THE SYNTHESIS, CHARACTERISATION AND ELECTRICAL CONDUCTIVITY OF POLY(STYRENE-CO-ACETYLENE)

by

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SUMMARY

A novel metathesis catalyst for the polymerisation of acetylene has been developed. The polyacetylene produced by this new catalyst has been characterised by infra-red and NMR spectroscopy. The conductivity of the pristine material has been studied as a function of temperature, pressure and frequency. The effect on the conductivity of doping the material has also been investigated.

The new metathesis catalyst has been incorporated into an anionic-to-metathesis transformation reaction. This novel reaction has been used to prepare samples of poly(styrene-co-acetylene). The copolymer has been characterised using U. V./visible, NMR, infra-red spectroscopy and the surface morphology looked at using scanning electron micrscopy. GPC was also used to give some idea of the molecular weights of the materials prepared. The conductivity of the copolymer has been studied as a function of temperature, pressure and frequency. The effect of doping on the conductivity the material has also been investigated.

The conductivity results obtained from both materials have been used to try and gain an insight into the mechanism of the conduction processes occuring within the materials.

An attempt has also been made to synthesise polyacetylene oligomers (polyenes) by modifying the Ziegler/Natta type catalysts commonly used to synthesise polyacetylene. The polyenes were characterised using U.V./Visible and infra-red spectroscopy together with GPC and GCMS.

KEYWORDS

POLYACETYLENE,
ANIONIC-TO-METATHESIS TRANSFORMATION REACTION
POLYACETYLENE COPOLYMERS
METATHESIS
CONDUCTING POLYMERS.

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CHAPTER 1

LITERATURE SURVEY

1.1 INTRODUCTION

Organic compounds have conductivities which are typically many orders of magnitude less than those of metals, with the polymeric sub-group of compounds being at the lower end of this conductivity range; polytetraflouroethene is one of the best insulating materials known. Although in most polymeric materials it is difficult to observe any electronic conductivity whatsoever, there is a special class of polymers that have a conjugated π-electron backbone which exhibit special electronic properties. Polyacetylene is the simplest member of this class and therefore has been studied most often, serving as a prototype for other conducting polymers.

Simplistically, polyacetylene can be regarded as a long chain of carbon atoms separated by alternating single and double bonds.(figure 1.1)

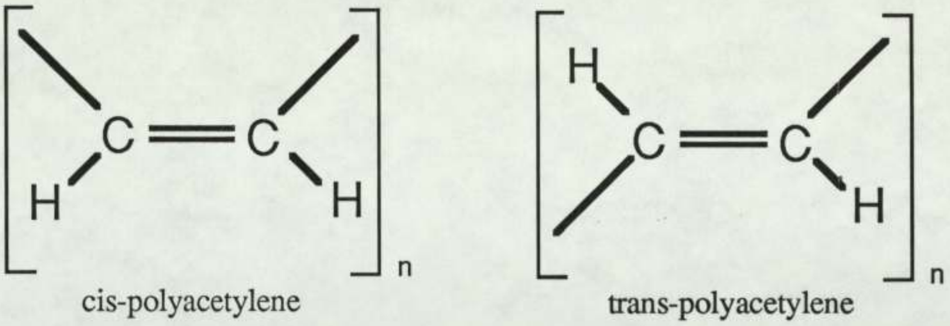


FIGURE 1.1 STRUCTURE OF POLYACETYLENE

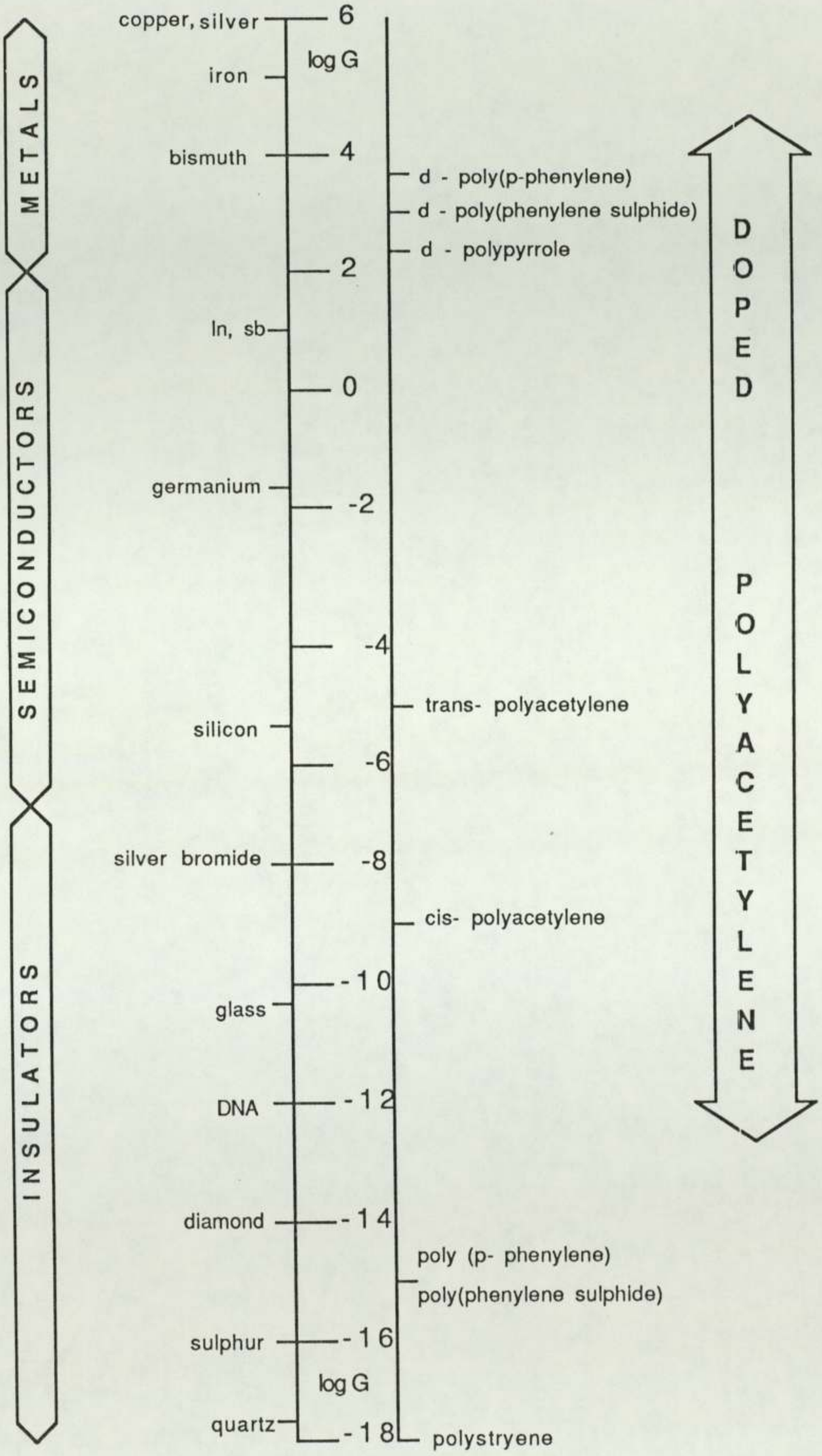
The first studies on acetylene polymerisation were reported in 1866 by Berthelot[1,2]. The first extensive investigations into the polymerisation of acetylene to high molecular weight polymers, using Ziegler/Natta catalysts, were not performed until 1958 by Natta and coworkers[3]. Since then there have been many reports on the synthesis, structure and doping of polyacetylene[4-6].

The class of polymer to which polyacetylene belongs exhibits "metallic" like conductivity when doped with materials such as iodine. This group of polymers has been the focus of considerable attention in recent years because of their electrical and electronic properties[7-15].

Polyacetylene that was produced in the early synthesis was in the form of a grey or black semi-crystalline powder that was insoluble in any solvent and decomposed before melting. It is difficult to prepare specimens, from these powdered samples, for the measurement of physical properties. It was not until Shirakawa and coworkers in 1974[14], produced thin films of polyacetylene that the physical properties of the material could be studied to any great extent. Both the cis- and trans- forms of polyacetylene may be prepared as these specular, flexible, polycrystalline semi-conducting films. Shortly after Shirakawa`s discovery MacDiarmid and Heeger[15] described the results of doping these films with both "p" and "n" type dopants, and showed that polymers possessing a wide range of conductivities could be created, ranging from insulator (10^{-10} $(\Omega\ \text{cm})^{-1}$) through to semi-conductor and metals (10^{3} $(\Omega\ \text{cm})^{-1}$), depending on the nature and amount of dopant incorporated. (figure 1.2) This disclosure sparked off an immense effort to discover more about doped polyacetylene, both with regard to the mechanism of its conductivity and possible applications[16-18].

At this stage in the development of these materials there was great hope that polymeric materials exhibiting this kind of conductivity could begin to replace

FIGURE 1.2 CONDUCTIVITIES OF SOME COMMON MATERIALS
d REPRESENTS DOPED MATERIALS



metals in industries such as electronics. Unfortunately the infusibility, instability and insolubility of polyacetylene have impeded both the scientific characterisation and the development of practical applications for this material. For this reason there has been considerable research aimed at circumventing these difficulties. To date two main approaches have been used to achieve this end; the blending of polyacetylene with other polymers and the synthesis of block and graft copolymers containing polyacetylene segments, in the assumption that the soluble part of these materials would solubilise the previously insoluble polyacetylene. The use of soluble precursor polymers has also been exploited[18a]. Of these two main approaches the block/graft copolymers have provided materials that are both soluble and highly conducting. It is the purpose of this introduction to outline the preparation and properties of these materials.

1.2 COPOLYMERS CONTAINING POLYACETYLENE

The initial driving force for the production of copolymers containing polyacetylene was to use them to facilitate the characterisation of polyacetylene and to provide information such as molecular weight, molecular weight distribution and steric homogeneity. For these reasons Wegner and coworkers[19] copolymerised acetylene with a number of 1-alkynes using the Shirakawa catalyst[14]. It was found that with increasing comonomer content of the feed solution the fraction of the copolymer that was soluble in toluene increased. These soluble copolymers had average molecular weights within the range 500-1500.

The first attempt to produce an electrically conducting copolymer containing polyacetylene was made by Chien and coworkers in 1981[20]. The synthetic techniques used were similar to those pioneered by Shirakawa[14]. A concentrated solution of $AlEt_3/Ti(OBu)_4$ in toluene was shaken in a flask so that the walls became coated with the catalyst. A gaseous mixture of acetylene and methyl acetylene was admitted and a copolymer film formed instantly both on the walls of the flask and on the surface of the catalyst solution. The composition of the film was determined by the composition of the gaseous mixture admitted. Doping with iodine or arsenic pentaflouride caused the copolymer films to become conductive reaching a maximum conductivity of 45 $(\Omega\ cm)^{-1}$ for a copolymer containing 55% polyacetylene, doped with arsenic pentaflouride. The electrical conductivity of the copolymers decreases with increasing methyl acetylene content[21]. This was probably due to steric interactions which reduce planarity and π orbital overlap. The copolymers showed different physical characteristics compared with those of homo-polyacetylene; they showed no fibrillar morphology, swelled in toluene and pentane, were highly elastic when wet, though they were insoluble and did not exhibit melting behaviour.

"Soluble" copolymers of a high molecular weight were synthesised by two groups of workers at roughly the same time. Baker and Bates[22,23] prepared graft copolymers containing polyacetylene with either polyisoprene or polystyrene as the solubilising block. The polyacetylene retained the electrical and spectroscopic properties of the homo-polymer, but it was claimed that the polyacetylene chains were now present as isolated entities in solution, effectively removing the chain-chain and inter fibril perturbations of the single chain properties of polyacetylene. However in recent years some workers have published evidence for aggregation of the copolymer chains in solution[49].

The starting point for production of the copolymer was a carrier polymer (either polyisoprene or polystyrene) which was nearly monodisperse, with a number average molecular weight of 2×10^5 , modified by oxidation to contain electrophilic sites. The electrophilic sites were epoxides introduced by oxidation with m-chlorobenzoic acid, without chain scission. Acetylene was polymerised using a $Ti(OBu)_4/AlEt_3$ catalyst in a toluene solution of the carrier polymer. The graft step is believed to be a result of nucleophilic attack of a growing polyacetylene chain on the electrophilic site on the carrier polymer.

In later work[24] the term "solubilised polyacetylene" refered to polyacetylene copolymers which were able to pass through filters with pore sizes as small as .2 µm and which were not readily separated from the carrier homo-polymer by centrifugation. The oligomers were prepared by a room temperature polymerisation of acetylene in the presence of acetone; the polymerisation reaction was initiated by the addition of $AlEt_3$ and was quenched quickly . These low molecular weight polymers are soluble in most organic solvents. To simulate these conditions 15-50 graft sites, which were either ketones or epoxides, were produced on a carrier polymer chain, so that when acetylene polymerisation takes place the polyene chain became attached to the carrier polymer. The ketone or epoxide sites were able to react in the same way as acetone to produce oligomeric polyacetylene, which in this case was pendant to the backbone polymer chain.

The most difficult characterisation question is the microscopic state of the solubilised polyacetylene. Small amorphous aggregates, micro crystals or single chains are all possible states for the system. A recent light scattering study[25] found the persistence length of the polyacetylene block was approximately 350 Å, while the hydrodynamic radius of the entire polymer was approximately 1050 Å. This suggests that the sample consists of aggregates of graft copolymer in solution although the arrangements of the polyacetylene segments within the aggregates has yet to be determined. The arrangements have been described as "worm like" in thin films of the copolymer[47].

NMR spectroscopy is a powerful tool for determining the micro structure and state of a polymer in solution . Baker and Bates failed to detect a ^{13}C NMR signal from solutions of the solubilised polyacetylene. This result is of no real surprise since previous NMR experiments[26] on styrene-butadiene block copolymers in hexane (a poor solvent for polystyrene) have revealed that the styrene portion of the copolymers escapes detection because of the restricted motion of the chains. In the same way the polyacetylene segments in the solubilised polyacetylene may have restricted motion within the aggregate resulting in an extremely broad signal. A dried sample of the solubilised polyacetylene was examined by solid state NMR and a signal attributable to trans-polyacetylene[27-29] was observed at 138ppm relative to $SiMe_4$, in addition to the spectrum for the carrier polymer.

Since the polyacetylene content in the dried samples is only a few percent and this is present in isolated domains within an insulating matrix, it is not surprising that the oxidation of the samples, with typical doping agents, such as the halogens, did not lead to an increase in bulk conductivity.

At around the same time Wnek and coworkers published a series of papers connected with the synthesis of other copolymers[30-36]; two synthetic routes were devised. Firstly the use of doped polyacetylene as a macromolecular initiator for the synthesis of graft copolymers and secondly the use of a transformation reaction as a route to block copolymer synthesis.

