Journal of the American Chemical Society, 104, 7491-7496, 1982.

113) Muetterties,E.L., Mechanism for the olefin metathesis reaction, Inorganic chemistry Vol. 14, No. 4, 951, 1975.

114) Sehra,J.C., Gundiah,S., Cycloolefins in mechanistic studies of olefin metathesis, Journal of Scientific and Industrial Research, Vol. 42, 250-260, May 1983.

115) Schrock,R.R., Depue,R.T., Feldman,J., Yap,K.B., Yang,D.C., Davies,W.M., Park,L., Dimare,M., Schofield,M., Anhaus,J., Walborsky,E., Evitt,E., Kruger,C., Betz,P.,

Further studies of imido alkylidene complexes of tungsten, well characterized olefin metathesis catalysts with controllable activity, Organometallics, 9, 2262-2275, 1990.

116) Kress,J., Wesolek,M., Osborn,J.A., Tungsten (IV) carbenes for the metathesis of olefins. Direct observation and identification of the chain carrying carbene complexes in a highly active catalyst system, Journal of the Chemical Society: Chemical Communications, No. 9, 514, 1982.

117) Wang,J.L., Menapace,H.R., Metathesis of 2-pentene by a binary catalyst system of tungsten hexacholride and n-butyllithium, Journal of Organic Chemistry, 33, 3787-3794, 1968.

118) Bilhou,J.L., Basset,J.M., Mutin,R., Graydon,W.F., A stereochemical study of metathesis and cis-trans isomerisation of 2-pentenes, The Journal of the American Chemical Society, 99, 4083, 1977.

119) Katz,T.J., Hersh,W.H., The stereochemistry of the olefin metathesis reaction, Tetrahedron Letters, 6, 585, 1977.

120) Thoi,H.H., Reddy,B.S.R., Rooney,J.J., Some aspects of stereoselectivities and kinetics in the ring opening polymerisation of Norbornenes using metathesis catalysts, Journal of the Chemical Society: Faraday Transactions I, 78, 3307-3317, 1982.

121) Ivin,K.J., Rooney,J.J., Bencze,L., Hamilton,J.G., Lam,L.M., Lapienis,G., Reddy,B.S.R., Thoi,H.H., Some recent applications of ^{13}C spectroscopy to the study of the ring opening polymerisation of cycloalkenes and related reactions initiated by metathesis catalysts, Pure and Applied Chemistry, Vol.54, No.2, 447-460, 1982.

122) Blackmore,P.M., Feast,W.J., The synthesis of stereoregular fluoropolymers via ring opening metathesis polymerisation of fluorinated bicyclo[2.2.1]heptenes and heptadienes: A review of possibilities and progress, Journal of Molecular Catalysis, 36, 145-152, 1986.

123) Overberger,C.G., Khattab,G., Effect of a trifluoromethyl group on the polymerisability of α-olefins by transition metalcatalysts, Journal of Polymer Science: Part A-1, Vol.7, 217-235, 1969.

124) Braendlin,H.P., Grindahl,G.A., Kim,Y.S., M^{c}bee,E.T., Stereochemistry of the diels-alder reaction. IV. Adducts between cyclopentadiene and fluorinated olefins, Journal of the American Chemical Society, 2112-2115, June 1962.

125) Bursics,A.R., Bursics,E., Murray,M., Stone,F.G.A., Trifluoromethyl substituted ring systems: Synthesis and reactivity towards metal carbonyls, Journal of Fluorine Chemistry, 7, 619-630, 1976.

126) Mcbee,E.T., Hsu,C.G., Pierce,O.R., Roberts,C.W., Diels-Alder reactions with fluorine containing olefins, Journal of the American Chemical Society, 77, 1955, 915.

127) Blackmore,P.M., Feast,W.J., Stereoregular fluoropolymers, Journal of Fluorine Chemistry, Vol.35, 235, 1987.

128) Feast, W.J., Millinchamp, I.S., Metathesis polymerisation of bicyclic fulvene derivatives, Journal of Molecular Catalysis, Vol.1 part 28, 331-336, 1985.

129) Fessenden and Fessenden p.288, Organic Chemistry second edition.

130) Hall,H.R., Yokoyama,Y., Ring opening polymerisation of atom-bridged and bond-bridged bicyclic ethers, acetals and orthoesters, Advances in Polymer Science, 42, 1982.

131) Gandini,A., Cheradame,H., Cationic polymerisation- initiation processes with alkenyl monomers, Advances in polymer science 34/35, 1980. .

132) Howells, R.D., M^{c}cown, J.D., Trifluoromethanesulfonic acid and derivatives, Chemical Reviews, vol. 77, No. 1, 69-92, 1977.

133) Ivin,K.J., Saegusa,T., General thermodynamic and mechanistic aspects, Vol 1, Elsevier Applied Science 1984.

134) Penczek,S., Kubisa,P., Matyjaszewski,K., Advances in polymer science, 37,- Cationic ring opening polymerisation of heterocyclic monomers, 1980.

135) Matyjaszewski, K., Cationinc polymerisation of alkenes and heterocyclics. More similarities than differences, Makromolekulare Chemie, Macromolecular Symposia, 54/55, 51-71, 1992.

136) Jaacks, V., Boehle,K., Ebenius,E., A method of determining the active centres in cationic polymerisation, applied to polymerisation of dioxolane, trioxane and formaldehyde, Die Makromolekulare Chemie, 118, 354-360, 1968.

137) Plesch,P.H., Westermann,P.H., The polymerisation of 1,3-dioxolane. 1. Structure of the polymer and thermodynamics of its formation, Journal of Polymer Science, Part C 16, 3837, 1968..

138) Andrews,J.M., Semlyen,J.A., Polymer, 13,142, 1942.

139) Szymonski, R., Kubisa, P., Penczek,S., Mechanism of cyclic acetal polymerisation. End of a controversy?, Macromolecules, 16, 1000-1008, 1983.

140) Okada,M., Yagi,K., Sumitomo,H., Cationic polymerisation of 2-methyl-1,3-dioxepane, Die Makromolekulare Chemie, 163, 225-234, 1973.

141) Altona,C., Van der Veek,A.P.M., Conformation of non-aromatic ring compounds: NMR spectra and dipole moments of some 2-substituted 1,3-dioxolanes, Tetrahedron, 24, 4377,1968.

142) Okada,M., Mita, K., Sumitomo, H., Polymerisability of methyl substituted 1,3-dioxalanes, Die Makromolekulare Chemie, 176, 859-872, 1975.

143) Kops, J., Larsen, E., Spanggard, H., Polymerisation of trans-7-oxabicyclo [4.3.0]nonane, Journal of Polymer Science, Symposium, No. 56, 91-100, 1976.

144) Kops, K., Spanggard, H., Polymerisation of cis- and trans-7,9-dioxabicyclo [4.3.0]nonane, Die Makromolekulare Chemie, 176, 299-313, 1975.

145) Riat,D.P.S., The ring opening polymerisation of ring strained cyclic ethers, PhD Thesis, Aston University, 1992.

APPENDIX PREPARATION OF MATERIALS

A.1 MATERIALS PREPARATION

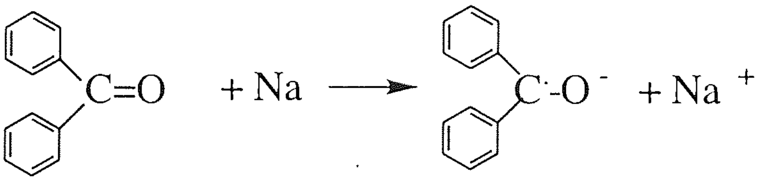
A variety of methods were employed to prepare the reagents for use:-

A.1.1 Method A

The liquid was dried by standing over calcium hydride for 48 hours, then degassed and stored under vacuum until required.

A.1.2 Method B

The radical anion complex, shown below, formed by heating sodium strips with benzophenone is very sensitive to moisture and oxygen and was used to indicate the efficiency of drying procedures. When the solvent, monomer etc. was degassed and dry the characteristic blue colour of the radical anion complex was observed but when the solvent contained air or moisture, the complex was green.



The liquid was distilled onto this complex and stored until required.

A.1.3 Method C

The liquid was dried by standing over calcium hydride for 48 hours then stored in a stoppered flask until required.

A.1.4 Method D

The reagent was used without further purification.

A.1.5 Method E

A solution in dichloromethane was prepared in a catalyst flask using the dry box.

A.1.6 Method F

The liquid was dried by standing over anhydrous magnesium sulphate for 48 hours, stoppered until required.

A.1.7 Method G

The reagent was refrigerated until required.

Table A.1 Preparation of materials.

Material	Drying procedure	Physical form	Supplier
cyclooctene	method A	liquid	95%
cyclohexane	method A	liquid	
tungsten hexachloride	method D	solid	Aldrich
aluminiumdiethyl chloride	method D	liquid	Aldrich solution in hexane
calcium hydride	method D	solid	Aldrich
cyclopentadiene	method D	liquid	
hexafluoro-2-butyne	method D	gas	Fluorchem
dicyclopentadiene	method D	liquid	Aldrich
hydroquinone	method D	solid	Aldrich
potassium dichromate	method D	solid	BDH
concentrated sulphuric acid	method D	liquid	Aldrich
toluene	method A	liquid	
sodium hydroxide	method D	pellets	BDH
acetone	method C	liquid	
dichloromethane	method A	liquid	stored in dark
sodium	method D	solid	Aldrich
benzophenone	method D	solid	BDH
tetrahydrofuran	method B	liquid	HPLC grade
tetraphenyltin	method D	solid	Aldrich
chlorobenzene	method A	liquid	
4-bromo-3,3,4,4-tetrafluorobut-1-ene	method A	liquid	Fluorochem

perfluorobutene	method D	gas	Fluorochem
1,1,3,3,3-pentafluoropropene	method D	gas	Fluorochem
hexafluoropropene	method D	gas	Fluorochem
molybdenum pentachloride	method D	solid	Aldrich
borontrifluoride etherate	method D and method E	liquid	Aldrich
ethanol	method F	liquid	Aldrich
2-chloro-2-methylpropane	method E	liquid	
2-amino-5-nitrobenzotrifluoride	method D	solid	Aldrich
2-nitro-5-aminobenzotrifluoride	method D	solid	Aldrich
paranitroaniline	method D	solid	Aldrich
oxetane	method G	liquid	Jannssen
1,2-methylenedioxybenzene	method A	liquid	Aldrich
1,4-benzodioxane	method A	liquid	Aldrich
trifluoromethane sulphonic acid	method E	liquid	Fluorochem
trifluoromethane sulphonic anhydride	method E	liquid	Fluorochem
tetrafluoroboric acid	method D	liquid	Fluka solution in diethyl ether
trimethylsilylchloride	method D	liquid	Aldrich
2-hydroxymethyl-1,4-benzodioxane	method D	solid	Aldrich
bis(trimethylsilyl) acetamide (BSA)	method G	liquid	Aldrich
bis(trimethylsilyl)tri fluoroacetamide (BSTFA)	method G	liquid	Aldrich
triethylamine	method C	liquid	
pyridine	method C	liquid	redistilled

A.2 HAZARDS OF CHEMICALS USED

Cyclohexane: flammable

Tungsten Hexachloride: corrosive, air and moisture sensitive, handle under nitrogen.

Aluminiumdiethyl Chloride: moisture sensitive, handle under inert atmosphere.

Calcium Hhydride: moisture sensitive, handle under nitrogen.

Cyclopentadiene: irritant.

Hexafluoro-2-butyne: toxic gas.

Dicyclopentadiene: irritant

Hydroquinone: irritant.

Concentrated Sulphuric Acid: heat evolved when in contact with water.

Toluene: flammable.

Sodium Hydroxide: heat evolved in contact with water.

Tetrahydrofuran: highly flammable.

Tetraphenyltin: light sensitive.

Chlorobenzene: flammable

4-Bromo-3,3,4,4-tetrafluorobut-1-ene: irritant.

Hexafluoropropene: toxic gas.

1,1,3,3,3-Pentafluoroprop-1-ene: toxic gas.

Molybdenum Pentachloride: moisture sensitive.

Perfluorobutene: toxic gas.

Borontrifluoride Etherate: Extremely moisture sensitive, handle under Argon.

Ethanol: flammable

2-Chloro-2-methylpropane: flammable

2-Amino-5-nitrobenzotrifluoride: irritant

2-Nitro-5-aminobenzotrifluoride: irritant

Paranitroaniline: irritant, highly toxic.

Oxetane: flammable

1,2-Methylendioxybenzene: irritant

1,4-Benzodioxane: irritant

Trifluoromethanesulfonic Acid: moisture sensitive, handle in a fumecupboard, corrosive.

Trifluoromethanesulfonic Anhydride: moisture sensitive, handle in a fumecupboard, corrosive.

Dichloromethane: flammable, toxic, irritant.

Tetrafluoroboric Acid: moisture sensitive.

Trimethylsilylchloride: flammable, corrosive, moisture sensitive.

2-Hydroxymethyl-1,4-benzodioxane: irritant.

Bis(trimethylsilyl)acetamide: flammable, moisture sensitive.

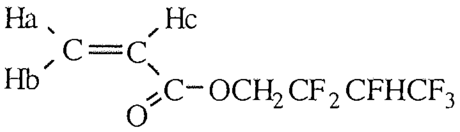
Bis(trimethylsilyl)trifluoroacetamide:flammable, moisture sensitive.

Triethylamine: flammable, corrosive.

Pyridine: flammable, irritant.

A3 2,2,3,4,4,4-HEXAFLUOROBUTYLMETHACRYLATE

A.3.1 Removal of Inhibitor from 2,2,3,4,4,4-Hexafluorobutyl methacrylate



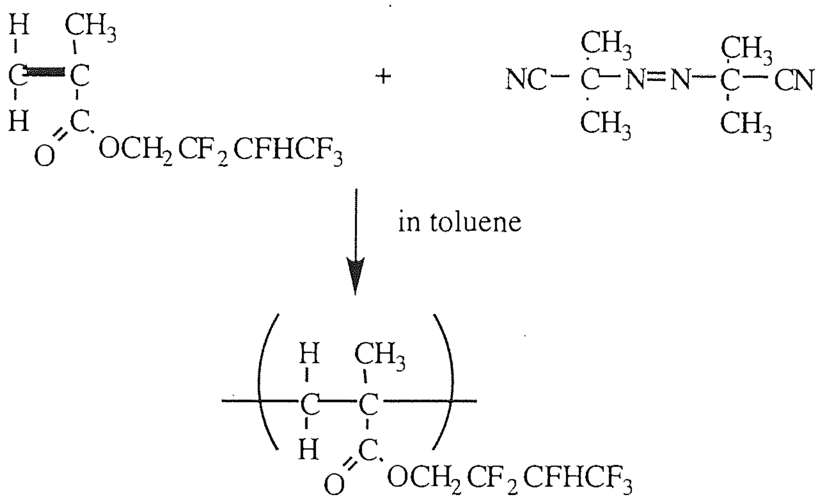
The monomer above was washed three times with approximately one third of its own volume of sodium hydroxide solution (10%), then twice with distilled water. The wet monomer was then dried over anhydrous magnesium sulphate and left standing over calcium hydride in a fridge.