The graft copolymer was synthesised by immersing a polyacetylene film in a 1M solution of sodium naphthalide in THF. The washed and dried films had compositions in the range $(CHNa_{0.2-0.25})_x$ and conductivities in the range 5-50 $(\Omega\ cm)^{-1}$. Exposure of these films to either liquid styrene or gaseous ethylene oxide resulted in polymerisation. It is thought that the primary reaction between the n-type polyacetylene and ethylene oxide is presumably attack of a carbanion on a methylene carbon resulting in ring opening and oxyanion formation, followed by successive monomer additions (figure 1. 3).

These polyacetylene/polyethylene oxide materials could be doped with iodine to give conductivities of the order of 1 $(\Omega cm)^{-1}$. This relatively low value is probably due to two factors ; (i) polyethylene oxide is an insulator compared polyacetylene doped with iodine and (ii) the polyethylene oxide grafts break up the conjugation in the polyacetylene backbone, which is expected to reduce intra chain hole mobility. Characterisation of these materials is by no means complete

The synthesis of the block copolymer, by Wnek was achieved by using a

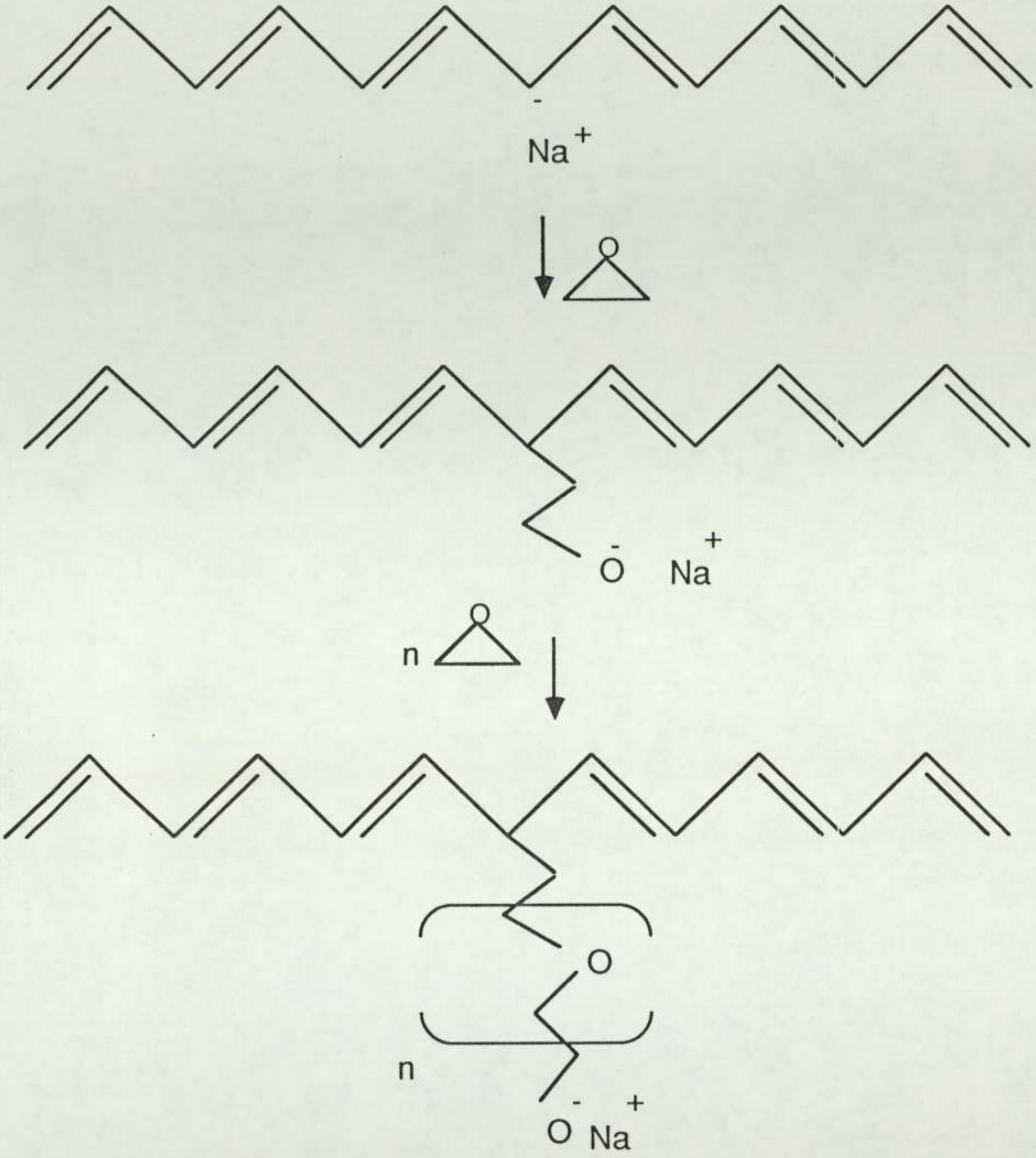


FIGURE 1.3 RING-OPENING POLYMERISATION OF ETHYLENE OXIDE

transformation reaction. "Living" polystyryl lithium was first prepared by conventional anionic techniques using n-butyl lithium as the initiator in THF at -78 °C. At this stage an anionic-to- Ziegler/Natta transformation reaction[37] was used to produce an active catalyst for acetylene polymerisation. In this case a catalytically active titanium based species was generated by the alkylation of $Ti(OBu)_4$ with polystyryl-lithium. (figure 1.4)

Gel-permeation chromatography (GPC) was used to show that the polystyryl-lithium had a number average molecular weight of around 28,000 initially, which after reaction with acetylene increased to 72,000. This was attributed to block copolymer formation. During the reaction it was noted that, when the styrene block length was increased the time taken for observable precipitation, in the reaction medium, to occur also increased, even when additional solvent was added to counteract viscosity effects, For example when the polystyryl lithium had a number average molecular weight of 32,000 it took 15 minutes before precipitation took place, when the number average molecular weight was increased to 42,000 it took 36 minutes for precipitation to occur.

Later studies have centered on radio labelling experiments in which polystyryl-lithium enriched with ^{14}C at the n-butyl terminus was used to alkylate $Ti(OBu)_4$. Acetylene was polymerised until particulate precipitation was observed, at which stage the reaction was terminated by the addition of tritiated methanol (MeOT). The product was purified and then counted. A control was carried out in which ^{14}C enriched polystyryl-lithium was terminated with MeOT to obtain a reference $^{14}C/^{3}H$ ratio. Block copolymer formation should result in a $^{14}C/^{3}H$

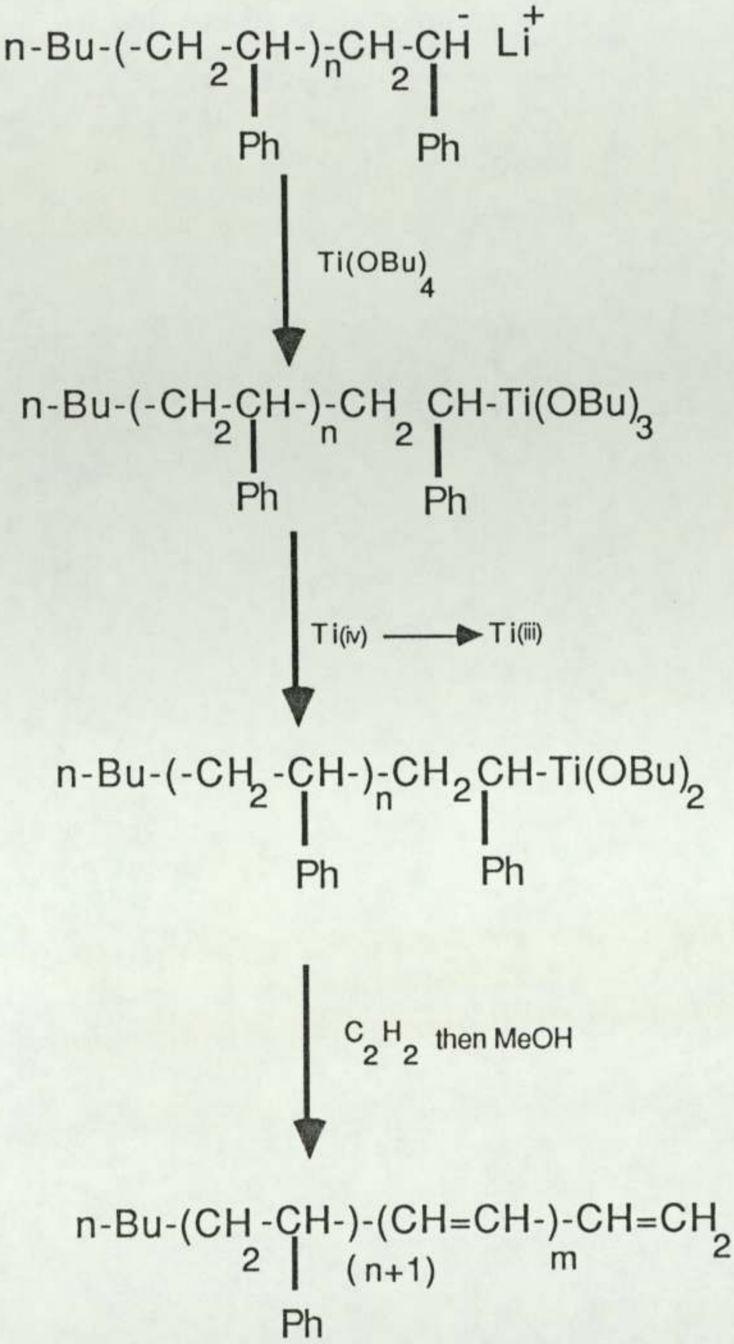


FIGURE 1.4 ANIONIC TO ZIEGLER/NATTA TRANSFORMATION REACTION

ratio similar to that of the control. The results given did not give definite proof of block formation, but the products did contain significant quantities of ^{14}C. The yield of block copolymer was only about 2-5%. This may have been because the solvent used was THF which can compete with acetylene for coordination with the active site. As yet diblock films, which have been cast from "apparently soluble" systems, have been found to be non-conducting, probably because an insulating layer of polystyrene surrounds the polyacetylene domains.

Block copolymers of polystyrene/polyacetylene, polyisoprene/polyacetylene and polyethylene/polyacetylene have been synthesised by Aldissi[38-42] using synthetic techniques similar to those already mentioned. The anionic section of the polymer was prepared using the normal conditions of n-butyl lithium initiation in toluene. The chain length of this part of the polymer could be controlled easily. An equimolar quantity of $Ti(OBu)_4$, based on the lithium concentration, was then added to the living polymer. When acetylene gas was admitted copolymers were formed as gels on the surface of the catalyst solution or as soluble materials in the reaction medium.

The length of the solubilising block plays an important part in determining the properties of the copolymer. Short anionic chains produce copolymer films that are conducting, medium length anionic chains produce soluble conducting copolymers and long anionic chains produce soluble insulating copolymers. In the case of the polyisoprene copolymers, soluble materials, where the content of polyene is below 10% w/w, are insulating. In the 10-20% w/w range the soluble materials exhibit conductivities in the range 1-10 $(\Omega cm)^{-1}$. Above

20 % w/w, insoluble materials are obtained, increasing conductivities are observed with an increasing relative amount of doped polyene. For the polystyrene copolymers lower amounts of polyene are required in order to obtain soluble material. In this case the amount of non-active component (polystyrene) is predominant and therefore insulating materials are obtained. In the range of insoluble polystyrene copolymers, the conductivity varies drastically with composition, in a manner similar to that for filled polymers (conducting composites). The morphology of the copolymers is also dependent upon the content of the solubilising block with the morphology becoming less fibrillar with increasing content of the insulating polymer.

Kminek and coworkers[43,44] have produced a copolymer containing polyacetylene and polymethyl methacrylate. The polyacetylene was produced by standard Shirakawa techniques from which a charge transfer complex of the form $[Na_{.057}(CH)_x]$ was prepared by reacting the polyacetylene with sodium dihydronaphthylide. This charge transfer complex was then used as an initiator for the anionic polymerisation of methyl methacrylate. By these means a soluble form of polyacetylene was produced but only when the molar ratio MMA: $(CH)_x > 1.5$. Gel permeation chromatagraphic data showed that the copolymer possesses a broad molecular weight distribution. This was probably due to the considerable chain transfer and auto termination that occured when methyl methacrylate was polymerised with organo-sodium compounds.

This soluble form of polyacetylene exhibited photoelectric behaviour and, from the absorbtion spectra threshold, the energy gap (E_g), was estimated as 1.6 ev. A disadvantage of the system is the limitation of the charge carrier transport by the methyl methacrylate barriers which could be overcome by doping.

Soluble graft copolymers were also synthesised by Bolognesi and coworkers[45-50] by grafting polyenic chains on to a soluble polymer matrix. Two methods of preparation were used based upon the technique of preparing catalytic sites on a polymeric backbone followed by subsequent polymerisation of a newly added monomer .

The first method involves a reaction between the catalytic system $Ti(OBu)_4/AlEt_3$ and the vinyl side groups of the polymer carrier. in which a titanium atom is bound to a matrix. A polyenic chain grows on this newly formed Ti-C bond via successive insertions of acetylene. (figure 1.5). The carrier polymers are either polybutadiene or polyisoprene. It should be noted that it is the quantity of titanium in the reaction mixture that dictates the number of sites activated.