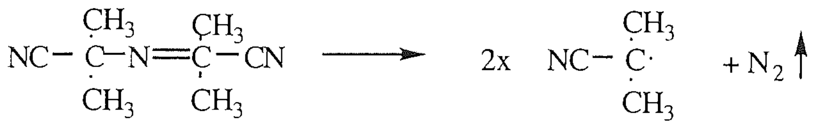
A 3.2 The Free Radical Polymerisation of ,2,2,3,4,4,4-Hexafluorobutylmethacrylate.

A3.2.1 The Recrystallization of Azoisobutyronitrile (AZBN)

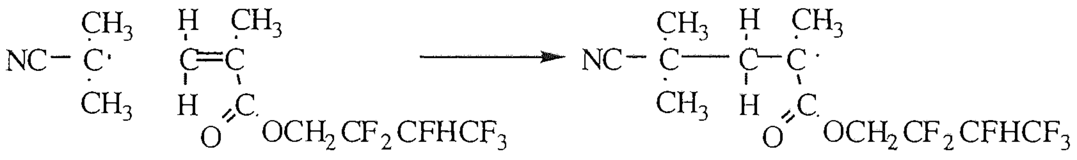
AZBN (10g) was dissolved in chloroform (40cm^3) and warmed to 40 °C. Methanol (75cm^3) was added and the solution cooled. The recrystallised AZBN was filtered off washed with methanol, dried under vacuum and stored in deep freeze until required.

A.3.2.2 Experimental Procedure for the Free Radical Polymerisation of 2,2,3,4,4,4-Hexafluorobutylmethacrylate





AZBN



AZBN was placed into a clean, dry, reaction vessel, which was then evacuated. Toluene ($50cm^3$) and hexafluorobutylmethacrylate (5g) were distilled into the vesssel which was then left overnight at 60°C. The polymer precipitated as it was produced. Methanol was added to dissolve the polymer, this was later evaporated to produce a fine white powdery polymer, which was dried in a vacuum oven. It was unusual that this polymer was insoluble in toluene, but very soluble in methanol, as methacrylates are usually soluble in toluene and insoluble in methanol. This solubility difference may be due to the fluorine atoms in the side chain, they could possibly be influencing the polarity of the polymer.

A.3.2.3 G.P.C.

Mw=26690, Mn=20930, Polydispersity= 1.27

A.3.3 The Anionic Polymerisation of 2,2,3,4,4,4-Hexafluorobutylmethacrylateusing Aluminium Porphyrin Solution

[M]:[I]=200:1

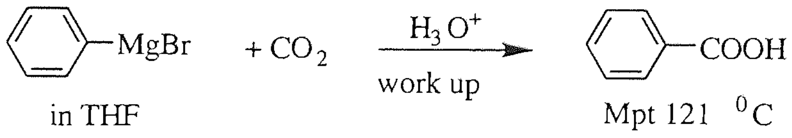
A.3.3.1 Experimental Procedure

2,2,3,4,4,4-Hexafluorobutylmethacrylate (0.0422moles) was distilled into a clean, dry reaction vessel, aluminium porphyrin solution (0.05moldm^{-3}:4.25cm^3) was injected into the reaction vessel through a subaseal. The vessel was then placed in a water bath at 60°C over night. We attempted to precipitate any polymer produced with methanol and then hexane, but no polymer was produced, even after evaporation of the solvent.

A.3.4 The Polymerisation of 2,2,3,4,4,4-Hexafluorobutyl methacrylate using a Grignard Reagent

A.3.4.1 The Synthesis of Grignard Reagent

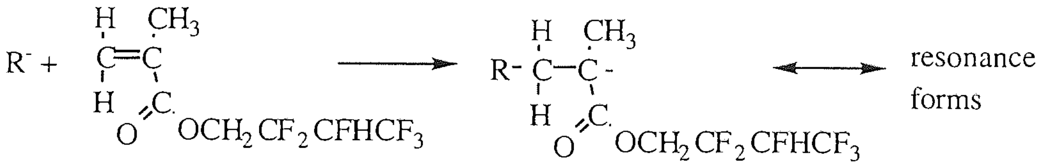
Magnesium (2g) was placed in the bottom of a round bottomed three-necked flask, to which a condenser, a stoppered dropping funnel containing bromobenzene in THF and a nitrogen line were attached. THF (50ml, dried over calcium hydride) was poured into the round bottomed flask, through the condenser along with a small quantity of the solution in the dropping funnel (1-2cm^3) and the reaction mixture stirred. When the mixture was refluxing the remainder of the solution in the dropping funnel was added dropwise to maintain the refluxing. To test the concentration of the prepared Grignard solution, an aliquot (5cm^3) was syringed onto cardice in an open beaker



A.3.4.2 The Polymerisation of 2,2,3,4,4,4-Hexafluorobutyl methacrylate

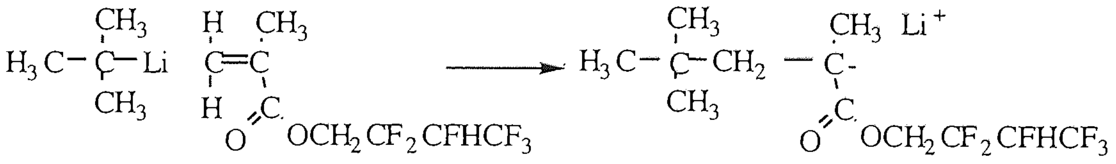
Hexafluorobutylmethacrylate (5g) and THF (2cm^3) were distilled into a clean, dry reaction vessel. Grignard solution (3.6cm^3; 0.55moldm^{-3}) was injected into the vessel which was then placed in a cooling solution of dry ice/methanol at -80°C. After evaporation of solvent, no polymer appeared.

Neither aluminium porphyrin or phenylmagnesiumbromide led to the production of polyhexafluorobutylmethacrylate. Aluminium porphyrin is known for generating immortal systems and experiments have been carried out using methylmethacrylate and U.V. light. Our polymerisations were carried out at 60°C without U.V. light and this is possibly why no polymerisation occurred. It was expected that an anionic mechanism would be succcessful in the polymerisation of hexafluorobutylmethacrylate, as the negative charge on the growing polymer could be stabilised by resonance.



Anionic polymerisations generally proceed better at lower temperatures, but even conducting the polymerisations at -80°C did not encourage polymerisation to take place.

A.3.5 Polymerisation of 2,2,3,4,4,4-Hexafluorobutylmethacrylate using Buli



Hexafluorobutylmethacrylate (3.8g) and THF (3.6g) were distilled into a clean, dry reaction vessel. Buli (0.2cm^3; 2.0moldm^{-3}) was injected through a subaseal which gave a [M]:[I] ratio of 100:1. The pale yellow solution was then left overnight. After this time the solution was deeper yellow in colour and more viscous. Methanol was added to precipitate the polymer, which was dried in a vacuum oven.

A3.5.1 GPC

Molecular Weight= 1629.75

A4 NMR SPECTRA

Figure A4.1 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene

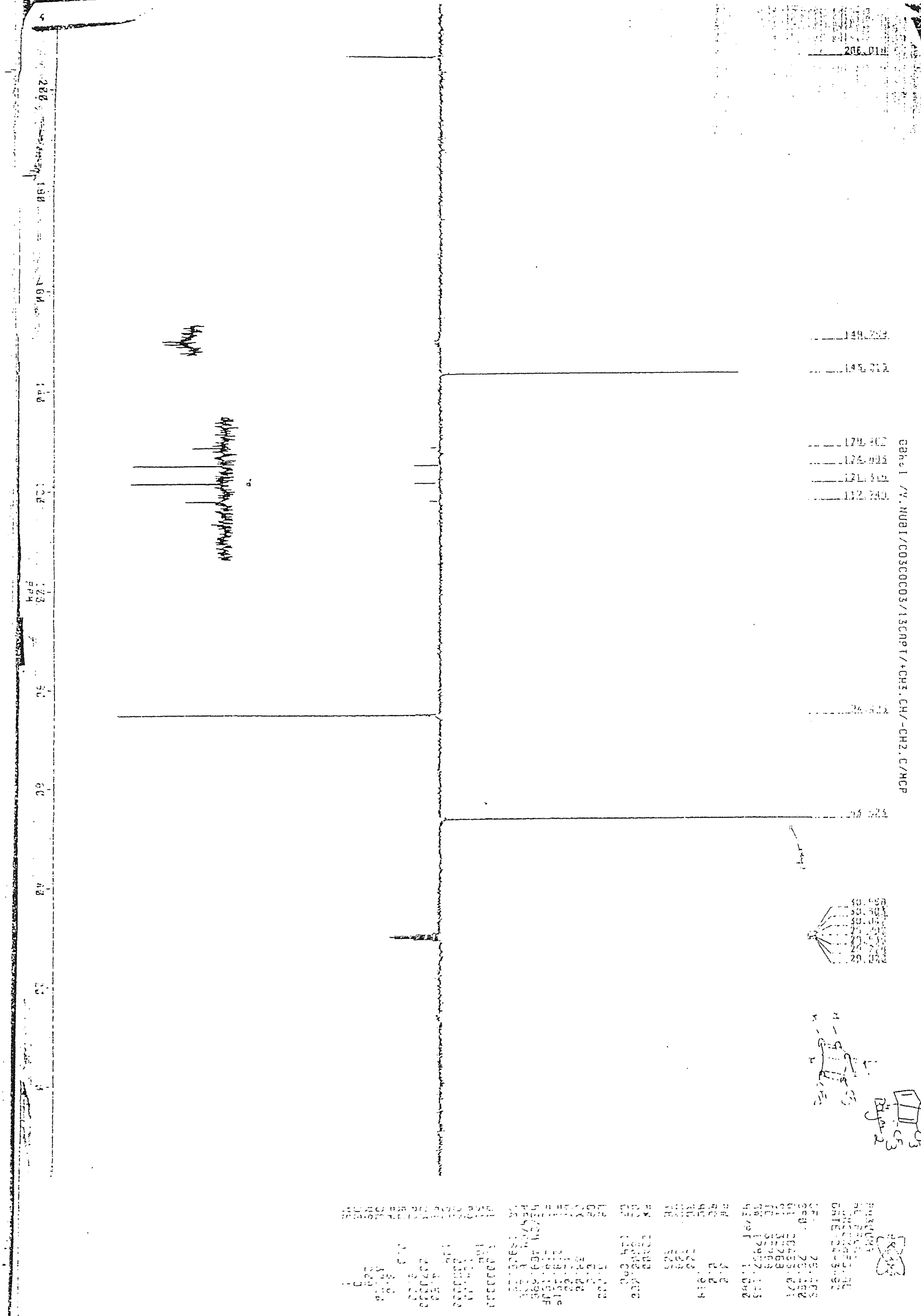


Figure A4.2 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene prepared using WCl_6/Sn(Ph)₄

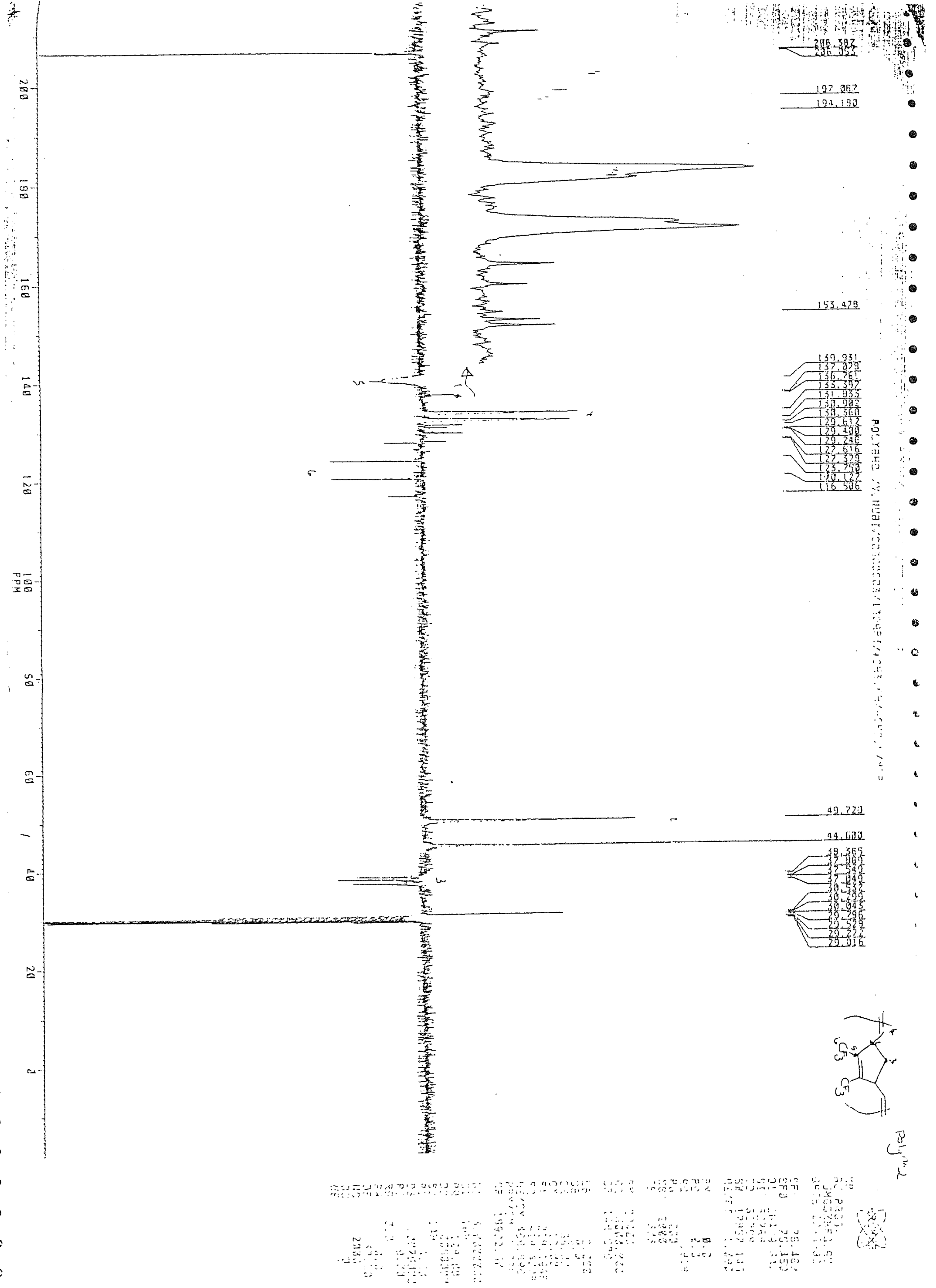
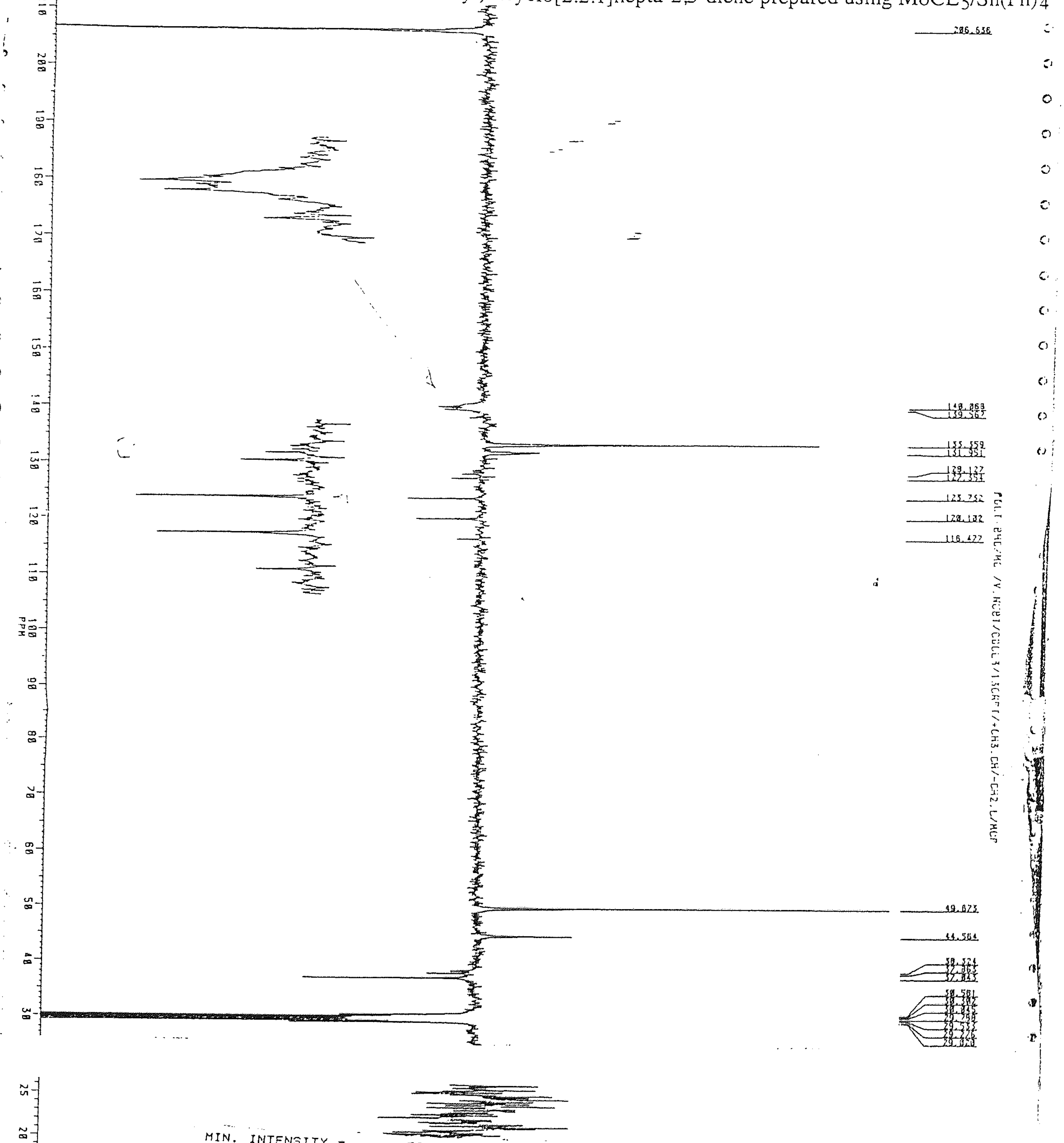


Figure A4.5 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene prepared using MoCL$_5$/Sn(Ph)$_4$



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INTENS. LEVEL  =        .538      MAXY  =  25.00000    PP CONSTANT =   1.00000
F1 =   16495.23 HZ =    .538      NOISE =    .09930    SENS. LEVEL =    .39721
                      218.5699 PPM       F2 =   -1378.26 HZ =   -18.2626 PPM

   #   CURSOR    FREQUENCY      PPM      INTENSITY
   1      808    15594.585    206.6358    -74.208
   2     5418    10570.751    140.0676     -1.249
   3     5452    10532.969    139.5670     -1.083
   4     5882    10064.493    133.3594      9.830
   5     5980     9958.186    131.9508      1.689
   6     6245     9669.598    128.1269      -.549
   7     6298     9611.291    127.3543      -.841
   8     6549     9337.957    123.7325     -2.122
   9     6800     9063.971    120.1020     -1.866
  10     7051     8790.387    116.4769      -.645
  11    11677     3748.791     49.6733     12.006
  12    12031     3363.189     44.5639      2.807
  13    12463     2892.260     38.3238      -.687
  14    12495     2857.462     37.8628     -1.381
  15    12551     2795.572     37.0427     -5.065
  16    13000     2306.383     30.5607     -3.981
  17    13018     2286.877     30.3022    -14.687
  18    13036     2267.497     30.0454    -29.122
  19    13054     2248.106     29.7885    -34.356
  20    13072     2228.789     29.5325    -29.361
  21    13089     2209.461     29.2764    -15.333
  22    13107     2190.083     29.0197     -5.400
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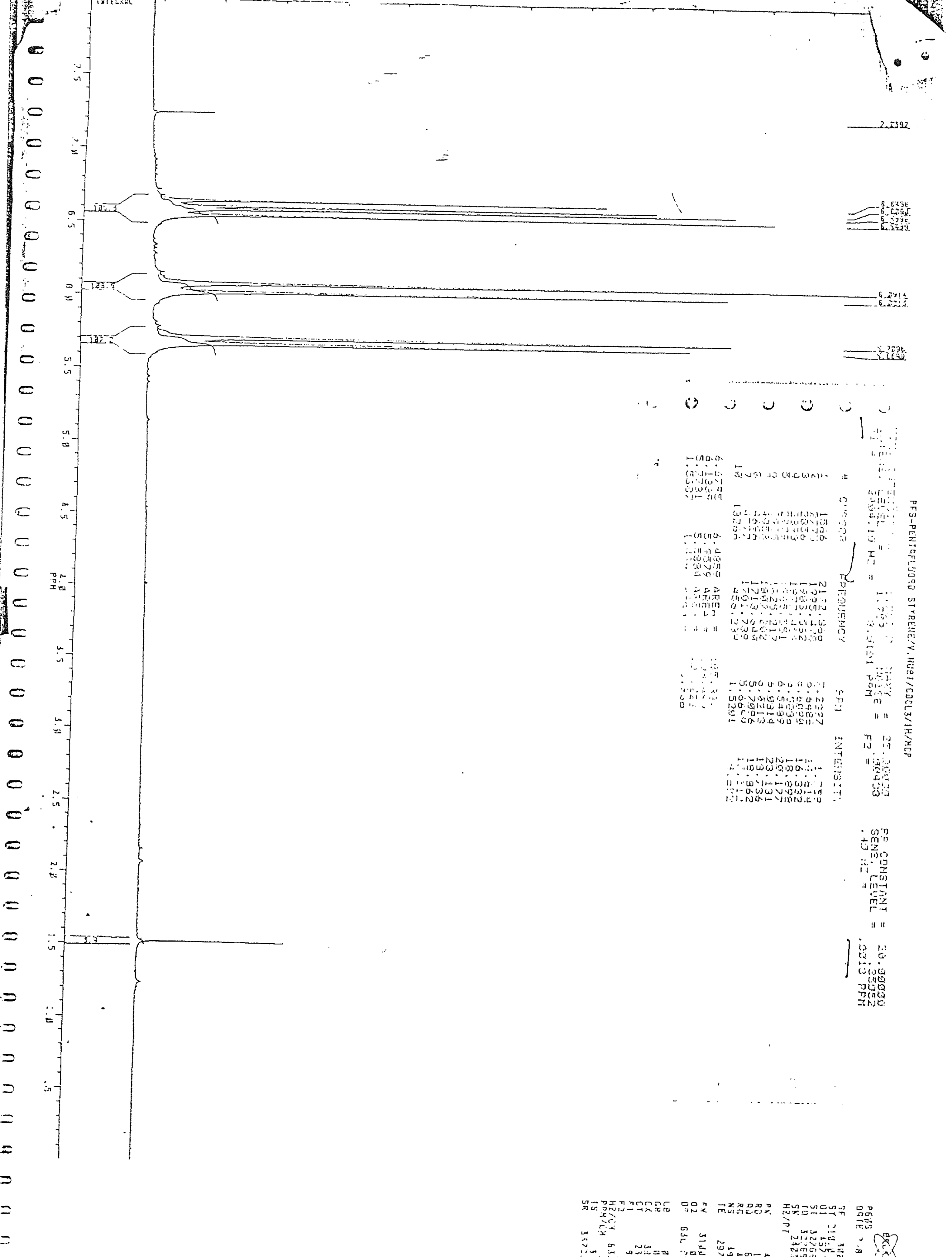
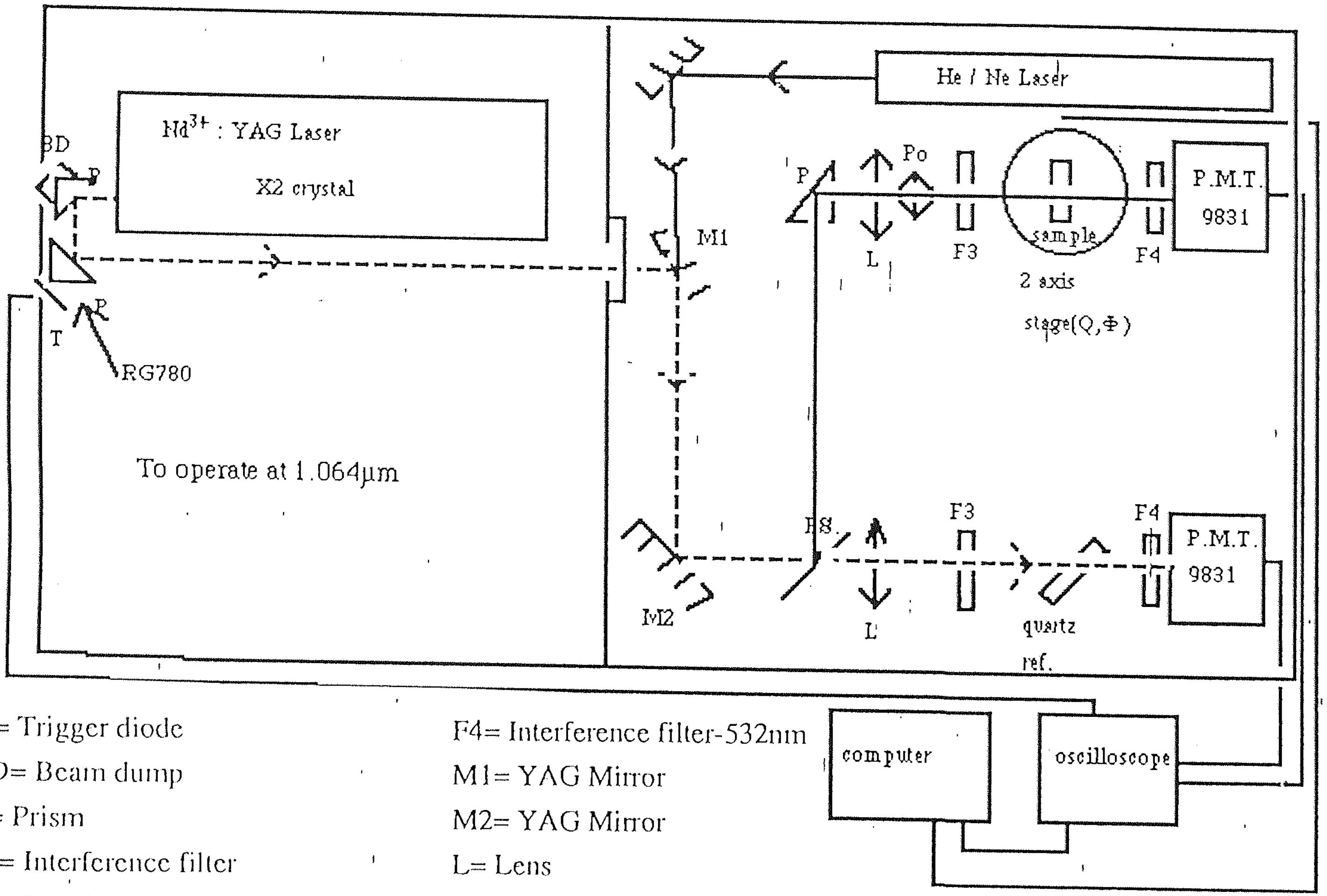
Figure A4.4 Pentafluorostyrene

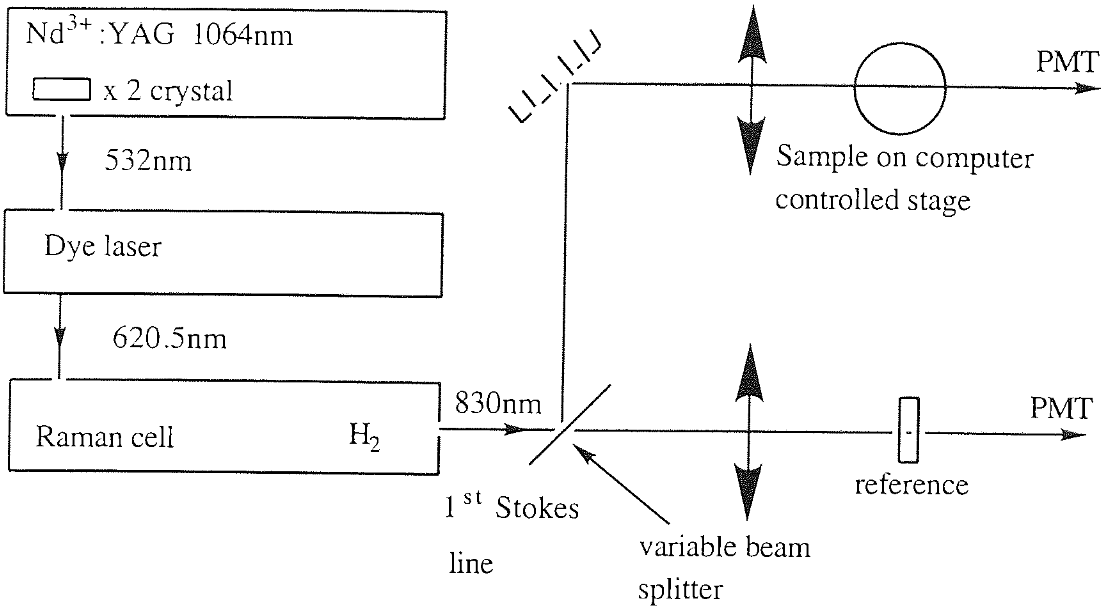




T= Trigger diode
BD= Beam dump
P= Prism
F2= Interference filter
F1= Interference filter/red glass filter
F3= Red glass filter
PMT= Photomultipliertube