The second preparation was based on the formation of carbanions on the carrier polymer and was a three step reaction (figure 1.6).(i) there was a reaction of s-butyl lithium with cis-1,4-polybutadiene in dry cyclohexane. The presence of TMEDA favours the formation of carbanions in the allylic positions of the polymer matrix. (ii) there was an exchange reaction between $Ti(OBu)_4$ and the polymeric lithiated compound to obtain a Ti-C bond on the polymer backbone; the Ti(iv) atoms bonded to the polymer were reduced to Ti(iii) species. Acetylene was then polymerised to produce a copolymer which was dark blue. Upon doping with iodine the coplymer had a conductivity of 1.4×10^{-3} $(\Omega\ cm)^{-1}$. Once again the conductivity depends

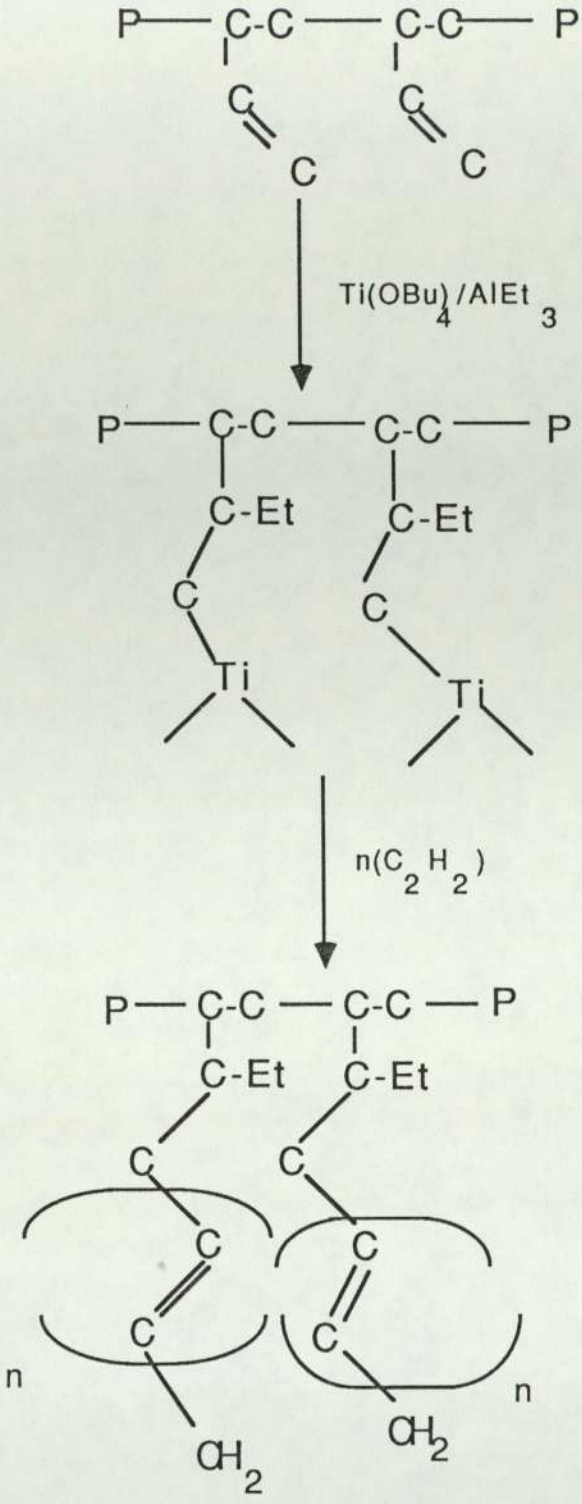


FIGURE1.5 REACTION BETWEEN $TI(OBu)_4$ / $AIET_3$ AND A VINYL SIDE GROUP FOLLOWED BY ACETYLENE POLYMERISATION

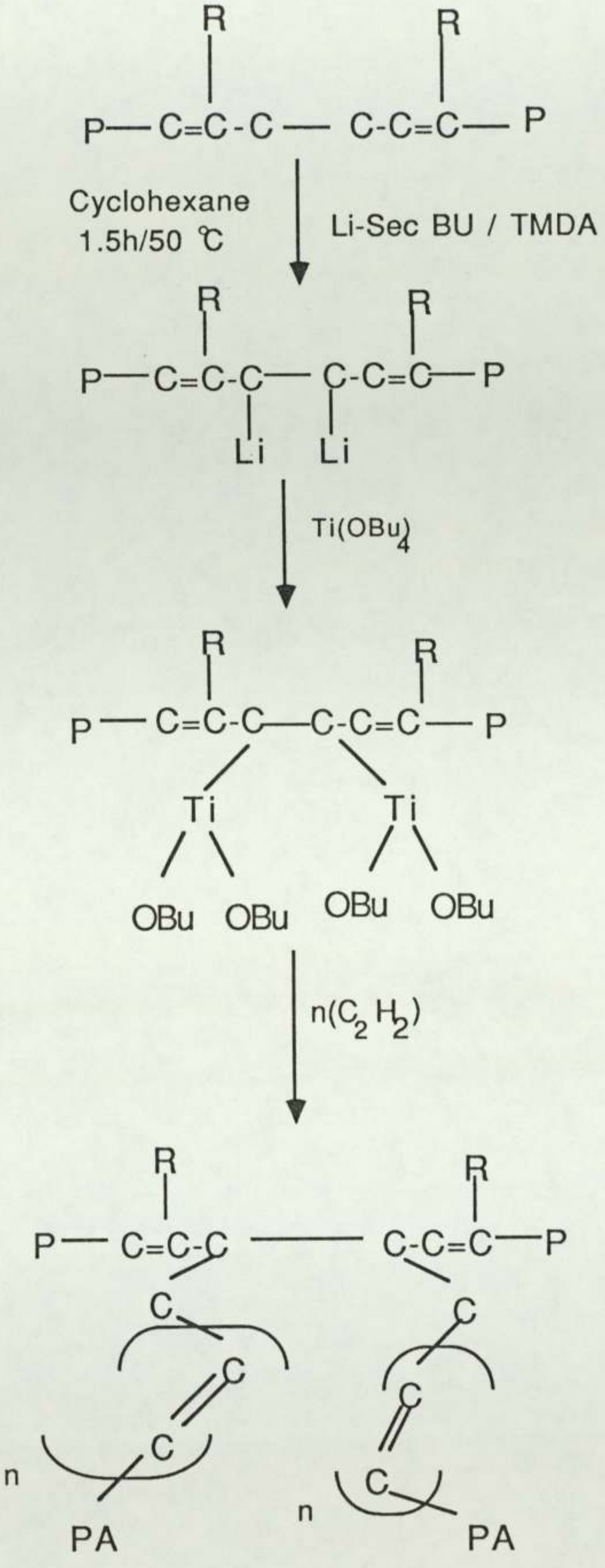


FIGURE 1.6 LITHIATION FOLLOWED BY REACTION WITH4 TI(OBu) AND ACETYLENE POLYMERISATION

directly on the quantity of polyene in the copolymer and the copolymer can be regarded as conductive spheres (polyacetylene microdomains) embedded in a dielectric medium (polybutadiene regions). Light scattering experiments carried out on the solubilised polyacetylene provide further evidence for aggregation in solution, with a radius of gyration of some 20 nm for the polyacetylene segment. (cf.6-7 nm for a higher molecular weight polybutadiene).

One of the most novel attempts to produce a copolymer containing polyacetylene was undertaken by McCarthy and Dias[51,52] . In their work they viewed poly(1,3-butadiene) $\{CH_2\text{-}CH_2\text{-}CH{=}CH\}_n$ as an alternating copolymer of acetylene and ethylene and as the enthalpically least stable isomer of poly(acetylene-co-ethylene) $\left[(CH_2\text{-}CH_2) \_\_ (CH{=}CH)_y\right]$. Their aim was to achieve a positional isomerisation of the double bond producing a more blocky poly(acetylene-co-ethylene). It was found that this could be achieved by using base catalysis in THF/DMSO solution. The mechanism for this isomerisation is thought to be as shown in figure 1.7.

The progress of the isomerisation was followed by IR and UV spectroscopy. The final product had a conductivity of 5×10^{-7} $(\Omega\,\mathrm{cm})^{-1}$, this low value can again be attributed to the presence of an insulating layer in this case polyethylene. The materials formed using potassium tert-butoxide as a catalyst, contain lengths of conjugation of approximately 10 double bonds. The conjugation length was not found to be a function of the temperature but is a function of the strength of the base used.

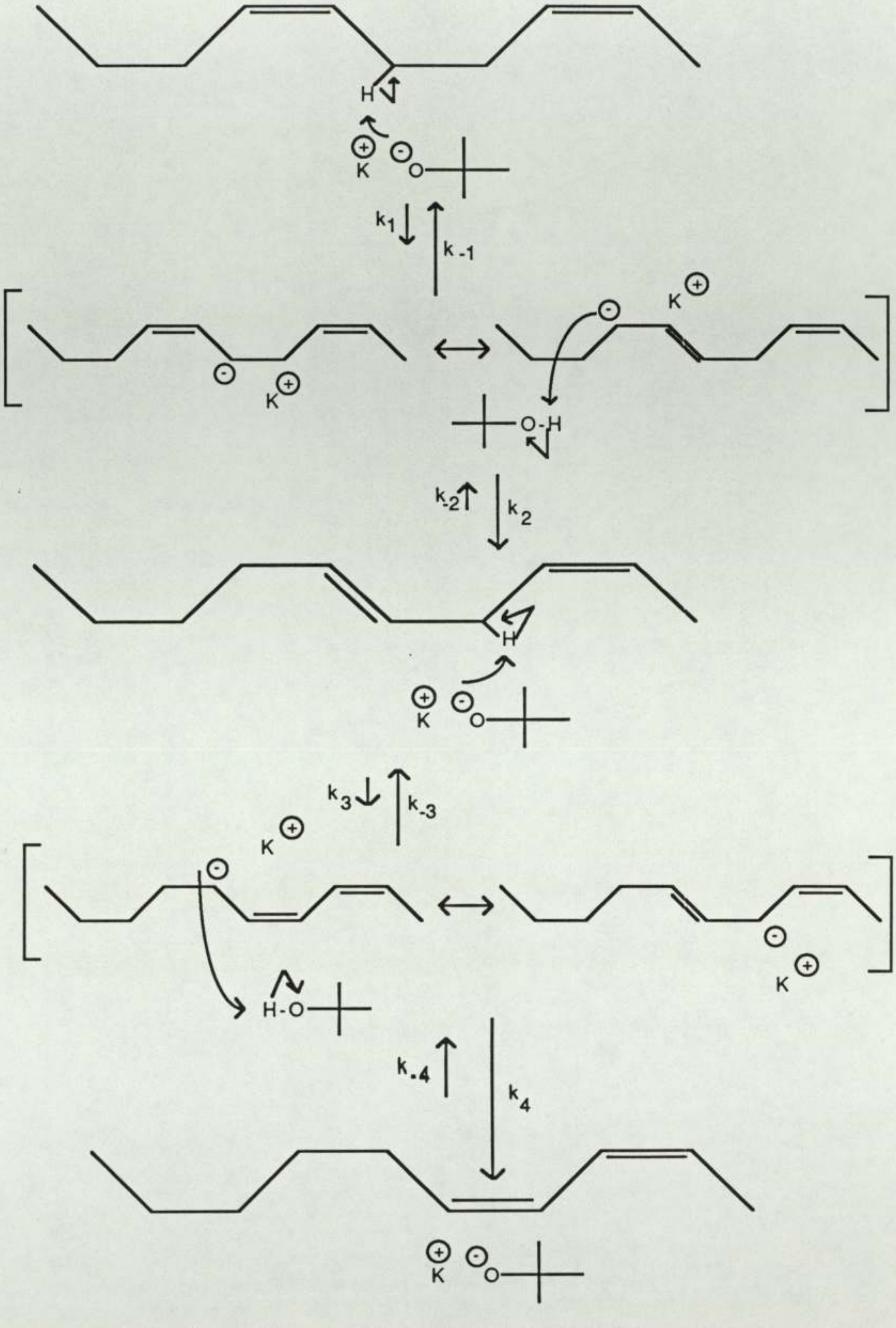


FIGURE 1.7 BASE CATALYSED ISOMERISATION OF ACETYLENE / BUTADIENE COPOLYMER

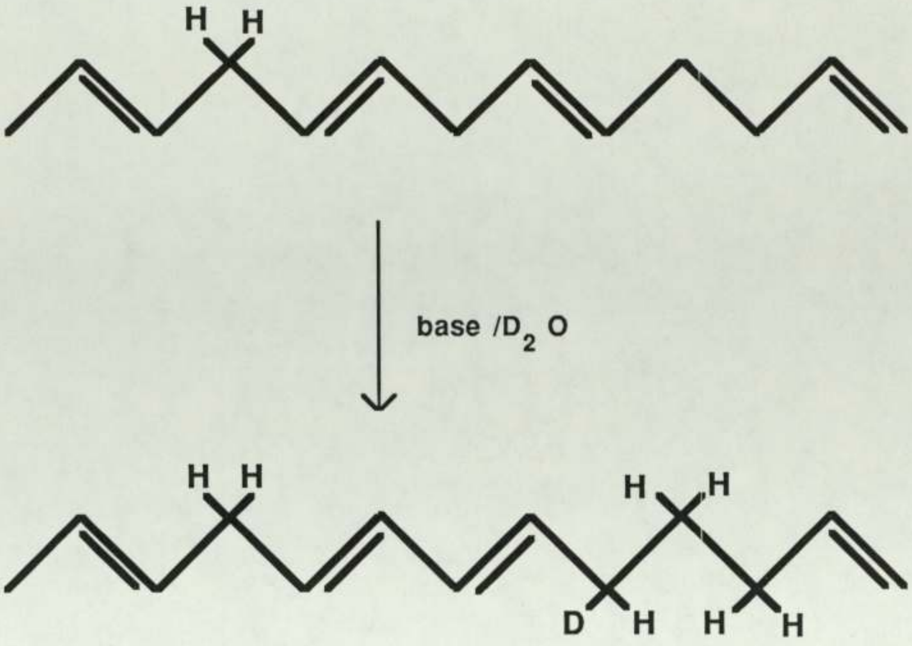


FIGURE 1.8 BASE CATALYSED ISOMERISATION OF POLY 1,3- BUTADIENE

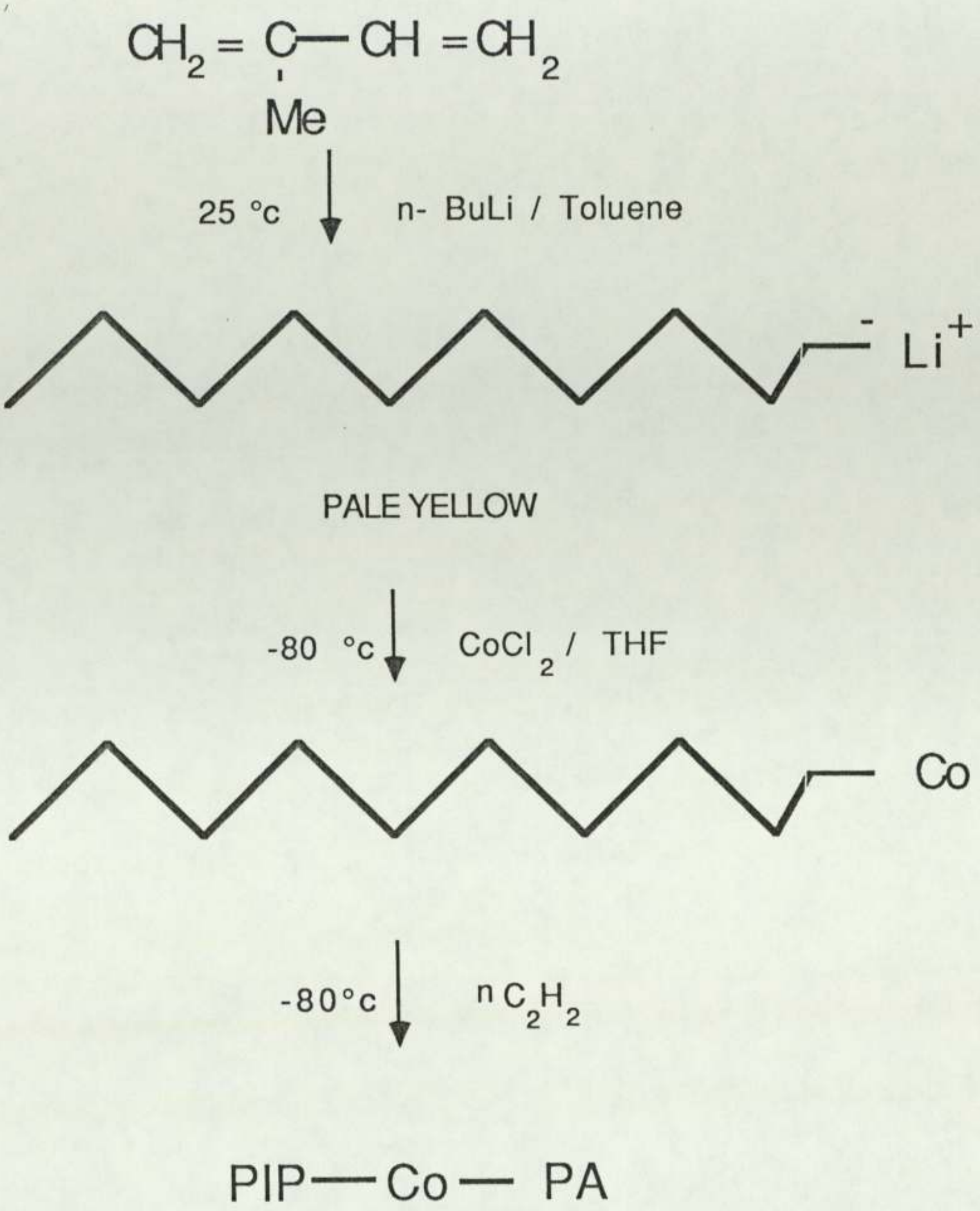
A similar modification technique was used by Tolbert and coworkers[53] on the random copolymer of acetylene and butadiene that was produced using the synthetic techniques developed by Furukawa in 1973[54]. The random copolymers were produced by passing a gas mixture (23% acetylene, 77% butadiene) into a solution of nickel napthenate/diethyl aluminium chloride in toluene. The purified polymer was either a yellow viscous liquid or a waxy polymer. This random copolymer can be readily deprotonated with alkyl-lithium to produce an anionic polymer with the expected spectroscopic characteristics. Reprotonation with D_2O generates a modified neutral polymer in which double bonds have been brought into conjugation (figure 1.8) .

Chien and Babu produced acetylene and carbon monoxide copolymers[55] using the $Ti(OBu)_4/AlEt_3$ catalyst and a gaseous monomer feed. These copolymers are completely amorphous with their back bone π-conjugation frequently interrupted by >C=O units.

The thermal degradation of vinyl chloride/acetylene copolymers has been studied by Braun and coworkers[56,57] . They showed that all copolymers are less stable than the component homo-polymer segments. The studies were aimed mainly at elucidating the mechanism of degradation and the nature of the inherent instability of the copolymers.

Light yellow polymer films were obtained from the plasma polymerisation of F-propene and acetylene gas mixtures[58]. The films formed were examined by elemental analysis and infra-red spectroscopy. Their chemical compositions depended on the composition of the original gaseous mixture. The gas permeability coefficients of these plasma films were determined for oxygen and nitrogen.

The novel catalyst system WCl_6/H_2O was used by Diets and coworkers[59] to produce acetylene/phenylacetylene copolymers. Both the physical and electrical properties of the copolymers were shown to vary with monomer content. The copolymers become wholly soluble in dichloromethane when containing greater than 40% of phenylacetylene. The conductivity of the iodine doped copolymer of this composition was 1.4×10^{-4} $(\Omega\,cm)^{-1}$ this rose to 5×10^{-1} $(\Omega\,cm)^{-1}$ for the insoluble copolymer containing 78% acetylene. None



PIP = Polyisoprene
PA = Polyacetylene

FIGURE 1.9 ANIONIC TO ZIEGLER / NATTA TRANSFORMATION USING COBALT CATALYSTS of the materials studied was stable in air for any length of time. The degradation process itself was found to be a two stage phenomenon involving a primary loss of iodine involved in charge transfer followed by an oxidation of the polyene backbone.

A novel Luttinger type cobalt catalyst system was used by Vincent and coworkers[60] to produce soluble polyacetylene -polyisoprene copolymers (figure 1.9). It is thought that the polyacetylene segment has a molecular weight of some 1200. The low temperature of the reaction resulted in an all cis-polyacetylene portion of the copolymer, though appreciable isomerisation to the trans- isomer was observed over a period of 23 hours at room temperature. As yet the electrical properties of this material have not been determined.

Although this relatively new area of polyacetylene chemistry has not produced a totally soluble and processable copolymer containing polyacetylene it has gone a long way towards that goal. The electrical properties of all the copolymers have been shown to depend on the polyene content, which is not surprising since conductivity is an inherent property of the polyene chain.

The electrical conductivity of the copolymers is not generally high enough to make them interesting to the electronics industry. This is not surprising since the solubilising segment is usually an insulator. With the development of new catalyst systems (e.g. anionic-to-Ziegler / Natta transformation reaction) this problem could be overcome enabling a new range of materials to be synthesised which may play a leading role in the industries of the future.

1.3 THE SEARCH FOR A NEW CATALYST SYSTEM

It can be seen from these attempts to produce block copolymers containing polyacetylene , that the predominantly used Ziegler catalyst appears to provide little control over the molecular weight of the acetylene block, leading to an insoluble polymer. There is therefore, a need to develope a new catalyst system that is active towards acetylene polymerisation.

It is noticeable that unlike vinyl polymers which have been extensively investigated and manufactured in large quantities, the polymerisation of acetylenes has not been the subject of much study, because of the difficulty of obtaining high molecular weight polymers by conventional free radical, cationic or anionic polymerisation[61]. Only a few transition metal catalysts are known to polymerise acetylenes by Ziegler/Natta or metathesis catalysis to yield high molecular weight polymers. For example $Ti(OBu)_4$ /$AlEt_3$ for acetylene[14] , WCl_6, $MoCl_5$, $W(CO)_6$, $Mo(CO)_6$, $Re(CO)_5X$ and some metal carbynes for phenyl acetylene and other substituted acetylenes,[62-69], and the halides of Nb(III) and Ta(III) for disubstituted acetylenes[70-71]. Two recently published reviews give a very good overview of the whole area of both the polymerisation of acetylene and substituted acetylenes.[4,6]

Tungsten hexachloride has been used in conjunction with tetra phenyl tin to polymerise acetylene [72,73] and the combination of WCl_6 and n-RLi has been known for a number of years as a catalyst for metathetic cyclo-olefin polymerisation[74]. The combination of these types of catalysts could lead to the formulation of a new catalyst reaction.

1.4 TRANSFORMATION REACTIONS

A commonly used route to the synthesis of block copolymers involves a process in which the mechanism of propagation can be changed after the first monomer, to one best suited to the polymerisation of the second . Such reactions have been called transformation reactions[37] and the techniques devised to prepare block copolymers using this technique would necessarily have a minimum of three stages i) polymerisation of monomer A by mechanism one, ii) isolation of polymer A, dissolution in a solvent suitable for mechanism two, iii) reaction or change of conditions, to transform the active end into a propagating species that will polymerise monomer B by mechanism two. Ideally the intermediate should be sufficiently stable to allow isolation and protracted storage. There have been several types of transformation reaction reported in the literature one of which has already been used to produce block copolymers containing polyacetylene.

1.4.1 ANIONIC TO ZIEGLER/NATTA TRANSFORMATION REACTIONS

Ziegler/Natta polymerisations can be envisaged to occur through a series of sequential steps beginning with the reduction of titanium (iv) with aluminium alkyls.

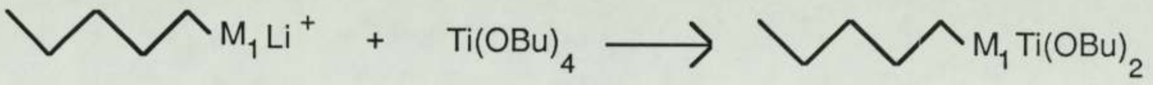
$$Ti(OBu)_4 + AlR_3 \rightarrow RTi(OBu)_3 + AlR_2(OBu)$$

$$2RTi(OBu)_3 \rightarrow 2Ti(OBu)_3 + 2R$$

$$Ti(OBu)_3 + AlR_3 \rightarrow RTi(OBu)_2 + AlR_2(OBu)$$

$$RTi(OBu)_2 + AlR_3 \rightarrow RTi(OBu)_2.AlR_3$$

Replacement of the R groups of the aluminium alkyl with polymer chains suggests another route to the synthesis of block copolymers via Ziegler/Natta reactions. Alternatively the aluminium alkyl could be replaced totally using the living anionic end to alkylate the titanium.



1.4.2 METATHETIC TRANSFORMATION REACTIONS

The metathesis of linear and cyclic olefins (in which acetylene is regarded as a two membered ring) is now believed to be initiated and propagated by metallocarbene / metallocyclobutane intermediates. In recent years there has been much work directed at attaining an understanding of how these intermediates are formed and how they direct the course, both kinetically and stereochemically, of the metathesis reaction. Most of this work has concentrated on the role played by the transition metal and has tended to ignore the role played by both the co-catalyst and the reactant olefin in the metathesis reaction. Whilst the presence of the co-catalyst may be necessary to help generate a metathetically "active species" it is not at all certain whether it plays any further role in such reactions. If the presence of the co-catalyst, or it's derivatives, could be detected in the products of a metathesis reaction then the importance of the role played by the co-catalyst would be determined.

An interesting, but as yet little studied, route to block copolymers is by an anionic-to-metathesis transformation reaction. It is envisaged that the incorporation of a metathetical catalyst into a transformation reaction mechanism will enable greater control to be exerted over the molecular weight of the polyacetylene segment thus enabling soluble copolymers of polyacetylene to be produced.

1.5 SCOPE OF THIS WORK

The purpose of this work is to develop a metathetical catalyst for the polymerisation of acetylene and to incorporate it into an anionic-to-metathesis transformation reaction which will yield soluble copolymers containing polyacetylene segments. These polymers will be characterised and the electrical properties determined. It is hoped that this work will provide some insight into the nature of the catalyst / co-catalyst / monomer interaction.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 INTRODUCTION

The purpose of this chapter is to explain some of the experimental techniques used throughout this study. The source and purification of the materials used will also be described. Table 1 shows the chemicals used in this study, their sources and some physical properties. In the table The British Oxygen Company is indicated by BOC and The British Drug House similarly by BDH.

2.2 VACUUM TECHNIQUES

Many of the catalysts used in both Ziegler/Natta and olefin metathesis are extremely sensitive to both oxygen and moisture. There are two general techniques for handling such unstable materials, blanket and vacuum techniques. Blanket techniques require manipulations in a nitrogen glove box which are clumsy and subject to leakage. It is for these reasons that for the major part of this work vacuum techniques were adopted.

2.2.1 THE VACUUM LINE

The vacuum line shown in figure 2.1 consisted of a main manifold which was evacuated by means of an Edwards rotary vacuum pump aided by a mercury diffusion pump. Liquid nitrogen cold traps were used to condense any organic vapours coming from the main manifold, preventing vapours contaminating the mercury and also stopping them and the mercury vapour getting into the atmosphere. Pressure as low as 10^{-4} mm Hg can be maintained for long

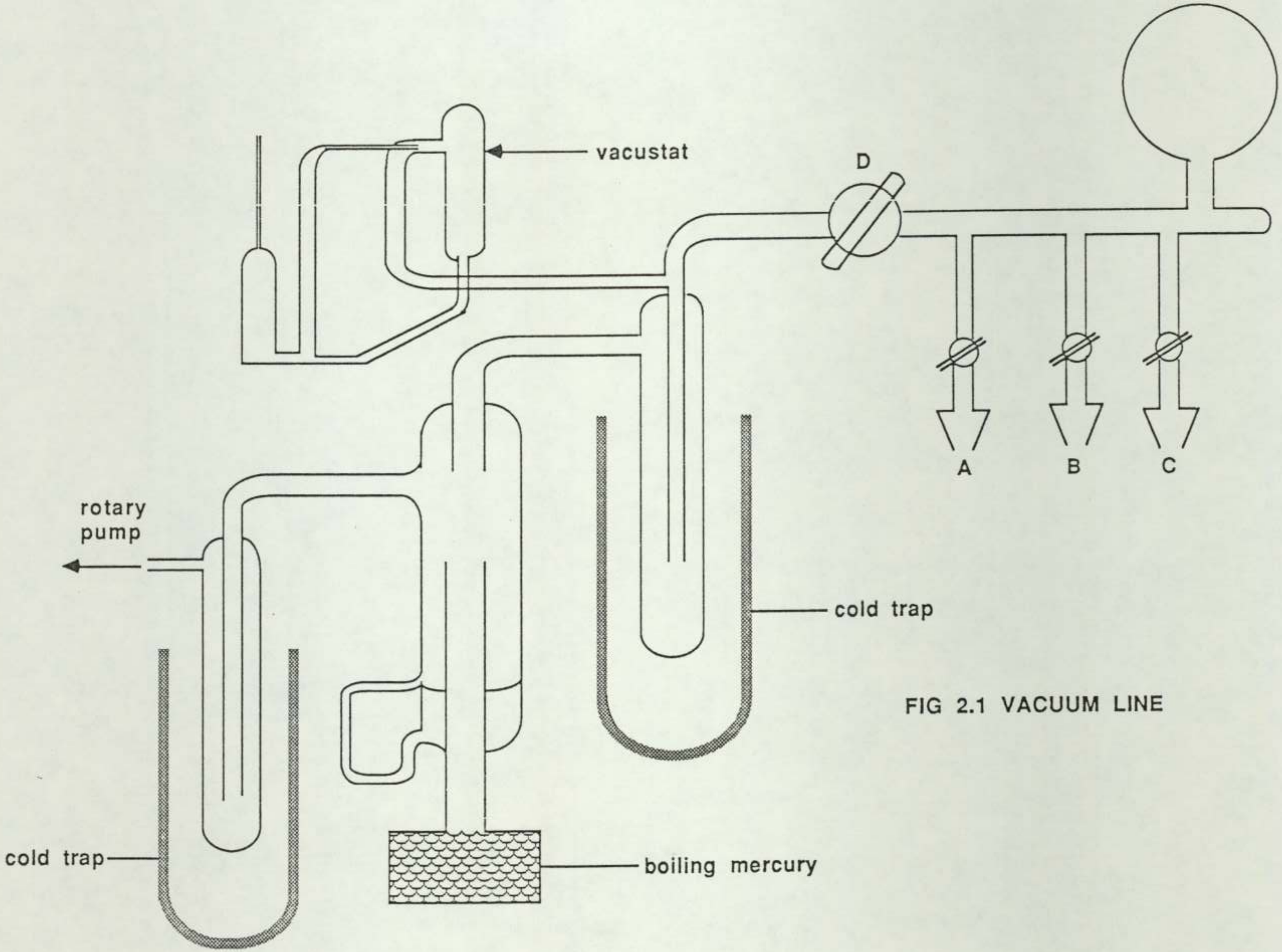


FIG 2.1 VACUUM LINE

Table 2.1 shows the chemicals used in this work, their sources and some physical properties

TABLE 2.1 LIST OF CHEMICALS

MATERIAL	FORMULA	SOURCE	MOL WT	MP °C	BP °C	DENSITY gm cm^{-3}
acetylene	$CH{\equiv}CH$	BOC	26	-80.8	-84.0	0.6208
toluene	$C_6H_5CH_3$	BDH	92.15	-95	110.6	0.867
cyclohexane	C_6H_{12}	Fissons	84.16	6.5	80.7	0.775
styrene	$CH_2{=}CHPh$	Aldrich	104.16	-30.6	145.2	0.906
tungsten hexachloride	WCl_6	Aldrich	396.6	275	346.7	3.52
n-butyl lithium	LiC_4H_9	Aldrich	64.06			.068
aluminium triethyl	$AlEt_3$	Fluka	114.19			
titanium tetrabutoxide	$Ti(OBu)_4$	Fluka	340.36			

All information is taken from the Handbook of Chemistry and Physics 67th Edition 1986-1987 periods with this system. The pressure in the system was estimated by use of a Vacustat gauge.