F4= Interference filter-532nm
M1= YAG Mirror
M2= YAG Mirror
L= Lens
Po= Polarizer
BS=Beam splitter

A5.1 Nd/YAG laser to operate at 1.064μm for film samples

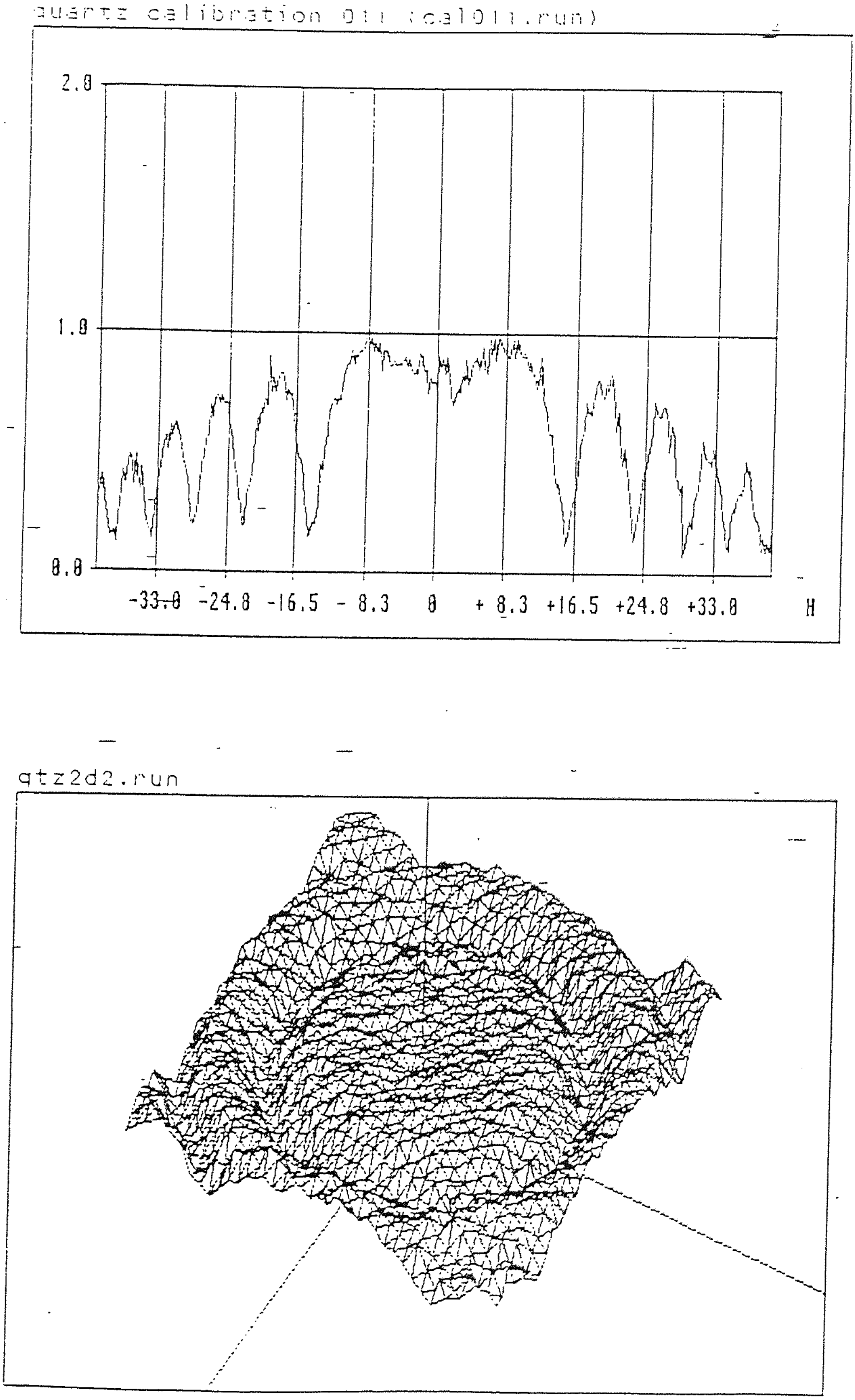


dye 626nm → 1300nm 2nd Stokes line

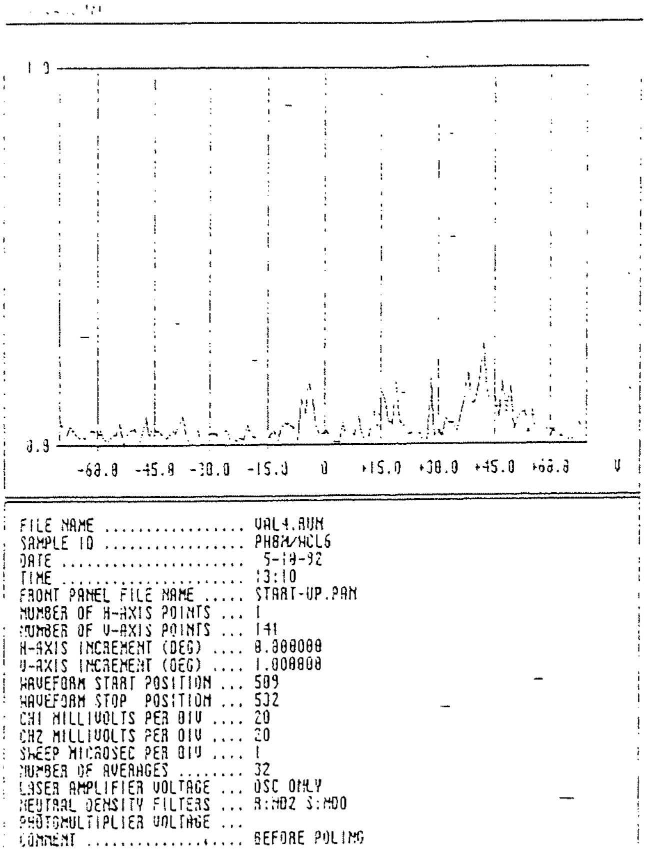
H_2 pressure is altered according to required Stokes line

PMT- Photomultiplier Tube

A5.2 Nd/YAG laser to operate at 1.064µm for powder samples



A5.3 Quartz calibration



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TIME ...................... 13:10
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NUMBER OF V-AXIS POINTS ... 141
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V-AXIS INCREMENT (DEG) .... 1.000000
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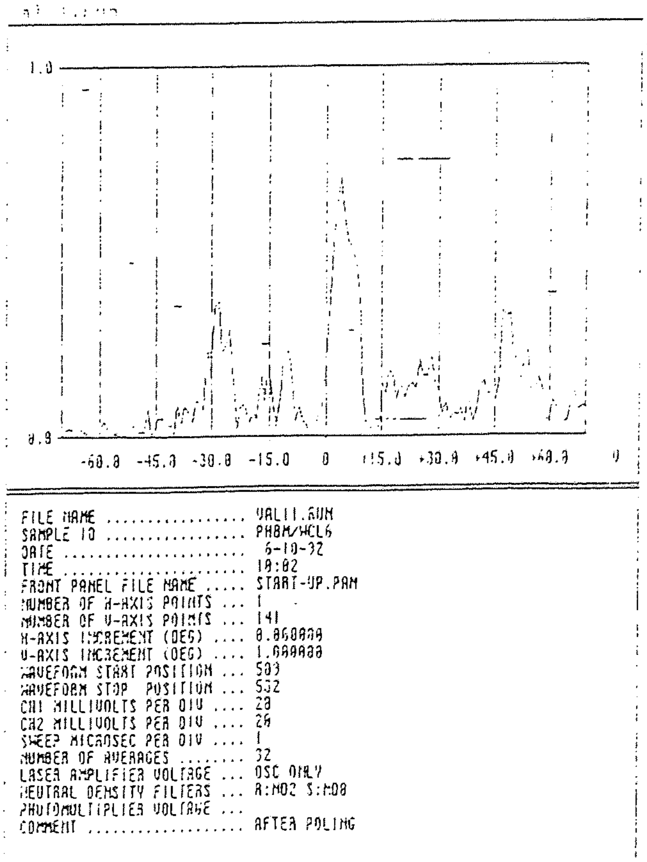
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... R:M02 S:M00
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... BEFORE POLING
```

A5.4 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex before poling



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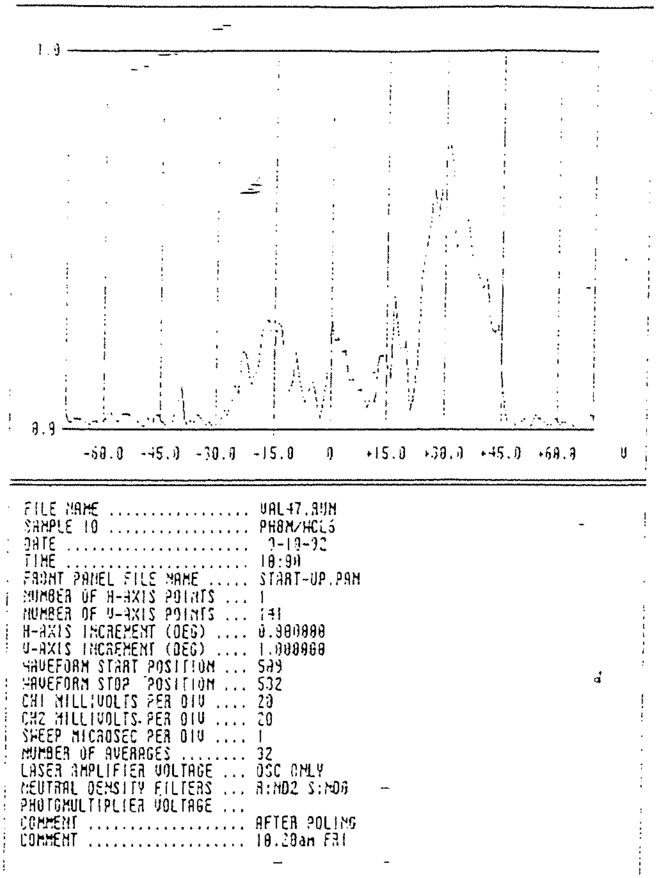
FILE NAME ................. VAL11.RUN
SAMPLE ID ................. PHBM/HCL6
DATE ......................  6-10-92
TIME ...................... 10:02
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 503
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... R:M02 S:M00
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... AFTER POLING
```