2.2.2 DEGASSING SOLVENTS

In order for solvents to be distilled under vacuum they must first be degassed. This is achieved by repeated freeze-pump-thaw cycles. Dried solvent was placed in a flask, shown in figure 2.2, and connected to the manifold at (B) and was gradually cooled by immersion in liquid nitrogen. When the solvent had frozen, the flask was evacuated by opening tap (H). After a high vacuum had been attained tap (H) was closed and the solvent was allowed to thaw at room temperature. As the solvent thawed, gas trapped in the frozen solid was released and equilibrated in the atmosphere above the solvent. This process of freeze-pump-thaw was repeated until a high vacuum was observed at two consecutive pump phases.

2.2.3 TRAP TO TRAP DISTILLATION

Prior to vacuum distillation, the solvent to be distilled was degassed as described in section 2.2.2. The flask containing the degassed solvent was connected to the main manifold of the vacuum line via tap A. A second flask was also connected to the vacuum line, at tap B and evacuated. When a high vacuum had been obtained in the system, both the empty receiver flask and the main manifold were flamed to remove the last traces of moisture from the interior surfaces of the equipment.

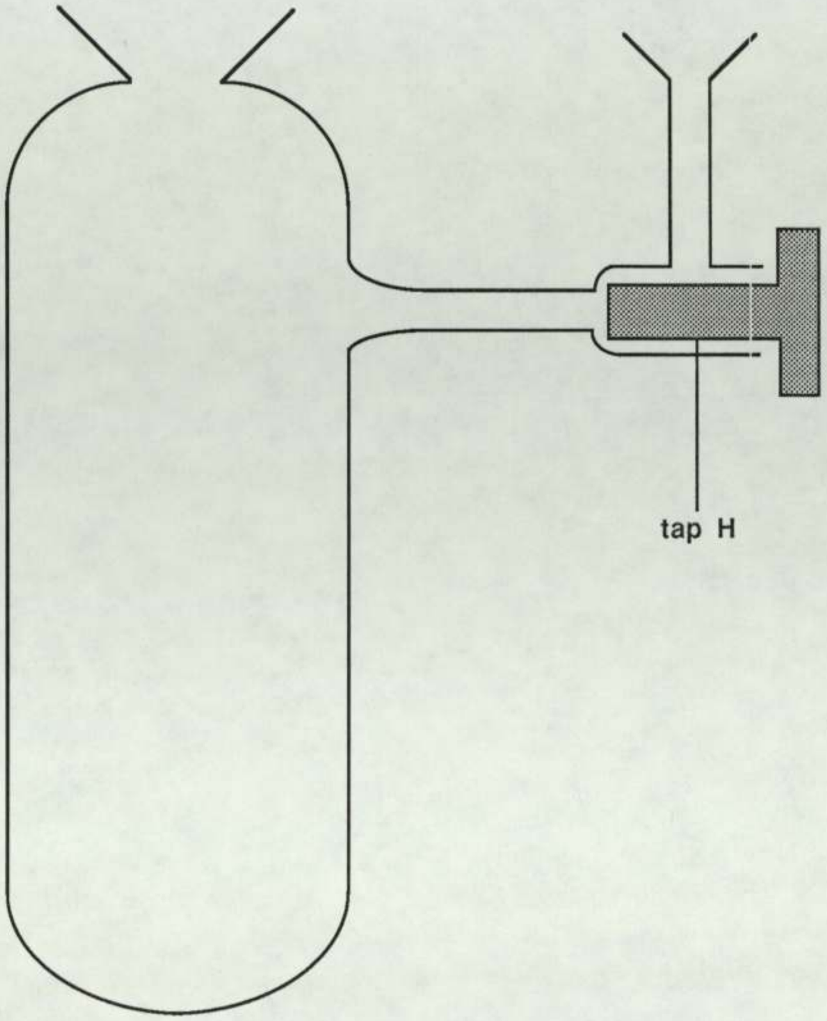


FIGURE 2.2 REAGENT STORAGE FLASK

The receiver flask was gradually cooled in a Dewar containing liquid nitrogen. Tap D of the main manifold was then closed and tap (H) opened to allow solvent to distill from the warm flask to the cold flask. To hasten distillation both the main manifold and the solvent flask could be warmed with a hot air blower.

2.3 PURIFICATION AND DRYING OF MATERIALS

Since the majority of the catalyst materials used in this study are very sensitive to impurities and moisture it is essential that all the materials used are purified to a high degree.

2.3.1 ACETYLENE

Acetylene was stored in a cylinder as a solution in acetone. The gas was purified by passing it through two concentrated sulphuric acid bubblers, a drying column containing alumina and charcoal and finally through a U - tube containing calcium chloride. The acetylene required for the polymerisation reaction was stored in a 2 dm^3 flask fitted with greasless taps and Quick fit® joints.

2.3.2 TOLUENE

Toluene was fractionally distilled from sodium pellets through an electrically heated 2 meter long fractionation column filled with glass beads. The first 70cm^3 of the distillate from the initial 1.5 dm^3 of solvent was discarded and the subsequent distillate was collected for further drying. The distillate was stored in a flask (figure 2.2) containing calcium hydride. The toluene was degassed and subsequently distilled into a second flask containing slivers of fresh sodium and benzophenone. Within 24 hours the solution became dark blue due to the formation of a sodium benzophenone complex. This complex formation indicates that the toluene was completely dry and oxygen free. The toluene was stored under vacuum and distilled from the flask when required. The sodium benzophenone reagent acts by the following sequence of reactions.

$$\text{Na} + \text{Ph-CO-Ph} \rightarrow \text{Na}^+[\text{Ph-CO-Ph}]^- \qquad \text{equ. 2.1}$$

$$\text{Na}^+[\text{Ph-CO-Ph}]^- + H_2O \rightarrow \text{NaOH} + 0.5H_2 + \text{Ph-CO-Ph} \qquad \text{equ. 2.2}$$

2.3.3 CYCLOHEXANE

The procedure for the purification and drying of cyclohexane is exactly the same as that employed for toluene.

2.3.4 STYRENE

Styrene contains 10-15 ppm of t-butyl catechol to prevent thermally initiated polymerisation. The catechol was removed by washing 100 cm^3 of styrene three times with 30cm^3 aliquots of 10% sodium hydroxide solution. The monomer was then rinsed several times with distilled water. The wet styrene was dried initially over anhydrous calcium chloride for 24 hours and then stored over powdered calcium hydride in a typical reagent flask (fig 2.2). After 24 hours the styrene was degassed and distilled on to slivers of fresh sodium and benzophenone. The styrene was stored under vacuum and distilled as required.

2.4 PREPARATION OF SOLUTIONS

This section describes the techniques used to prepare solutions of the sensitive reagents used in this study.

2.4.1 TUNGSTEN HEXACHLORIDE

A known amount of tungsten hexachloride (usually about 0.3g) was introduced, under nitrogen, into a flask similar to that shown in figure 2.3. The main body of the flask was then cooled and evacuated after being attached to the vacuum line. The required amount of cyclohexane was distilled into the flask under vacuum to produce a solution with a tungsten hexachloride, the concentration of which was approximately 1.5×10^{-2} M The volume of solvent distilled was determined by weight difference.

2.4.2 ALUMINIUM TRIETHYL

A known amount of pure dry toluene was distilled under vacuum into part A of a clean dry flask of the type shown in figure 2.3. Part B of the flask was then purged with oxygen free nitrogen and the tap was removed, whilst keeping a slow stream of nitrogen flowing through the flask. A measured volume of aluminium triethyl was then injected by syringe into part B of the flask. The tap was then replaced and the tap separating parts A and B opened allowing the aluminium triethyl and toluene to mix.

2.4.3 TITANIUM TETRABUTOXIDE

Solutions of $Ti(OBu)_4$ were prepared in a similar way to those of aluminium triethyl.

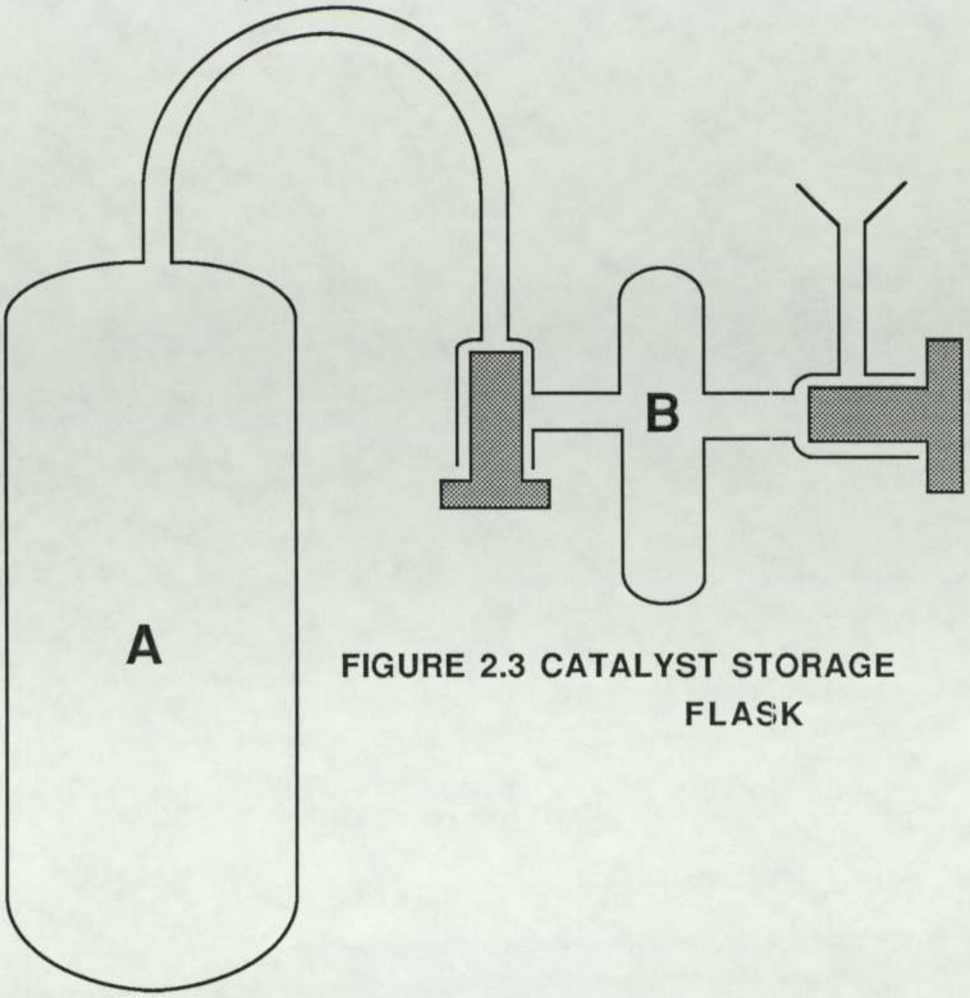


FIGURE 2.3 CATALYST STORAGE FLASK

2.5 POLYMERISATION REACTIONS

This section describes the polymerisation techniques used to prepare the polymers in this study.

2.5.1 POLYSTYRYL LITHIUM

A known amount of pure dry styrene was distilled under vacuum into part A of a clean dry flask of the type shown in figure 2.4. A known amount of pure dry cyclohexane was then distilled into part B. A solution of butyl lithium in hexane was injected into the cyclohexane via the Subaseal. The whole flask was then placed in an ice bath to equilibrate. After 30 minutes the solvent and monomer were mixed and the whole flask immersed in a water bath at 60°C and left for 24 hours.

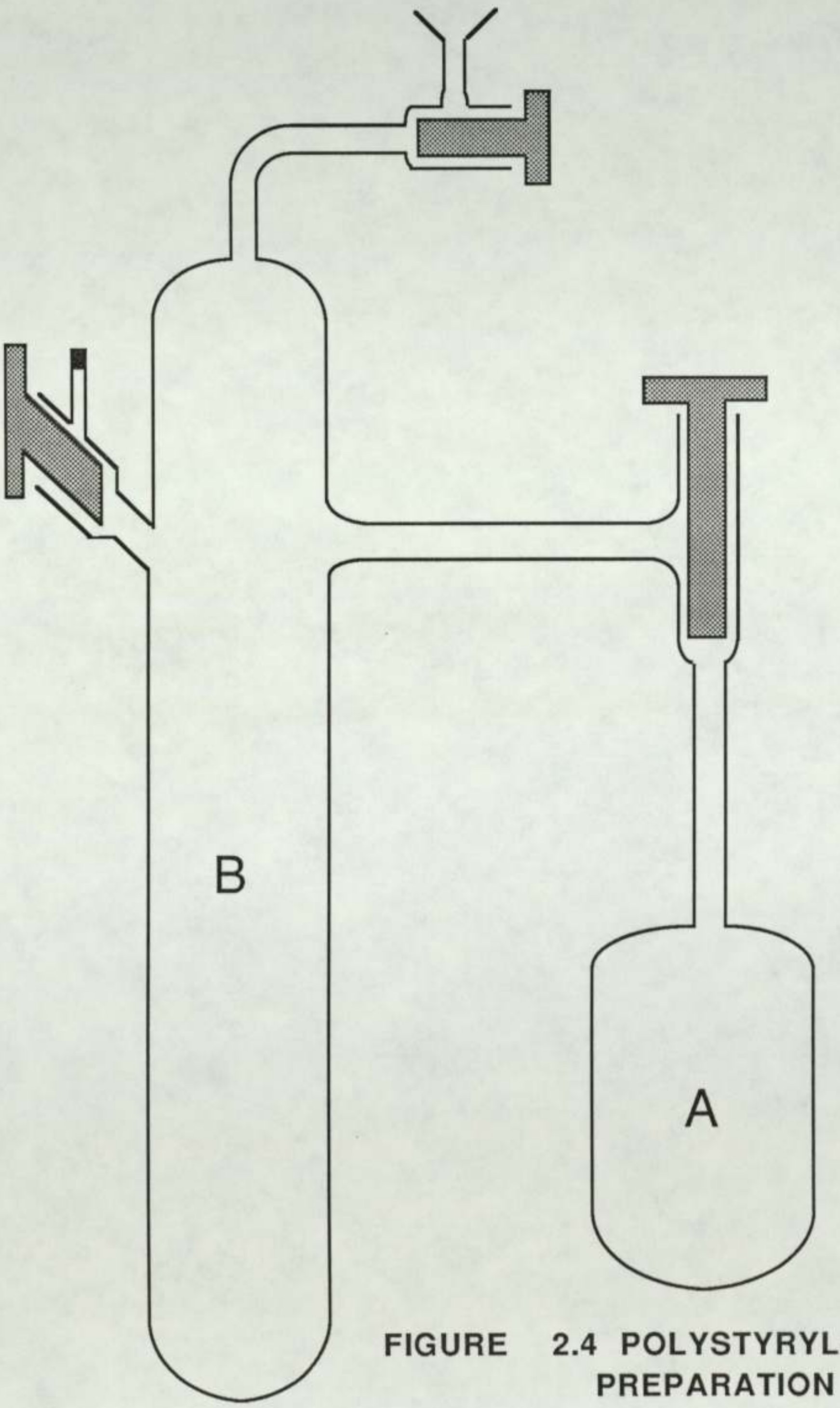


FIGURE 2.4 POLYSTYRYL-LITHIUM PREPARATION FLASK

The solution, which was originally clear, gradually turned orange red, which is typical of the polystyryl anion in non polar solvents. The polystyryl lithium was transferred under vacuum into a flask similar to that shown in figure 2.3 for storage.

2.5.2 ZIEGLER / NATTA POLYMERISATION OF ACETYLENE

A reaction vessel of the type shown in figure 2.5 was evacuated and flamed to remove traces of moisture. To the flask were added 5cm^3 aliquots of 1.22 M aluminium triethyl and 0.28 M titanium tetrabutoxide The catalyst mixture was allowed to stand for about 60 seconds before the flask was attached to the vacuum line via tap A and cooled slowly in liquid nitrogen. The vessel was degassed and a 2dm^3 bulb containing the acetylene was attached. The catalyst solution was allowed to warm up to room temperature at which time the monomer was admitted via tap B . Immediately the gaseous acetylene formed a purple film on the surface of the catalyst solution. The polymerisation was interrupted by evacuating the system.

Purification of the film was achieved by removing the excess catalyst solution remaining under the newly formed film by means of a syringe, followed by repeated washing with toluene, until the the solution became colourless. The film was removed from the vessel and dried in a vacuum oven for 24 hours . Samples were stored under nitrogen at room temperature in screw top glass jars.

2.5.3 PREPARATION OF POLYACETYLENE OLIGOMERS

Toluene (80 cm^3) was distilled from benzophenone/sodium into the reaction flask (figure 2.5). To this was added 2.79 gms of $Ti(OBu)_4$ by means of a syringe. The flask was cooled in liquid nitrogen and the solution, when frozen, was degassed. A 2 dm^3 storage bulb containing acetylene was attached to the flask and the connecting tube evacuated.

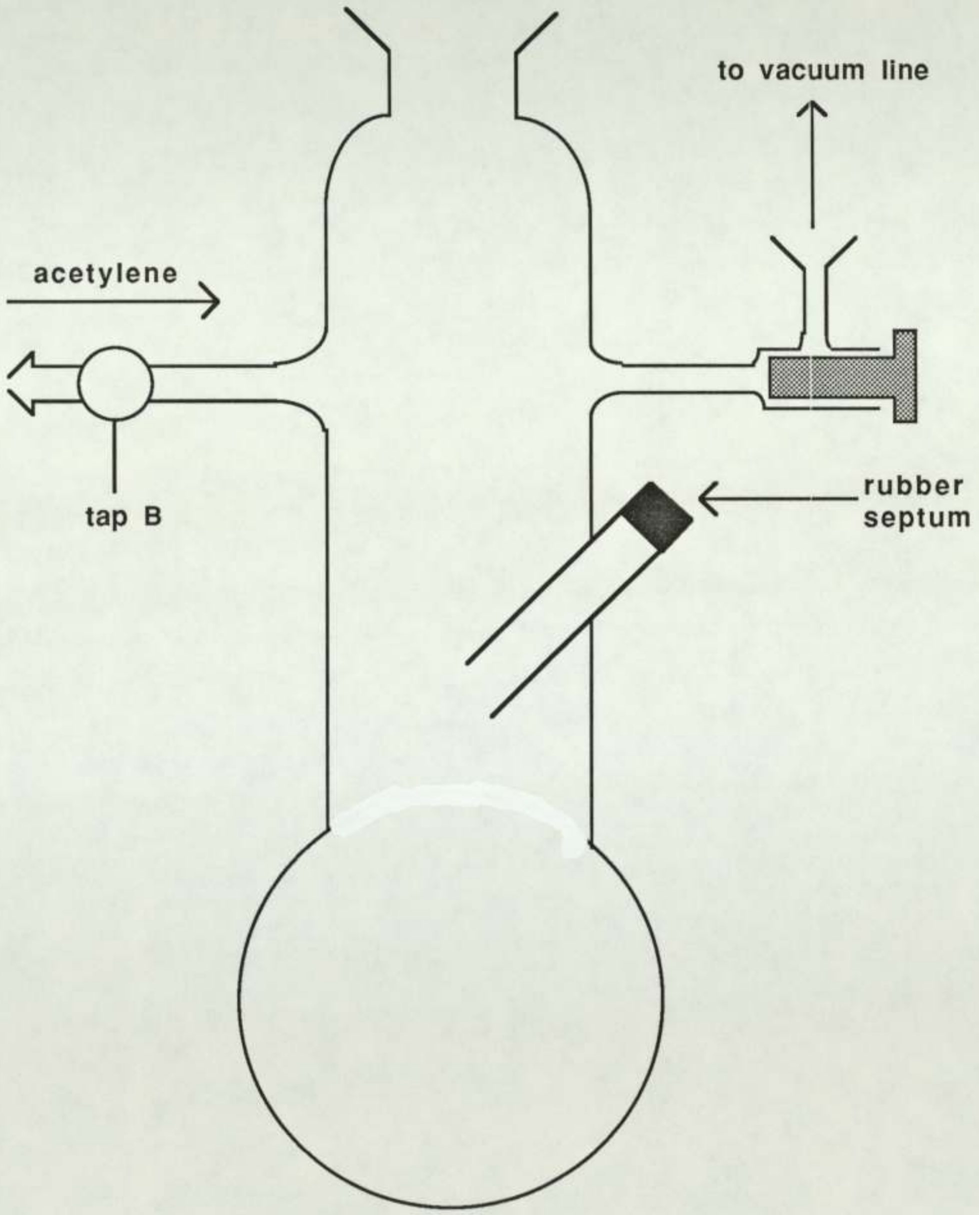


FIGURE 2.5 REACTION FLASK

The reaction flask was then allowed to return to room temperature and at this stage a quencher was added in the form of either acetone or ethyl benzoate. (In a normal preparation 5-10 cm^3 of ethyl benzoate was added). 18 cm^3 of 1.22 M $AlEt_3$ in toluene was added, with vigorous stirring, over a period of about 10 minutes. During this time the colour of the reaction mixture changed from clear to yellow, deepening to red and finally through to brown. The final solution contained black particles of polyacetylene. The reaction was terminated by the addition of 5 cm^3 of methanol followed by careful addition of 50 cm^3 of 2M HCl (care is needed as the solution becomes hot)

The product was filtered to remove the precipitated salts and powdered polyacetylene. These residues were washed with toluene and all the filtrates collected together and washed with water, a dilute solution of sodium hydrogen carbonate and finally distilled water. The organic layer was separated off and dried over anhydrous magnesium sulphate overnight. After filtering the solution was evaporated on the vacuum line yielding about 2-3 cm^3 of a viscous yellow / orange liquid. The product was stored under nitrogen until it was needed.

2.5.4 METATHESIS POLYMERISATION OF ACETYLENE

50 cm^3 of pure dry solvent (either toluene or cyclohexane) was distilled under vacuum into a reaction flask of the type shown in figure 2.5. The flask was cooled in liquid nitrogen until frozen and then evacuated. A 2 dm^3 glass bulb containing acetylene was attached and the connecting tube evacuated. The solvent was allowed to return to room temperature and form a saturated solution with the admitted monomer. Tungsten hexachloride (2.1×10^{-4} moles)

in cyclohexane was injected into the reaction flask followed by 4.07× 10^{-4} moles of aluminium triethyl in toluene. The reaction system showed all the colour changes that are normally associated with the metathesis reaction *i.e.* blue → green/brown → blue/black. After approximately 30 minutes at ambient temperature a black precipitate began to form in the reaction vessel. Polymerisation was allowed to proceed for 48 hours after which time the reaction was terminated by the addition of ethanol to destroy the catalyst completely. The reaction system was then filtered and the polymer obtained was washed with fresh cyclohexane and dried in a vacuum oven for 24 hours. Separate reactions were also carried out in which the individual catalyst components were added to the solvent to ensure that acetylene polymerisation could not be initiated by one of the components on its own.

2.5.5 PREPARATION OF POLY(STYRENE-CO-ACETYLENE)

A reaction flask of the type shown in figure 2.5 was attached to the vacuum line and evacuated. 10cm^3 of 1.7× 10^{-2} M polystyryl lithium solution in cyclohexane was introduced by syringe into the reaction flask via the Subaseal. The reaction flask was again attached to the vacuum line and cooled in liquid nitrogen. The bulb containing the acetylene was attached and the flask evacuated .The flask was allowed to return to room temperature and 3 cm^3 of 1.26 × 10^{-2} M tungsten hexachloride solution is added using a syringe. The catalysts were allowed to mix for 2 to 3 minutes before the acetylene was admitted to the flask. The system showed all the colour changes associated with metathesis reactions. After 30 minutes the the solution appeared blue and after an hour a blue/black precipitate could be observed. After 24 hours the product was precipitated in methanol and dried in a vacuum oven overnight. The product was stored under nitrogen in glass vials until required

2.6 ANALYTICAL TECHNIQUES

This section describes some of the analytical techniques used to characterise the polymers produced in this study.

2.6.1 ELEMENTAL ANALYSIS

Carbon and hydrogen contents, of the polymers obtained from the preparations, were carried out using a Carlo-Erba CHN analyser. 10 samples were ashed in order to produce an average value for each polymer.

2.6.2 INFRA-RED SPECTRA

The infra-red spectra of the polymers obtained were produced by a Perkin-Elmer 1710 Fourier Transform Infra-Red (FTIR) spectrometer. Small amounts of the polyacetylene or copolymer were ground with potassium bromide (KBr) powder until a homogeneous mixture was produced. Discs of this material were prepared in the normal fashion by means of a hydraulic press and a die. These discs were then used to produce the infra red spectra. The KBr was kept in an oven at 120 °C in order to keep it completely dry.

2.6.3 U.V./VISIBLE SPECTRA

The U.V./Visible spectra of the copolymers obtained from the reactions were produced by a Beckman DU7 U.V./Visible spectrometer. In general, samples were taken directly from the reaction mixture and injected into 1 cm pathlength cuvets. In order to record the absorbance due to the polyacetylene segments the samples were run against a background of polystyryl-lithium in cyclohexane.

2.5.4 COMBINED GAS CHROMATOGRAPHY-MASS SPECTROSCOPY

Preliminary G.L.C. examination of the polyenes was carried out on a Pye Unicam 304 gas chromatagraph fitted with a 1m × 0.5cm (iD) SE30 glass column and flame ionisation detector. All G.C.-M.S. analysis was performed on a V. G. Micromass 12000 series quadropole mass spectrometer fitted with a 30m× 0.3cm (ID) bonded phase fused silica column.

Components separated on the column were fed into the source of the mass spectrometer (maintained at 200 °C) where they were ionised by a 70eV electron beam. Mass spectra were generated and recorded every two seconds on a digital PDP8a microcomputer running V. G. release 8MSI2000 software.

Samples of the polyene mixture were injected directly into the gas chromatagraph in the normal manner, although in many cases the samples first had to be diluted in a solvent such as chloroform, in order to stop the column becoming overloaded.

2.6.5 GEL PERMEATION CHROMATOGRAPHY

Gel permeation chromatography (G.P.C.) is a technique used to separate polymer molecules according to their random coil dimensions in solution. Separation occurs in a column (or series of columns) filled with beads of a rigid porous 'gel' of highly crosslinked polystyrene. As a polymer solution flows past the beads, polymer molecules diffuse into the internal pore structure of the gel; the extent of diffusion is governed by the size of the polymer molecule and the pore size distribution in the gel. Larger molecules can enter only a small fraction of the internal portion of the gel, or are completely excluded, smaller molecules penetrate a larger fraction of the internal pores of the gel. Larger molecules therefore spend less time inside the gel and so are eluted quickly from the column. Smaller molecules spend more time in the pore structure of the gel and so are eluted more slowly from the column.

After eluting from the column the polymer solution passes through a series of detectors which produce a responses proportional to the concentration of the polymer in solution. Nowadays most G.P.C. equipment is fitted with both ultra violet (U.V.) and a differential refractometer (R.I.) detectors. The U.V. detector measures the U.V. absorbtion of the polymer containing chromophoric groups along the back bone of the polymer chain at a pre-determined wavelength, or polymers having chromophoric end groups. Refractive index detectors function by detecting changes in refractive index between a sample of the polymer solution eluting from the G.P.C. columns and a sample of pure solvent. This detector is independent of the nature of the polymer in solution. If the response of detectors is plotted against retention time (fig 2.6) then the familiar G.P.C.

chromatogram is obtained.