A5.5 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex after poling



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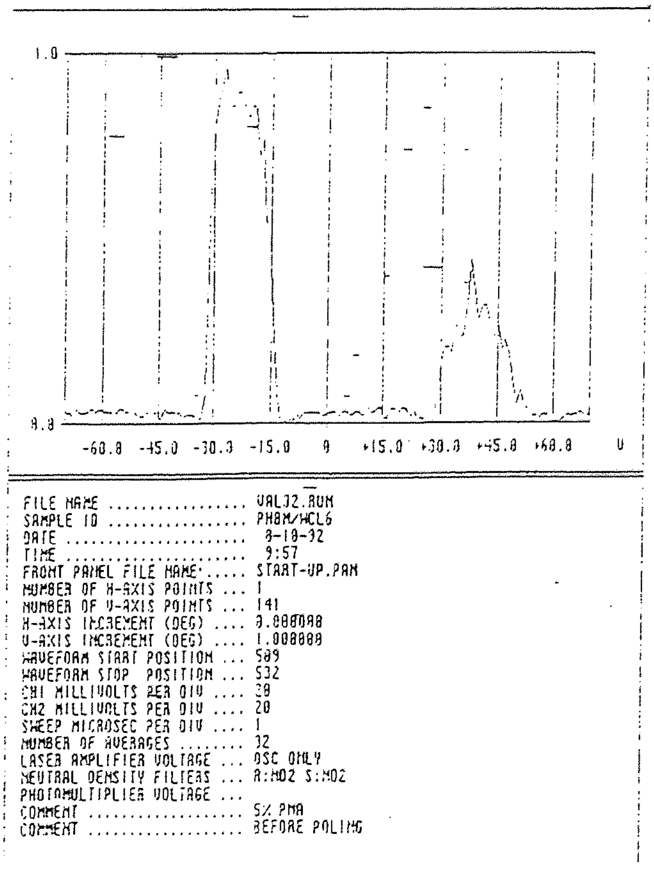
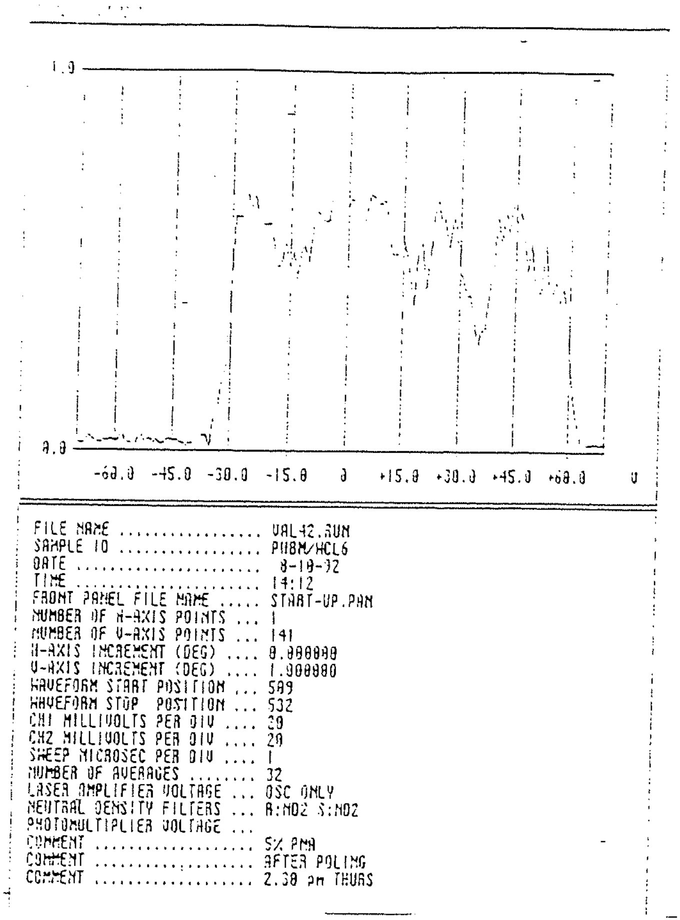
FILE NAME ................ VAL47.RUN
SAMPLE ID ................ PH8M/HCL6
DATE .....................  9-10-92
TIME ..................... 10:00
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... R:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT .................. AFTER POLING
COMMENT .................. 10.20am FRI
```

A5.6 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex after poling after 72 hours



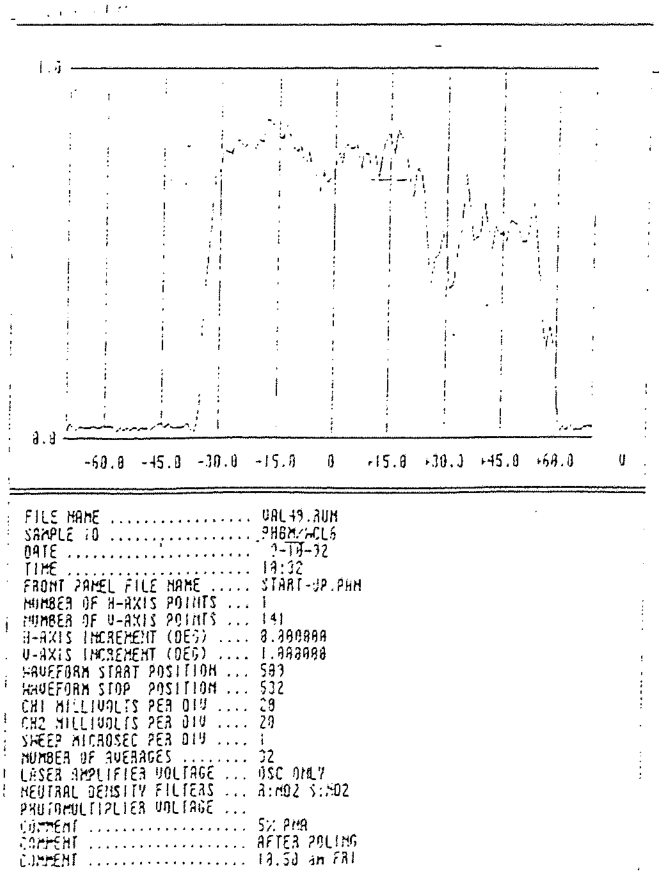
```
FILE NAME ................ VAL32.RUN
SAMPLE ID ................ PH8M/HCL6
DATE .....................  8-10-92
TIME .....................  9:57
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... R:ND2 S:ND2
PHOTOMULTIPLIER VOLTAGE ...
COMMENT .................. 5% PNA
COMMENT .................. BEFORE POLING
```

A5.7 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 5% paranitroaniline before poling



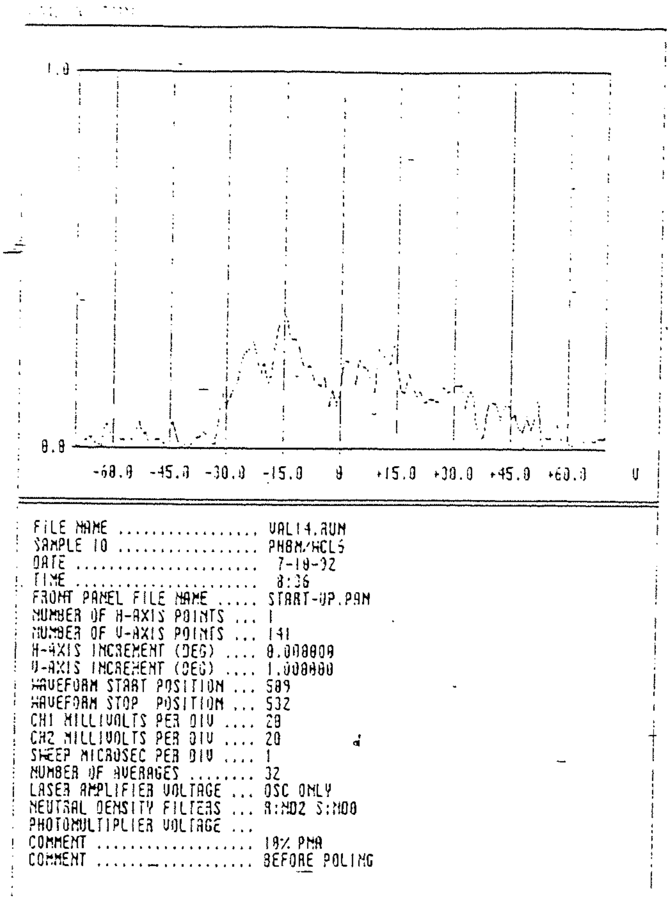
```
FILE NAME ................. VAL42.RUN
SAMPLE ID ................. PUBM/HCL6
DATE ......................  9-10-92
TIME ...................... 14:12
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... A:ND2 S:ND2
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... 5% PNA
COMMENT ................... AFTER POLING
COMMENT ................... 2.30 pm THURS
```

A5.8 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 5% paranitroaniline after poling



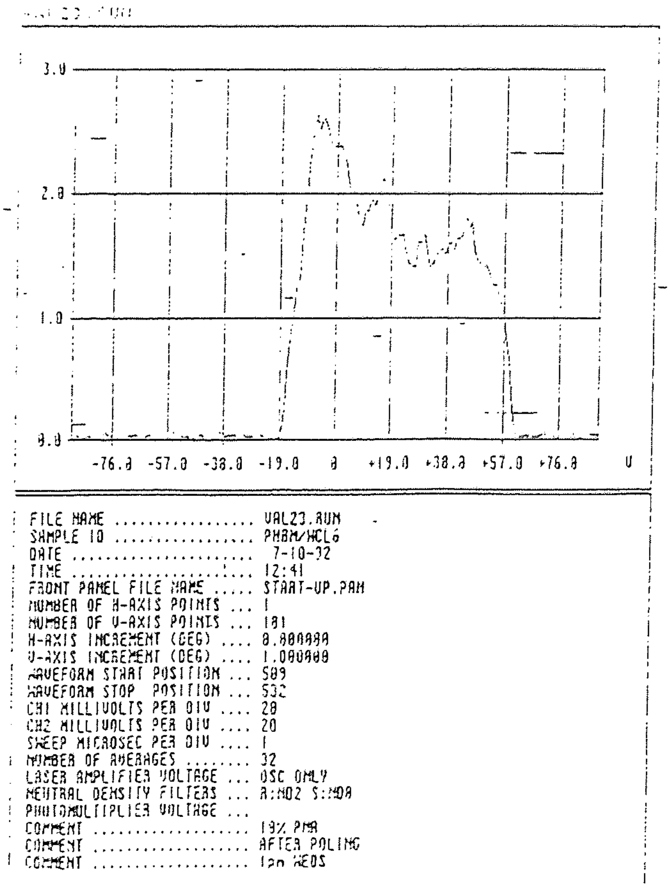
```
FILE NAME ................. VAL49.RUN
SAMPLE ID ................. PHBM/HCL6
DATE ......................  9-10-92
TIME ...................... 10:32
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 503
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... A:ND2 S:ND2
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... 5% PNA
COMMENT ................... AFTER POLING
COMMENT ................... 10.50 am FRI
```

A5.9 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 5% paranitroaniline after poling after 24 hours



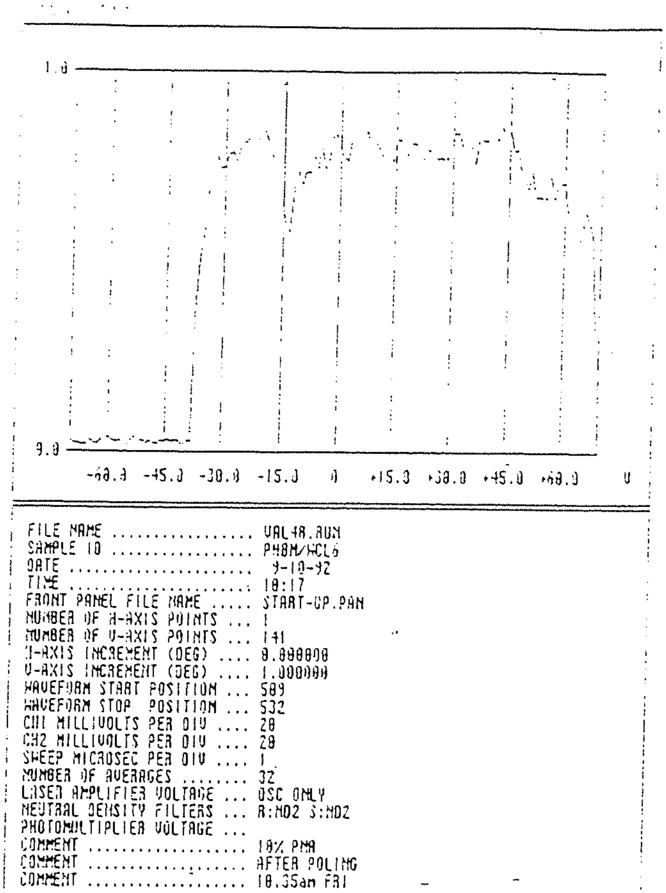
```
FILE NAME ................. VAL14.RUN
SAMPLE ID ................. PHBM/HCL5
DATE ......................  7-10-92
TIME ......................  8:36
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... A:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... 10% PNA
COMMENT ................... BEFORE POLING
```

A5.10 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 10% paranitroaniline before poling



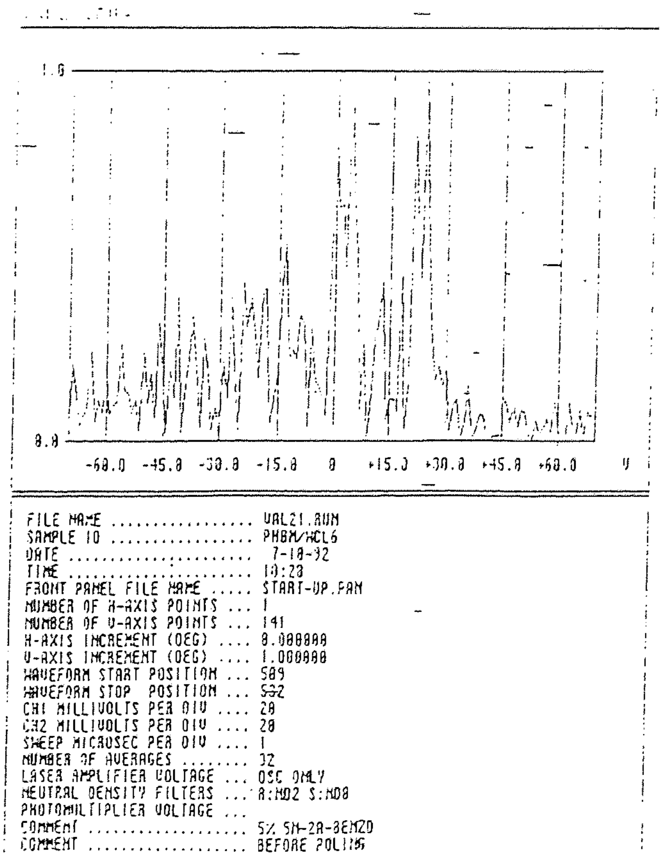
```
FILE NAME ................. VAL23.RUN
SAMPLE ID ................. PHBM/HCL6
DATE ......................  7-10-92
TIME ...................... 12:41
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 181
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... A:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... 10% PNA
COMMENT ................... AFTER POLING
COMMENT ................... 1an WEDS
```

A5.11 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 10% paranitroaniline after poling



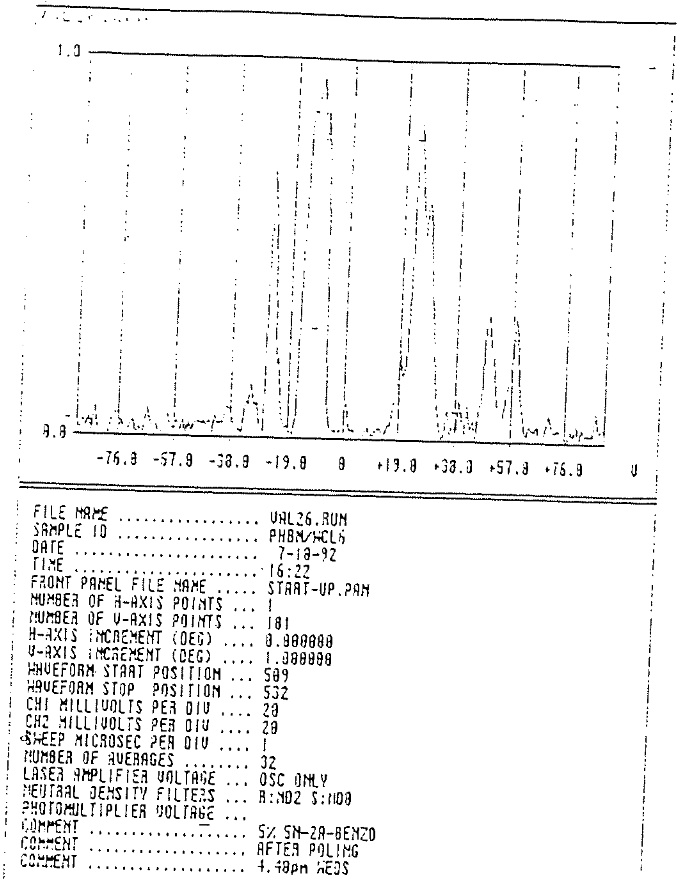
```
FILE NAME .................. VAL48.RUN
SAMPLE ID .................. PHBM/HCL6
DATE .......................  9-10-92
TIME ....................... 10:17
FRONT PANEL FILE NAME ...... START-UP.PAN
NUMBER OF H-AXIS POINTS .... 1
NUMBER OF V-AXIS POINTS .... 141
H-AXIS INCREMENT (DEG) ..... 0.000000
V-AXIS INCREMENT (DEG) ..... 1.000000
WAVEFORM START POSITION .... 509
WAVEFORM STOP  POSITION .... 532
CH1 MILLIVOLTS PER DIV ..... 20
CH2 MILLIVOLTS PER DIV ..... 20
SWEEP MICROSEC PER DIV ..... 1
NUMBER OF AVERAGES ......... 32
LASER AMPLIFIER VOLTAGE .... OSC ONLY
NEUTRAL DENSITY FILTERS .... R:ND2 S:ND2
PHOTOMULTIPLIER VOLTAGE ....
COMMENT .................... 10% PNA
COMMENT .................... AFTER POLING
COMMENT .................... 10.35am FRI
```

A5.12 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 10% paranitroaniline after poling after 48 hours



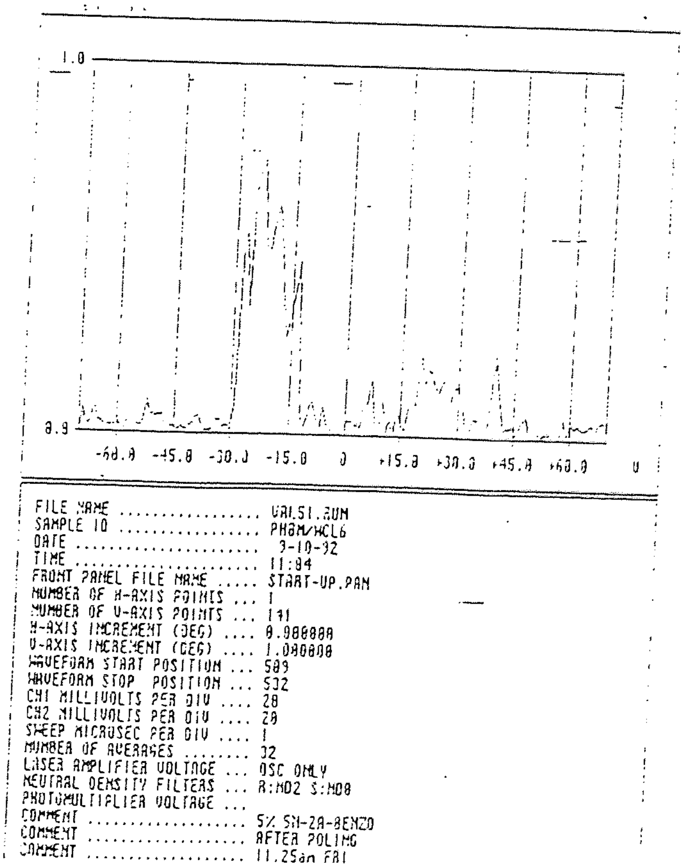
```
FILE NAME .................. VAL21.RUN
SAMPLE ID .................. PHBM/HCL6
DATE .......................  7-10-92
TIME ....................... 10:28
FRONT PANEL FILE NAME ...... START-UP.PAN
NUMBER OF H-AXIS POINTS .... 1
NUMBER OF V-AXIS POINTS .... 141
H-AXIS INCREMENT (DEG) ..... 0.000000
V-AXIS INCREMENT (DEG) ..... 1.000000
WAVEFORM START POSITION .... 509
WAVEFORM STOP  POSITION .... 532
CH1 MILLIVOLTS PER DIV ..... 20
CH2 MILLIVOLTS PER DIV ..... 20
SWEEP MICROSEC PER DIV ..... 1
NUMBER OF AVERAGES ......... 32
LASER AMPLIFIER VOLTAGE .... OSC ONLY
NEUTRAL DENSITY FILTERS .... R:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ....
COMMENT .................... 5% 5N-2A-BENZO
COMMENT .................... BEFORE POLING
```

A5.13 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 5% 5-nitro-2-aminobenzotrifluoride before poling



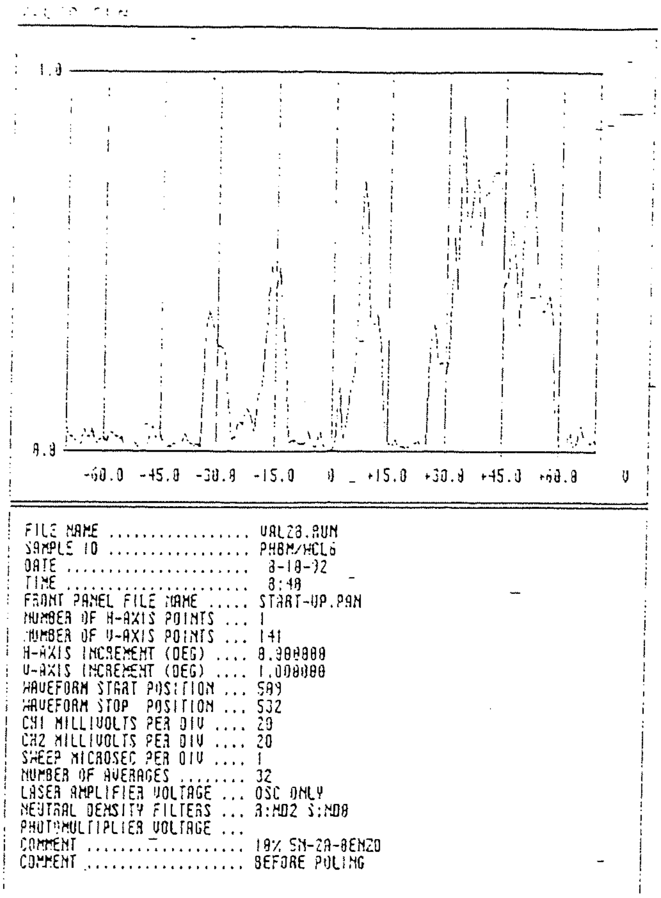
```
FILE NAME .................. VAL26.RUN
SAMPLE ID .................. PHBN/HCL6
DATE .......................  7-10-92
TIME ....................... 16:22
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 181
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... R:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... 5% SN-2A-BENZO
COMMENT ................... AFTER POLING
COMMENT ................... 4.40pm WEDS
```

A5.14 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 5% 5-nitro-2-aminobenzotrifluoride after poling



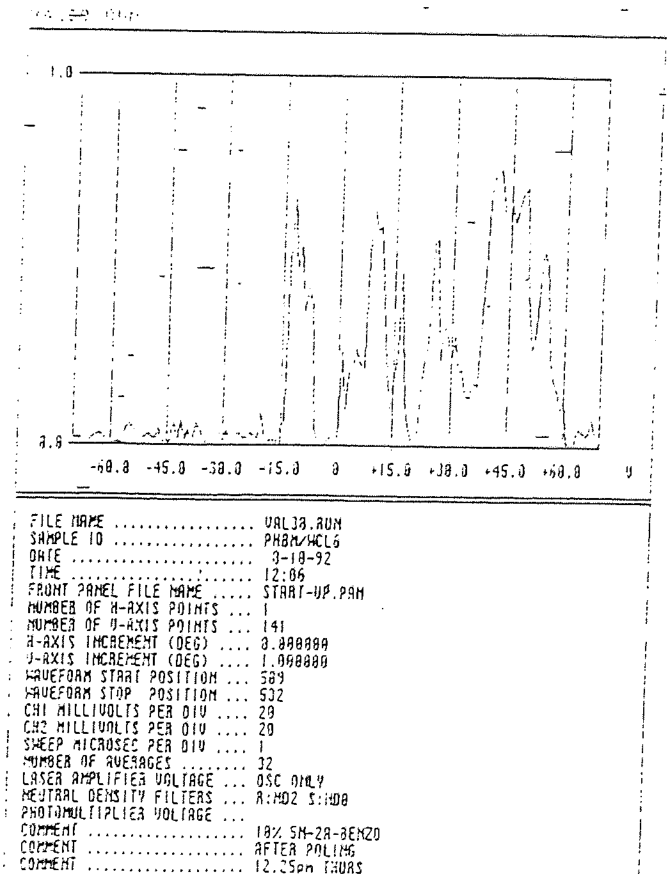
```
FILE NAME .................. VAL51.RUN
SAMPLE ID .................. PHBN/HCL6
DATE .......................  9-10-92
TIME ....................... 11:04
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... R:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... 5% SN-2A-BENZO
COMMENT ................... AFTER POLING
COMMENT ................... 11.25am FRI
```

A5.15 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 5% 5-nitro-2-aminobenzotrifluoride after poling after 48 hours



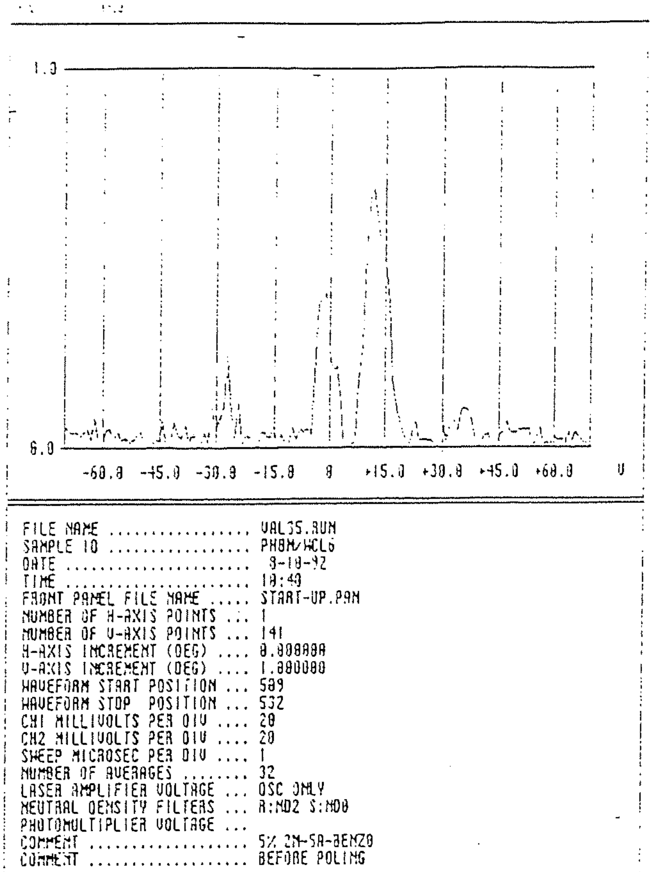
```
FILE NAME ................. VAL20.RUN
SAMPLE ID ................. PHBM/HCL6
DATE ......................  3-10-92
TIME ......................  8:40
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... R:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... 10% SN-2A-BENZO
COMMENT ................... BEFORE POLING
```

A5.16 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 10% 5-nitro-2-aminobenzotrifluoride before poling



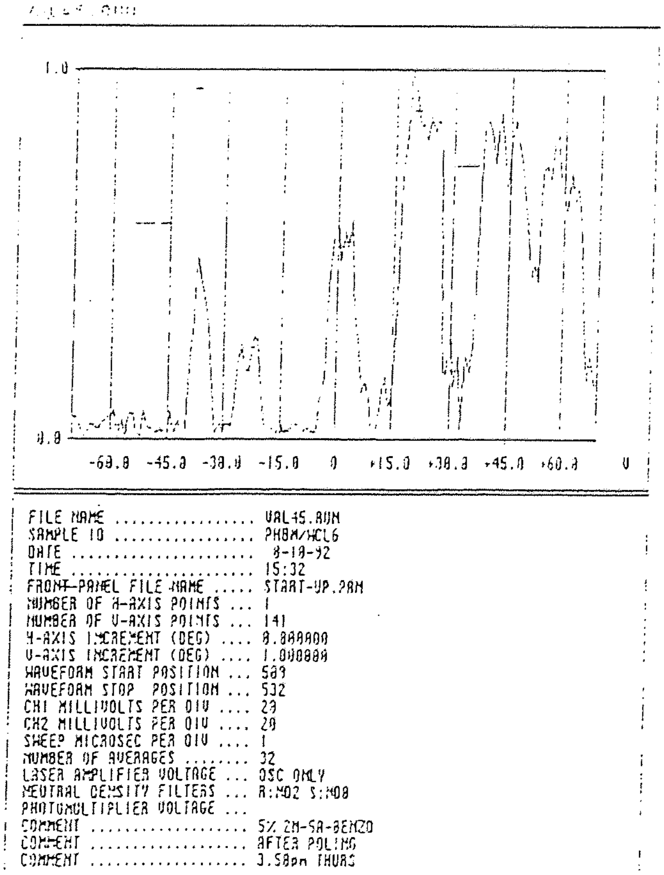
```
FILE NAME ................. VAL30.RUN
SAMPLE ID ................. PHBM/HCL6
DATE ......................  3-10-92
TIME ...................... 12:06
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... R:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... 10% SN-2A-BENZO
COMMENT ................... AFTER POLING
COMMENT ................... 12.25pm THURS
```

A5.17 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 10% 5-nitro-2-aminobenzotrifluoride after poling



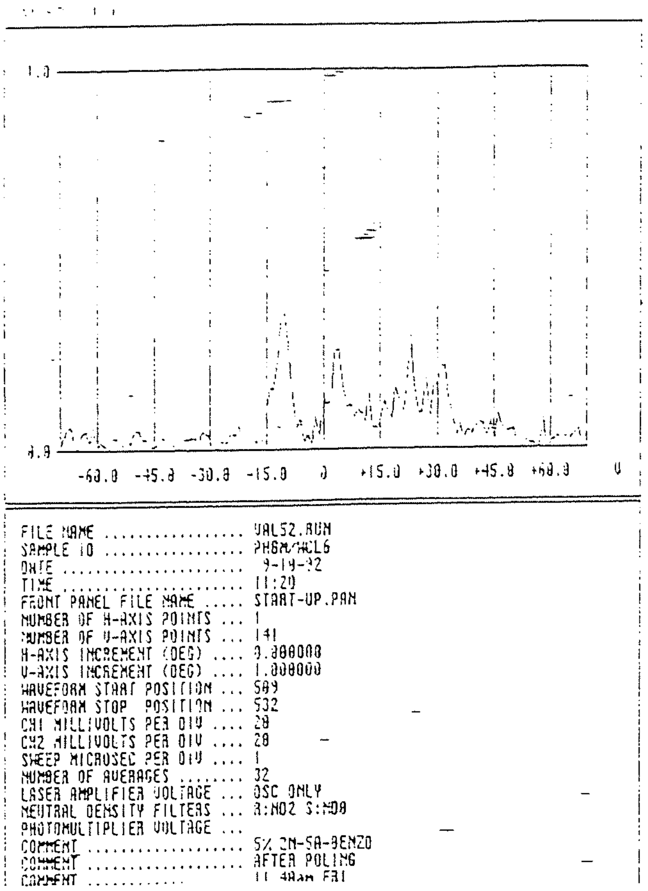
```
FILE NAME ................. VAL35.RUN
SAMPLE ID ................. PHBN/HCL6
DATE ......................  8-10-92
TIME ...................... 10:40
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... R:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... 5% 2N-5A-BENZO
COMMENT ................... BEFORE POLING
```

A5.18 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 5% 2-nitro-5-aminobenzotrifluoride before poling



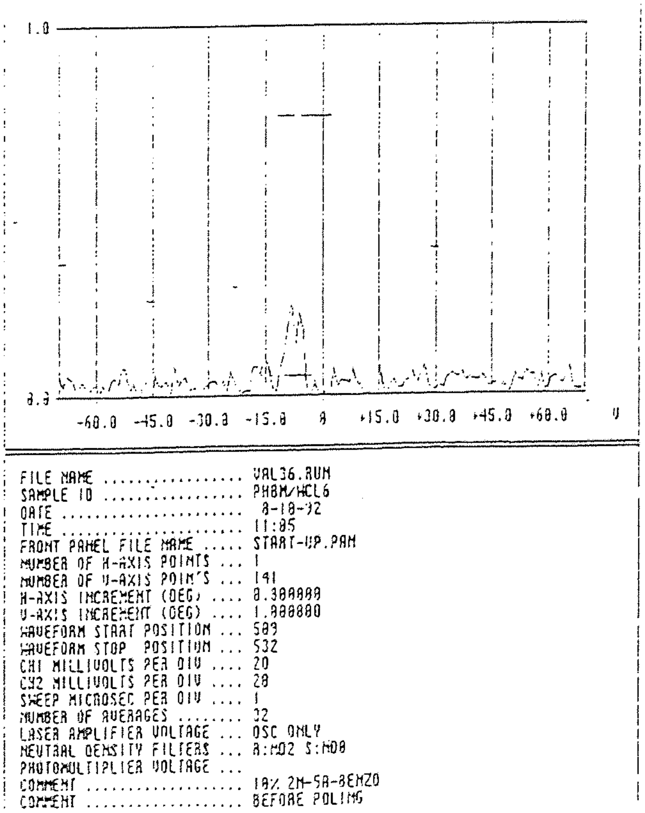
```
FILE NAME ................. VAL45.RUN
SAMPLE ID ................. PHBN/HCL6
DATE ......................  8-10-92
TIME ...................... 15:32
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... R:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... 5% 2N-5A-BENZO
COMMENT ................... AFTER POLING
COMMENT ................... 3.50pm THURS
```

A5.19 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 5% 2-nitro-5-aminobenzotrifluoride after poling



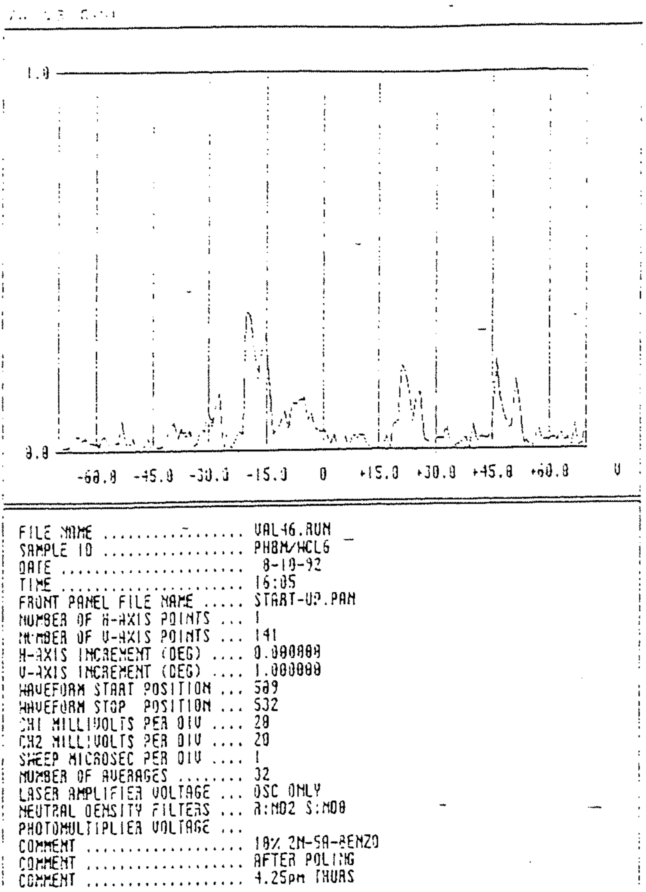
```
FILE NAME ................. VAL52.RUN
SAMPLE ID ................. PHBM/HCL6
DATE ......................  9-19-92
TIME ...................... 11:20
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... A:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... 5% 2N-5A-BENZO
COMMENT ................... AFTER POLING
COMMENT ..........          11 40am FRI
```

A5.20 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 5% 2-nitro-5-aminobenzotrifluoride after poling after 8 hours



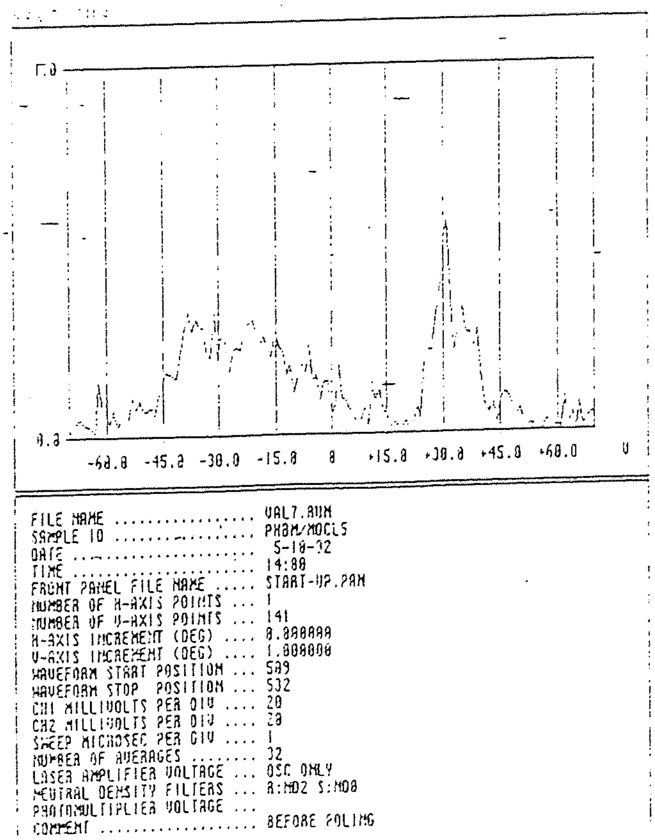
```
FILE NAME ................. VAL36.RUN
SAMPLE ID ................. PHBM/HCL6
DATE ......................  8-18-92
TIME ...................... 11:05
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POIN'S ... 141
H-AXIS INCREMENT (DEG) .... 0.300000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... A:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... 10% 2N-5A-BENZO
COMMENT ................... BEFORE POLING
```

A5.21 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 10% 2-nitro-5-aminobenzotrifluoride before poling



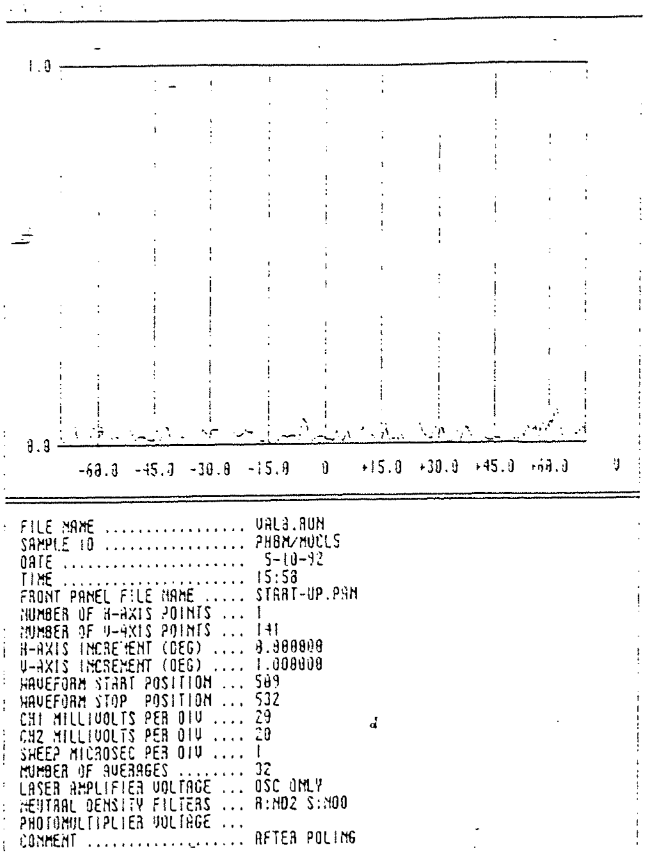
```
FILE NAME ................... VAL46.RUN
SAMPLE ID ................... PH8M/HCL6
DATE ........................  8-10-92
TIME ........................ 16:05
FRONT PANEL FILE NAME ....... START-UP.PAN
NUMBER OF H-AXIS POINTS ..... 1
NUMBER OF V-AXIS POINTS ..... 141
H-AXIS INCREMENT (DEG) ...... 0.000000
V-AXIS INCREMENT (DEG) ...... 1.000000
WAVEFORM START POSITION ..... 509
WAVEFORM STOP  POSITION ..... 532
CH1 MILLIVOLTS PER DIV ...... 20
CH2 MILLIVOLTS PER DIV ...... 20
SWEEP MICROSEC PER DIV ...... 1
NUMBER OF AVERAGES .......... 32