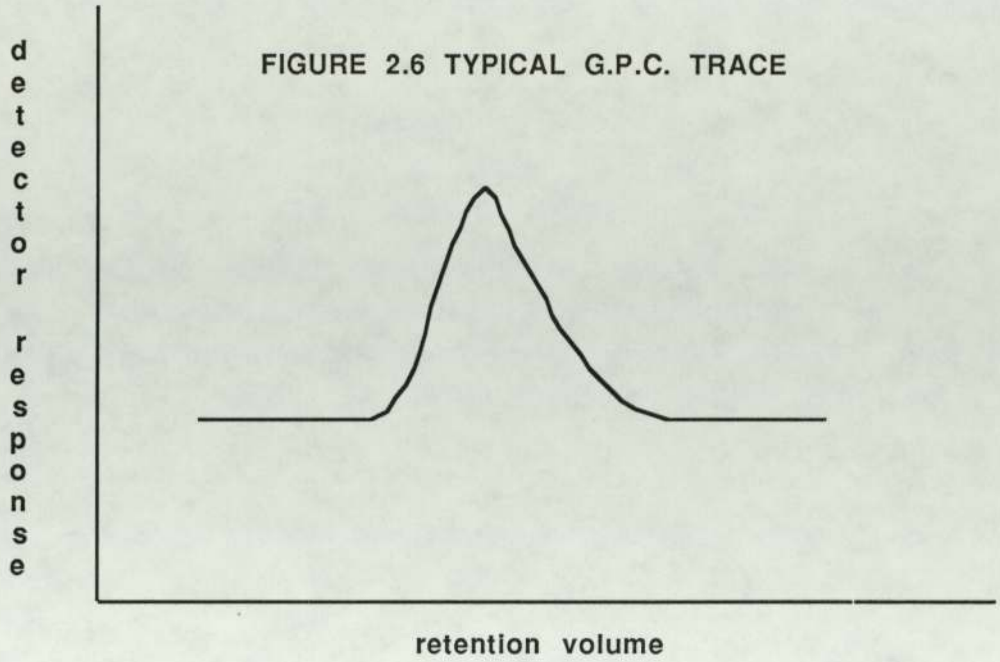
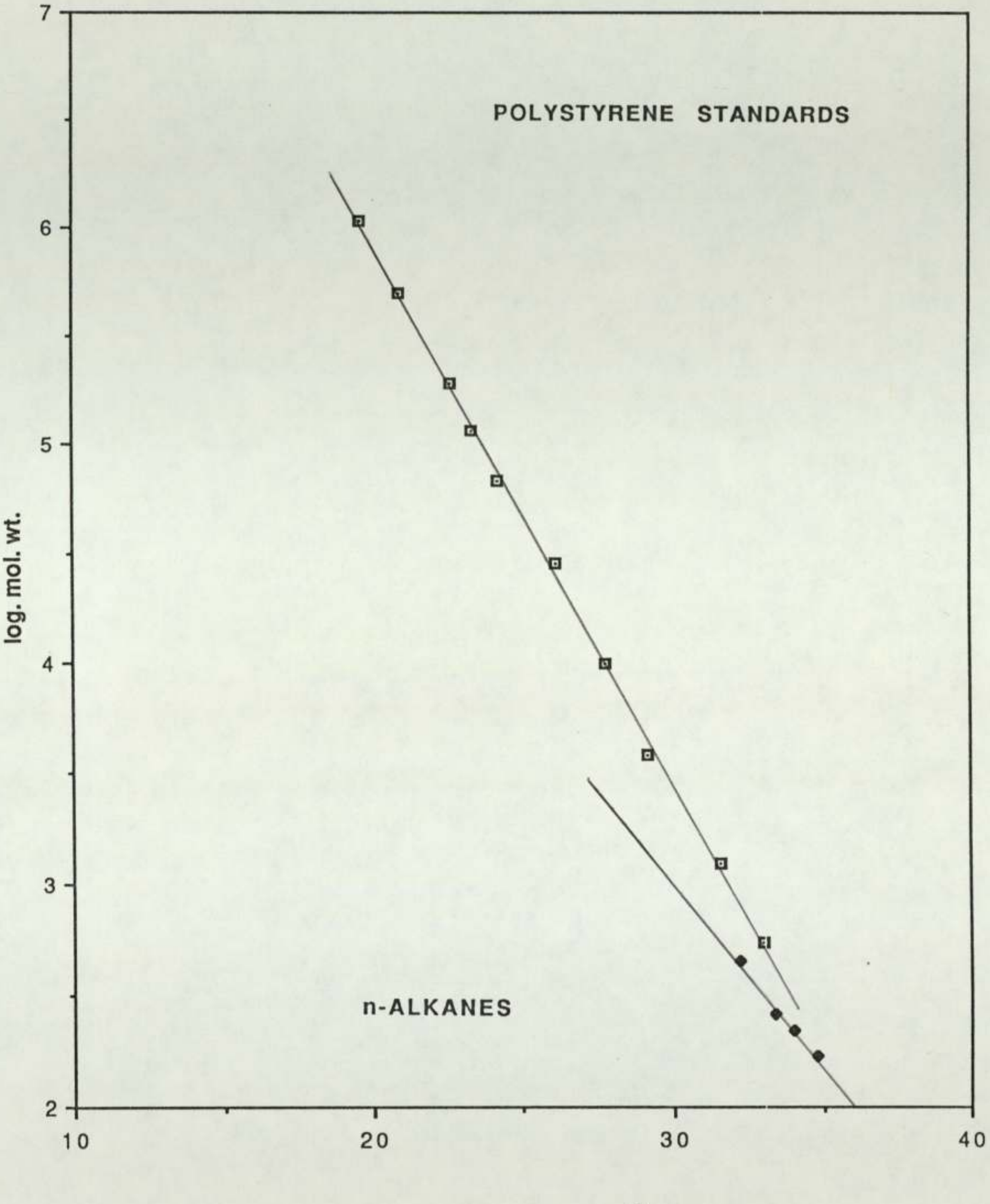


FIGURE 2.6 TYPICAL G.P.C. TRACE

Since there is no complete theoretical understanding of the relationship between molecular size and the elution rate of a polymer solution through a gpc column, the chromatogram provides only a semi-quantitative description of molecular size (and in most cases molecular weight) distribution of the polymer in solution. Quantitative information can be obtained by calibrating the series of G.P.C. columns with a set of narrowly dispersed polystyrenes of a range of molecular weights. From this calibration a plot of log molecular weight (polystyrene) against retention time (volume) figure 2.7 may be obtained. By comparing retention volumes of different polymers it is possible to obtain a polystyrene equivalent molecular weight for most linear polymers in solution.

All G.P.C. chromatagrams recorded for the copolymer were produced using a Perkin-Elmer series 10 liquid chromatagraph fitted with a Perkin-Elmer LC-85B spectrophotometric variable wavelength detector and a Knauer Differential

FIGURE 2.7 G.P.C. CALIBRATION GRAPH



refractometer detector. The columns used were 10^5, 10^4, 10^3 and 10^2 Å porosity 10μ gel from Polymer Laboratories 10PL gel.

The initial G.P.C. study on the polyene mixture was carried out using a column containing Sephedex LH-60 in conjunction with an applied chromatography pump and a Knauer detector.

2.6.6 SCANNING ELECTRON MICROSCOPY

Scanning electron micrographs were obtained using a Cambridge S-150 scanning electron microscope. The sample to be studied was mounted on an aluminium stud by means of double sided sticky tape. A very thin gold film was then introduced on to the surface of the sample by means of a gold sputterer. This is to stop the sample charging up in the electron beam and causing distortion of the image. Since the surface of the samples, in every case, was very uneven this coating process was very inefficient in certain areas. Nevertheless photographs of the surface morphology of the materials could then be obtained.

2.7 ELECTRICAL MEASUREMENTS

This section describes the techniques used to measure the electrical properties of the polymers produced in this study.

2.7.1 APPARATUS FOR THE MEASUREMENT OF PARALLEL RESISTANCE

The measurement of the parallel resistance, R_p , was carried out using a Gen Rad 1689 precision RLC Digibridge connected to a resistance cell containing the sample under test. Electrical connections between the digibridge and the resistance cell were made using a four terminal, guarded Gen Rad 1657-9600 extender cable. The cable was slightly modified with the replacement of the "high" and "low" banana plugs by BNC plugs. The guard plug was left unchanged. The corresponding BNC sockets were mounted on to a small Tufnol sheet and the two terminal resistance cell was connected to these sockets. Prior to the connection of the resistance cell a zeroing procedure was carried out on the digibridge and extender cable to compensate for any inbuilt resistance.

2.7.2 RESISTANCE CELLS

Two resistance cells were used in this study, one for use above room temperature and one for use below room temperature. These cells are shown in figures 2.8 and 2.9.

2.7.3 MEASUREMENTS ABOVE ROOM TEMPERATURE

Figure 2.8 shows a cross-sectional diagram of the stainless-steel resistance cell used for the measurement of parallel resistance at temperatures above room temperature The cell consists of a stainless-steel body with a central cavity. A sample of the dried powdered polymer was placed in the cavity and the cell "tapped" to produce an even distribution. The ram was then introduced into the PTFE sleeve and pushed down to make contact with the polymer. The cell was then placed between the jaws of a hydraulic press from which it was insulated by sheets of high density polyethylene. The press is then activated to produce the required pressure on the press rams. Electrical connections were made between the cell and a Gen Rad 1689 precision digital bridge. The sample was contained between the central ram and the base of the cell, which formed the cell terminals. The PTFE spacer was used to insulate both terminals electrically.

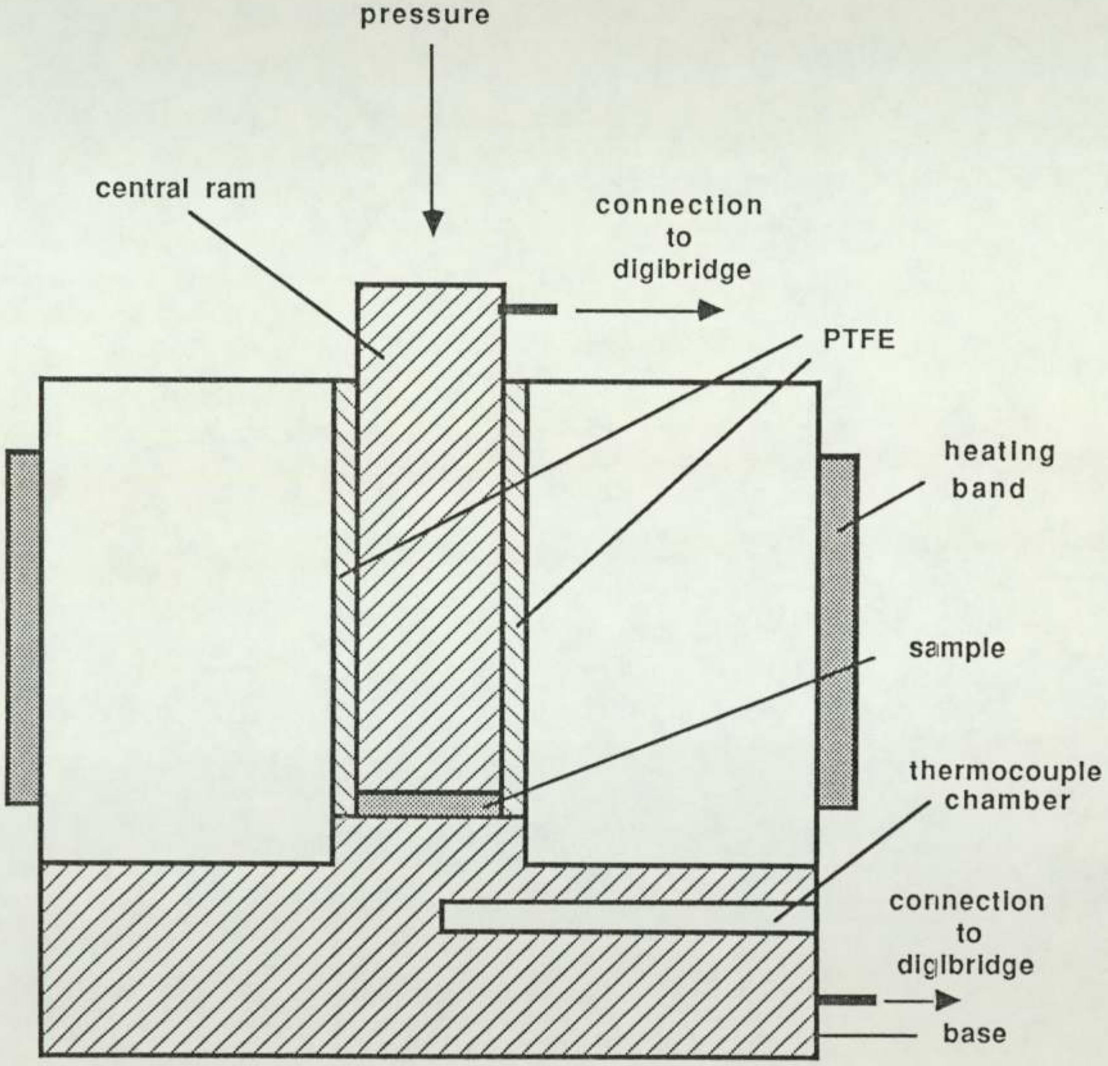


FIGURE 2.8 HIGH-TEMPERATURE STAINLESS-STEEL RESISTANCE CELL

The average of ten measurements was taken at each of thirteen spot frequencies in the range 12 Hz to 10^5 Hz. When a full range of measurements has been made the cell is allowed to cool to room temperature and is forced apart by means of Allan keys running through the base of the cell. The polymer disc is then removed from the cell and the thickness measured by a micrometer.