LASER AMPLIFIER VOLTAGE ..... OSC ONLY
NEUTRAL DENSITY FILTERS ..... A:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE .....
COMMENT ..................... 10% 2N-5A-BENZO
COMMENT ..................... AFTER POLING
COMMENT ..................... 4.25pm THURS
```

A5.22 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using tungsten/tin complex doped with 10% 2-nitro-5-aminobenzotrifluoride after poling



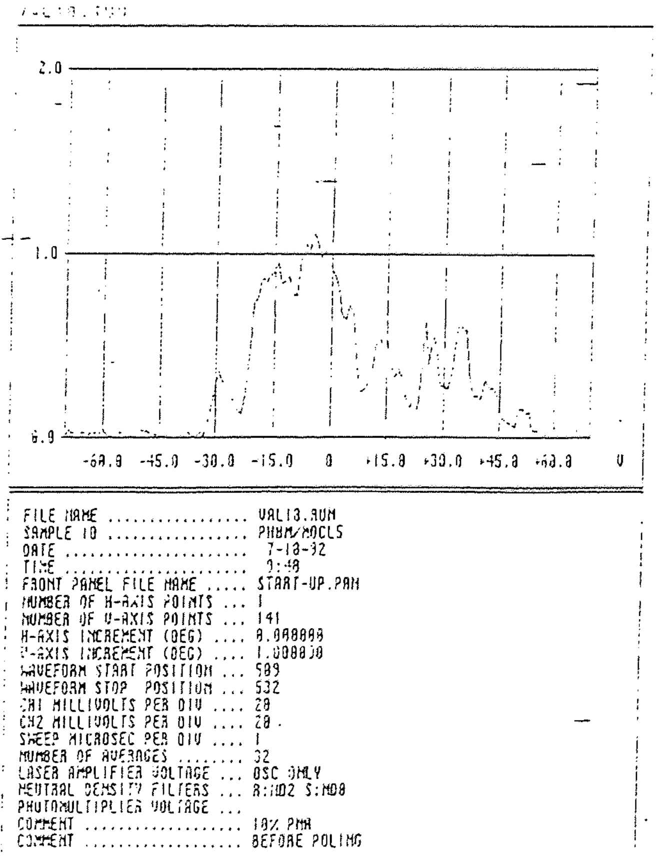
```
FILE NAME ................... VAL7.RUN
SAMPLE ID ................... PH8M/MOCL5
DATE ........................  5-10-92
TIME ........................ 14:00
FRONT PANEL FILE NAME ....... START-UP.PAN
NUMBER OF H-AXIS POINTS ..... 1
NUMBER OF V-AXIS POINTS ..... 141
H-AXIS INCREMENT (DEG) ...... 0.000000
V-AXIS INCREMENT (DEG) ...... 1.000000
WAVEFORM START POSITION ..... 509
WAVEFORM STOP  POSITION ..... 532
CH1 MILLIVOLTS PER DIV ...... 20
CH2 MILLIVOLTS PER DIV ...... 20
SWEEP MICROSEC PER DIV ...... 1
NUMBER OF AVERAGES .......... 32
LASER AMPLIFIER VOLTAGE ..... OSC ONLY
NEUTRAL DENSITY FILTERS ..... A:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE .....
COMMENT ..................... BEFORE POLING
```

A5.23 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2,1]hepta-2,5-diene using molybdenum/tin complex before poling



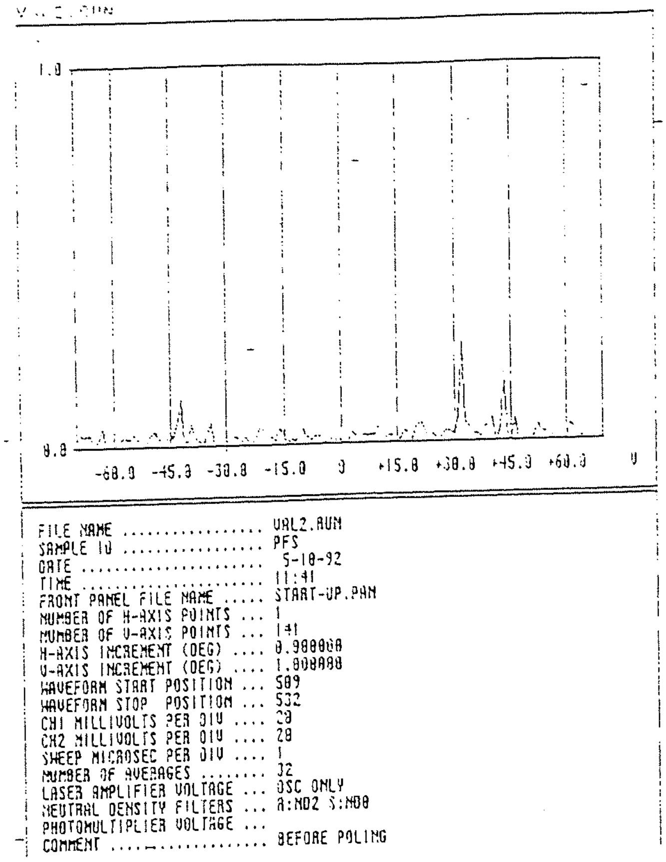
```
FILE NAME ................. VAL0.RUN
SAMPLE ID ................. PHBM/MOCLS
DATE ......................  5-10-92
TIME ...................... 15:50
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 29
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... A:ND2 S:N00
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... AFTER POLING
```

A5.24 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using molybdenum/tin complex after poling



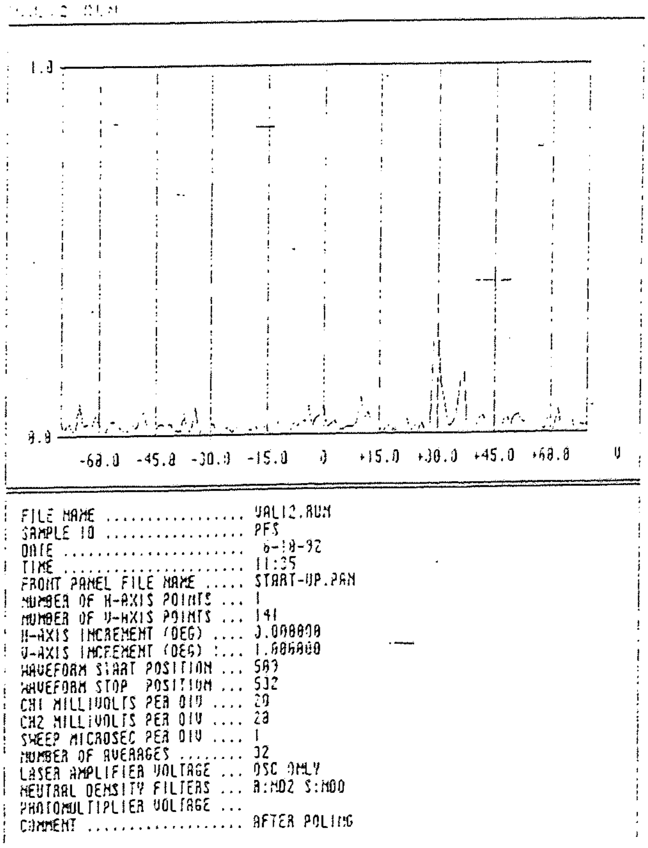
```
FILE NAME ................. VAL10.RUN
SAMPLE ID ................. PHBM/MOCLS
DATE ......................  7-10-92
TIME ......................  9:40
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... A:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... 10% PNA
COMMENT ................... BEFORE POLING
```

A5.25 Poly-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene using molybdenum/tin complex doped with 10% paranitroaniline before poling



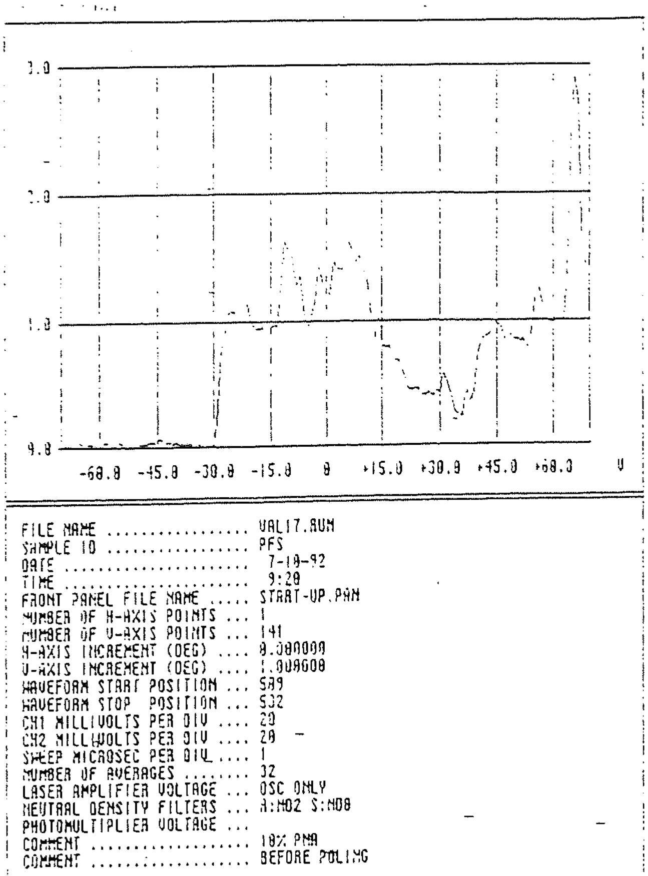
```
FILE NAME ................. VAL2.RUN
SAMPLE ID ................. PFS
DATE ......................  5-10-92
TIME ...................... 11:41
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... R:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... BEFORE POLING
```

A5.26 Polypentafluorostyrene before poling



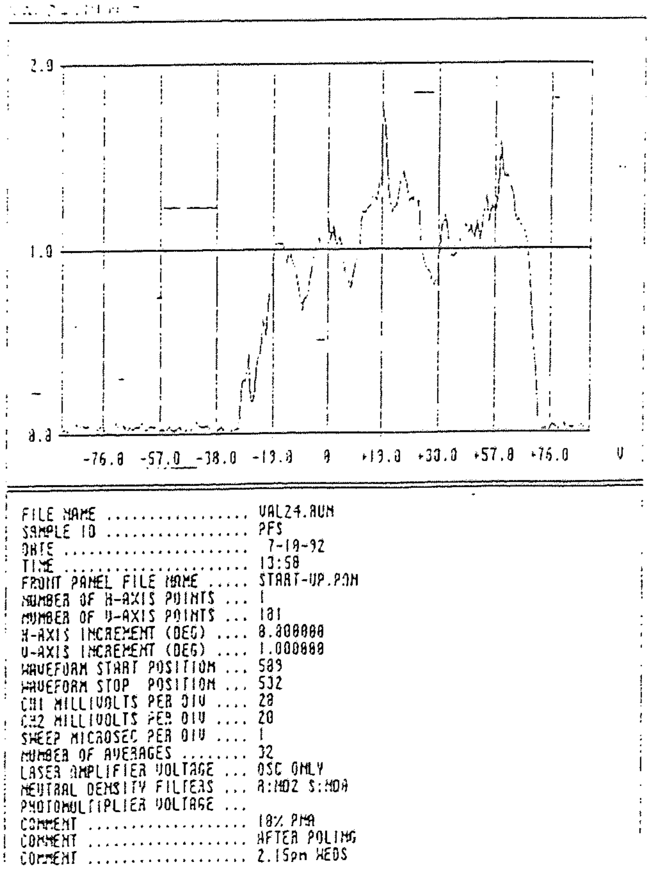
```
FILE NAME ................. VAL12.RUN
SAMPLE ID ................. PFS
DATE ......................  6-10-92
TIME ...................... 11:35
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... R:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... AFTER POLING
```

A5.27 Polypentafluorostyrene after poling



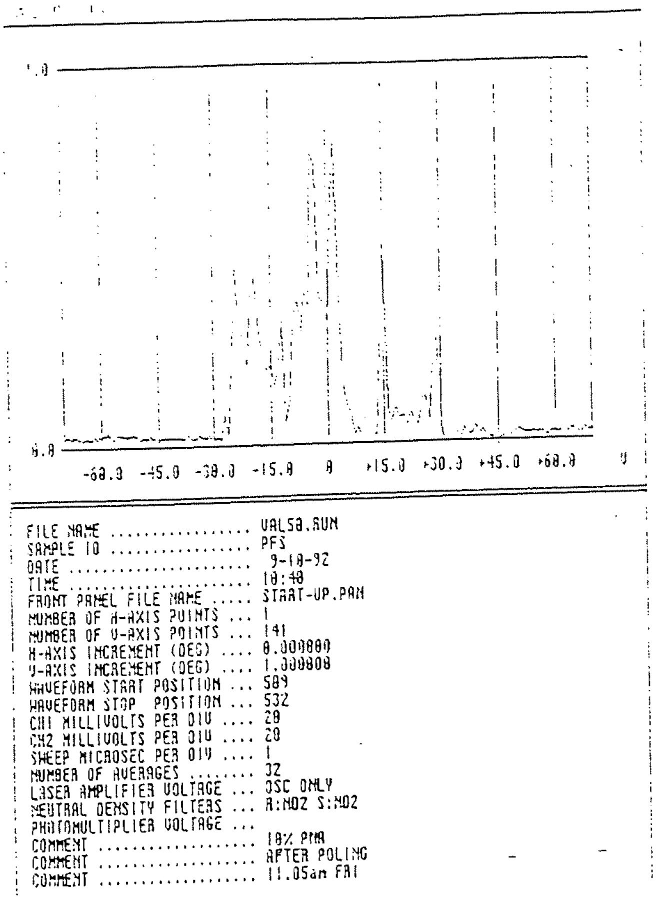
```
FILE NAME ................ VAL17.RUN
SAMPLE ID ................ PFS
DATE .....................  7-10-92
TIME .....................  9:20
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... A:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT .................. 10% PNA
COMMENT .................. BEFORE POLING
```

A5.28 Polypentafluorostyrene doped with 10% paranitroaniline before poling



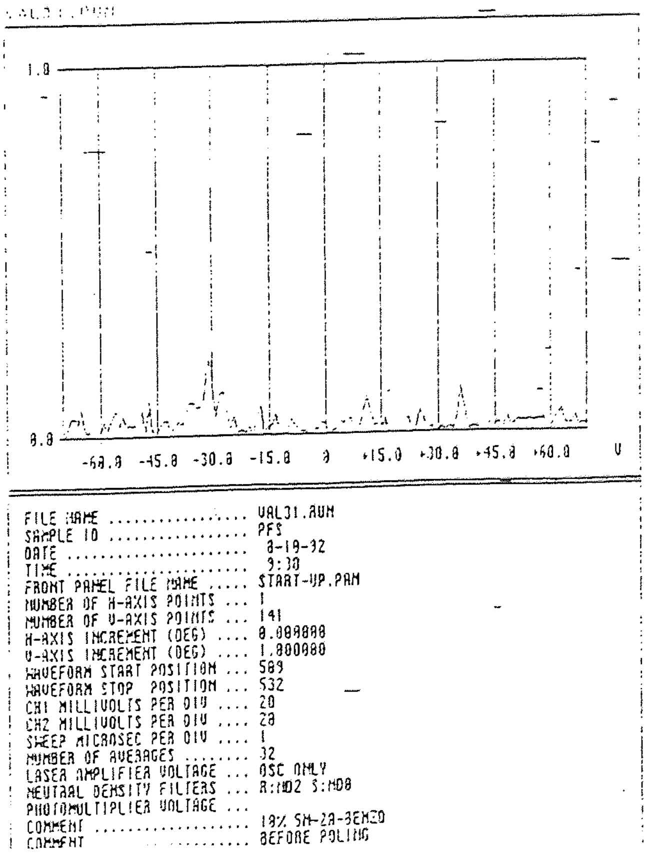
```
FILE NAME ................ VAL24.RUN
SAMPLE ID ................ PFS
DATE .....................  7-10-92
TIME ..................... 13:50
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 101
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... A:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT .................. 10% PNA
COMMENT .................. AFTER POLING
COMMENT .................. 2.15pm WEDS
```

A5.29 Polypentafluorostyrene doped with 10% paranitroaniline after poling



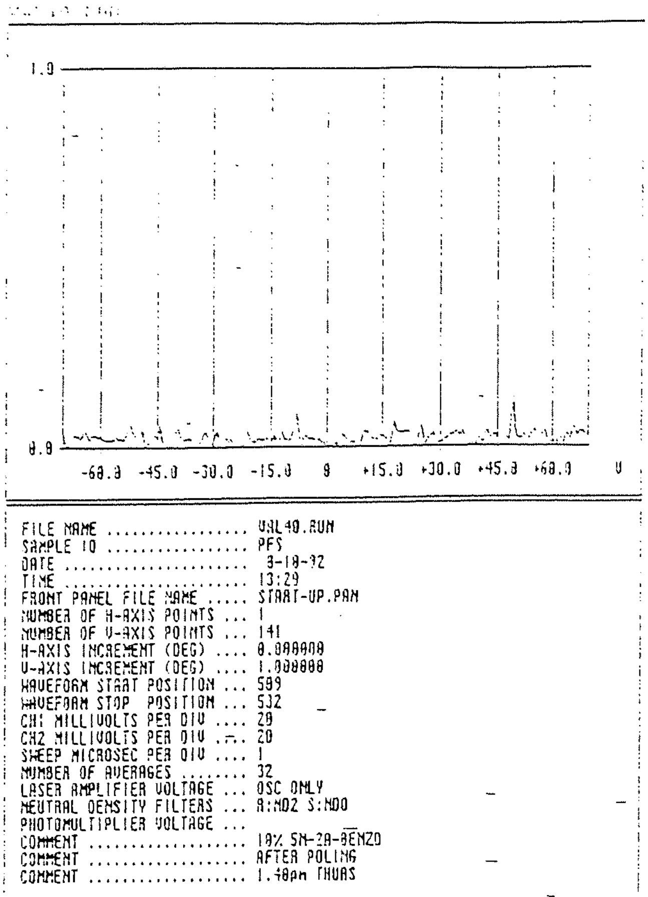
```
FILE NAME .................. VAL50.RUN
SAMPLE ID .................. PFS
DATE ....................... 9-10-92
TIME ....................... 10:40
FRONT PANEL FILE NAME ...... START-UP.PAN
NUMBER OF H-AXIS POINTS .... 1
NUMBER OF V-AXIS POINTS .... 141
H-AXIS INCREMENT (DEG) ..... 0.000000
V-AXIS INCREMENT (DEG) ..... 1.000000
WAVEFORM START POSITION .... 509
WAVEFORM STOP  POSITION .... 532
CH1 MILLIVOLTS PER DIV ..... 20
CH2 MILLIVOLTS PER DIV ..... 20
SWEEP MICROSEC PER DIV ..... 1
NUMBER OF AVERAGES ......... 32
LASER AMPLIFIER VOLTAGE .... OSC ONLY
NEUTRAL DENSITY FILTERS .... A:ND2 S:ND2
PHOTOMULTIPLIER VOLTAGE ....
COMMENT .................... 10% PNA
COMMENT .................... AFTER POLING
COMMENT .................... 11.05am FRI
```

A5.30 Polypentafluorostyrene doped with 10% paranitroaniline after poling after 48 hours



```
FILE NAME .................. VAL31.RUN
SAMPLE ID .................. PFS
DATE ....................... 8-19-92
TIME ....................... 9:30
FRONT PANEL FILE NAME ...... START-UP.PAN
NUMBER OF H-AXIS POINTS .... 1
NUMBER OF V-AXIS POINTS .... 141
H-AXIS INCREMENT (DEG) ..... 0.000000
V-AXIS INCREMENT (DEG) ..... 1.000000
WAVEFORM START POSITION .... 509
WAVEFORM STOP  POSITION .... 532
CH1 MILLIVOLTS PER DIV ..... 20
CH2 MILLIVOLTS PER DIV ..... 20
SWEEP MICROSEC PER DIV ..... 1
NUMBER OF AVERAGES ......... 32
LASER AMPLIFIER VOLTAGE .... OSC ONLY
NEUTRAL DENSITY FILTERS .... A:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ....
COMMENT .................... 10% 5N-2A-BENZO
COMMENT .................... BEFORE POLING
```

A5.31 Polypentafluorostyrene doped with 10% 5-nitro-2-aminobenzotrifluoride before poling



```
FILE NAME ................. VAL40.RUN
SAMPLE ID ................. PFS
DATE ......................  3-18-92
TIME ...................... 13:29
FRONT PANEL FILE NAME ..... START-UP.PAN
NUMBER OF H-AXIS POINTS ... 1
NUMBER OF V-AXIS POINTS ... 141
H-AXIS INCREMENT (DEG) .... 0.000000
V-AXIS INCREMENT (DEG) .... 1.000000
WAVEFORM START POSITION ... 509
WAVEFORM STOP  POSITION ... 532
CH1 MILLIVOLTS PER DIV .... 20
CH2 MILLIVOLTS PER DIV .... 20
SWEEP MICROSEC PER DIV .... 1
NUMBER OF AVERAGES ........ 32
LASER AMPLIFIER VOLTAGE ... OSC ONLY
NEUTRAL DENSITY FILTERS ... A:ND2 S:ND0
PHOTOMULTIPLIER VOLTAGE ...
COMMENT ................... 10% 5N-2A-BENZO
COMMENT ................... AFTER POLING
COMMENT ................... 1.40pm THURS
```

A5.32 Polypentafluorostyrene doped with 10% 5-nitro-2-aminobenzotrifluoride after poling