2.7.4 CONTROL OF THE TEMPERATURE IN THE RANGE 283 K TO 373K

The temperature of the cell was raised by an electrical heating band which was attached to the outside of the main body of the resistance cell. The heating band was connected to a Variac which enabled the current flowing through the band to be controlled giving a good temperature variation. The temperature in the cell was measured by means of a thermocouple, which was inserted in to the core of the cell below the sample chamber by means of a hole bored from the outside.The thermocouple was attached to a Keithley 616 digital electrometer which produced a voltage reading which could easily be converted to a temperature reading by means of a calibration chart. The temperature control of this apparatus was ± 1K

2.7.5 MEASUREMENTS BELOW ROOM TEMPERATURE

Electrical measurements below room temperature were made in the cell shown in figure 2.9 The temperature was controlled by a cryostat shown in figure 2.10. A compressed disc of the polymer was produced by placing a small amount of the powdered polymer into the cavity of the cell shown in figure 2.8. The ram

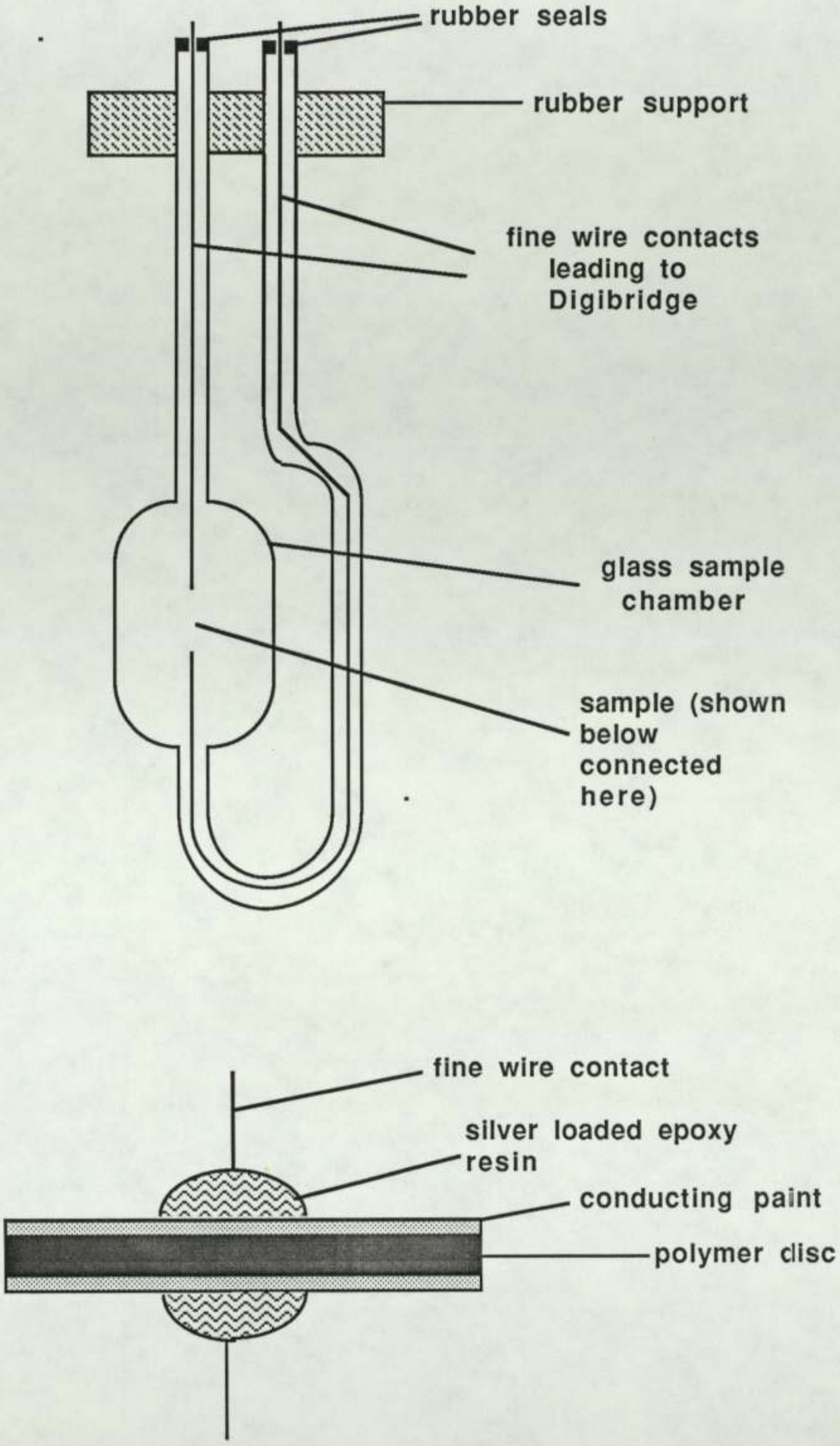


FIGURE 2.9 LOW TEMPERATURE RESISTANCE CELL AND SAMPLE DESIGN

was pushed into the cell and the cell placed in the hydraulic press. The press is actuated and the cell was held under pressure for 5-10 minutes.The pressure was released and the cell forced apart, to remove the polymer disc and measure its thickness. Both sides of the disc were carefully painted with conducting paint (RS components), which was allowed to dry overnight. Fine wires were attached to either side of the disc with silver loaded epoxy resin (RS components). The disc was located in the cell which is then placed in the cryostat. Electrical connections were made to the Gen Rad 1689 precision digital bridge as previously described. An average of 10 resistance measurements was taken at each of 13 spot frequencies in the range 12 Hz to 10^5 Hz.

2.7.6 CONTROL OF THE TEMPERATURE IN THE RANGE 283 K TO 213 K

Temperature control in this region was achieved using a "minus seventy" thermostat bath, bridge control model (Townson & Mercer Ltd., Croydon, UK). A cross-sectional diagram of this apparatus is shown in figure 2.10. The heat exchange vessel was half filled with acetone and solid CO_2 .The temperature control vessel was filled with acetone. A hole drilled into the lid of the temperature control vessel allowed the suspension of the low temperature resistance cell into the acetone. The temperature was measured by a total immersion alcohol thermometer. The temperature control of this apparatus was ±0.5K.

2.7.7 VOLUME RESISTIVITY AND VOLUME CONDUCTIVITY

Volume resistivity, ρ_v , is defined as

$$\rho_v = \frac{R_p A}{L}$$

Where R_p is the measured parallel resistance at a specific frequency, A is the cross-sectional area of the electrode and l is the thickness of the disc. Hence volume conductivity, σ_v, is given by $(\rho_v)^{-1}$.

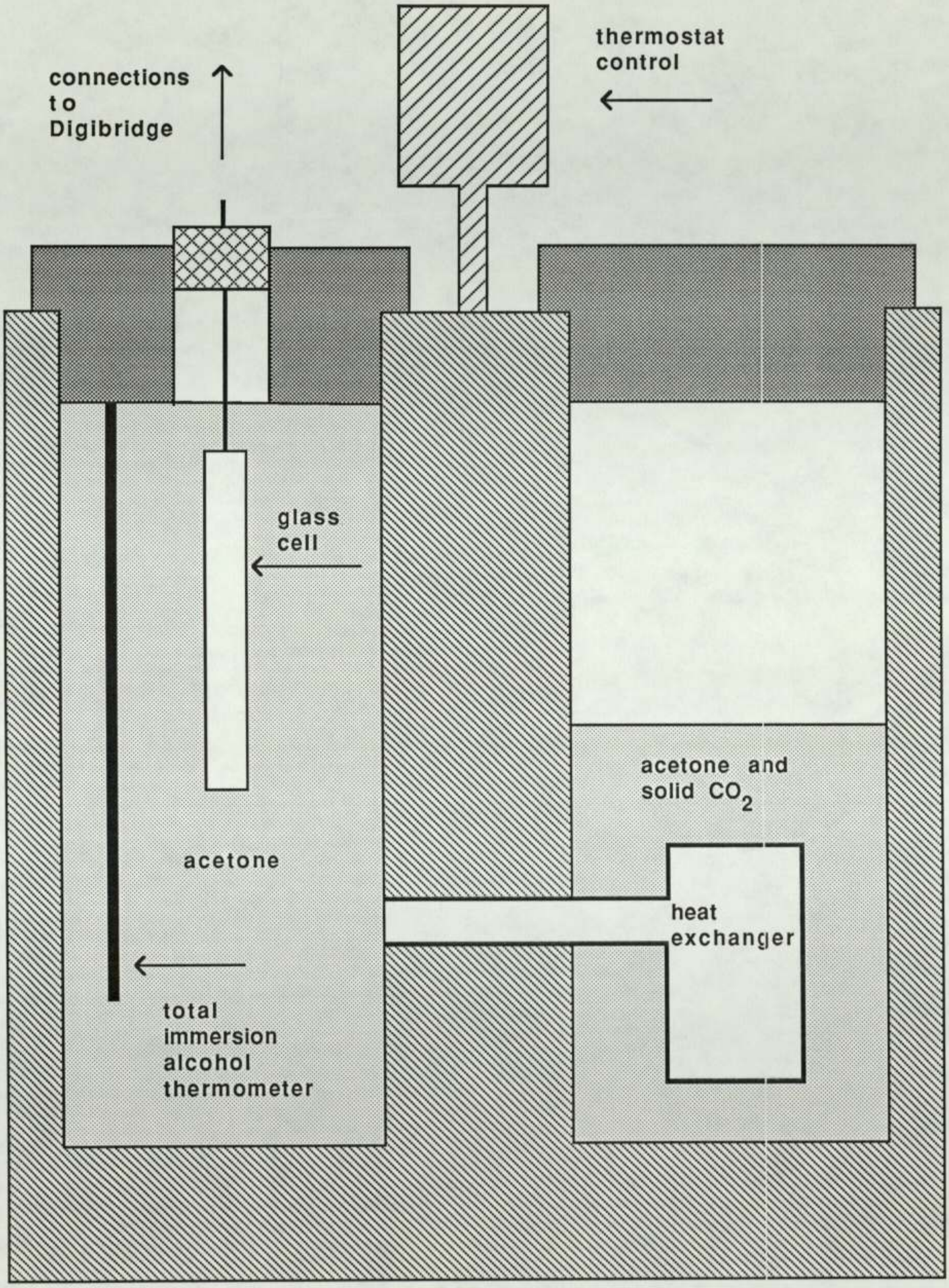


FIGURE 2.10 CROSS-SECTION OF THE "MINUS SEVENTY"BATH

CHAPTER 3

ACETYLENE POLYMERISATIONS

3.1 INTRODUCTION

Acetylene polymerisations have been initiated by radiation, plasma, and a variety of transition and rare-earth metal catalysts. There are many side reactions depending upon the method of initiation. One prominent side reaction is cyclisation to benzene; other processes lead to low molecular weight oligomers, branched and cross-linked polymers. Alhough it is easy to quantify the cyclisation yield, the extent of other reactions is difficult to measure because the products are insoluble.

Among the various catalyst systems the most extensively studied is the combination of $Ti(OBu)_4$ and $AlEt_3$. It has been the subject of these extensive studies because it is the most mechanistically complex of the catalyst systems. After three decades of intensive studies, the detailed mechanism of Ziegler/Natta polymerisations cannot be said to be known with any certainty.

3.2 THE MECHANISM OF ZIEGLER/NATTA POLYMERISATION OF ACETYLENE

From the work of Dawes and Dzhabiyev[75,76] it is known that when triethyl aluminium and titanium alkoxides are mixed, the initial reaction is the transfer of an alkyl group from the aluminium to the titanium. A complicating factor in defining the reaction scheme is the inclination of titanium alkoxides[77] and aluminium alkyls[78] to self-associate and form dimers and trimers in non polar solvents.

Titanium (iv) has been shown to be inactive toward the polymerisation of acetylene[79] , and Ti(iii) has been implicated as the oxidation state of the catalysts, [79-81] . Chien [82] and Baker [83] assigned the following structure- to the possible active sites for the polymerisation of acetylene.

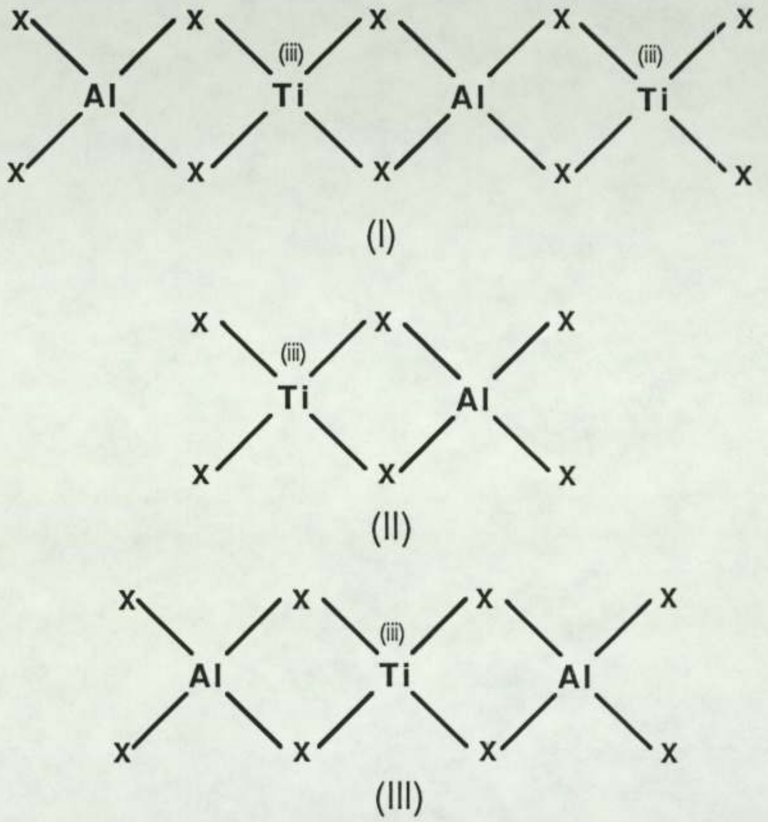


FIGURE 3.1 POSSIBLE STRUCTURE FOR ACTIVE SITES IN ZIEGLER/NATTA POLYMERISATION OF ACETYLENE

Since the butoxy group is a better bridging ligand than Et, it is more likely to be the bridging group. The remaining ligands comprise both OBu and Et depending upon the stoichiometric ratio of Al:Ti.

It has been postulated that it takes 4 moles of $AlEt_3$ to produce the most active catalytic species[84] and the following reactions are thought to lead to its formation.

$$Ti(OBu)_4 + AlEt_3 \rightarrow Ti(OBu)_3Et + AlEt_2(OBu) \quad \text{equ. 3.1}$$

$$2Ti(OBu)_3Et \rightarrow 2Ti(OBu)_3 + C_2H_4 + C_2H_6 \quad \text{equ. 3.2}$$

$$Ti(OBu)_3 + AlEt_3 \rightarrow Ti(OBu)_2Et + AlEt_2(OBu) \quad \text{equ. 3.3}$$

$$Ti(OBu)_2Et + AlEt_3 \rightarrow I + II \quad \text{equ. 3.4}$$

$$Ti(OBu)_2Et + 2AlEt_3 \rightarrow III \quad \text{equ 3.5}$$

Where I, II and III refer to the structures in figure 3.1

For Al:Ti ratios much less than 4:1, there is incomplete reduction of the titanium and little or no polymerisation of acetylene. For much larger ratios, Ti^{3+} is reduced to inactive lower oxidation states.

$$2Ti(OBu)_2Et \rightarrow 2Ti(OBu)_2 + C_2H_4 + C_2H_6 \quad \text{equ. 3.6}$$

The propagation process almost certainly involves the insertion of monomer into the Ti-C bond of the catalyst complex. Experimental support has been provided by D'Yachkovskii and co-workers [85] who showed by NMR that in the $(\pi\text{-}C_5H_5)_2TiCl_2$ / Me_2AlCl catalysed polymerisation of phenylacetylene the monomer was inserted into the Ti-Me bond. Furthermore, based on the structures of the polyenes produced by several workers [86-88], it was concluded that the monomer, after being activated on π-complexation, undergoes cis-opening of the triple bond, which has a Mobius transition state leading to addition to the Ti-C bond as shown in figure 3.2.

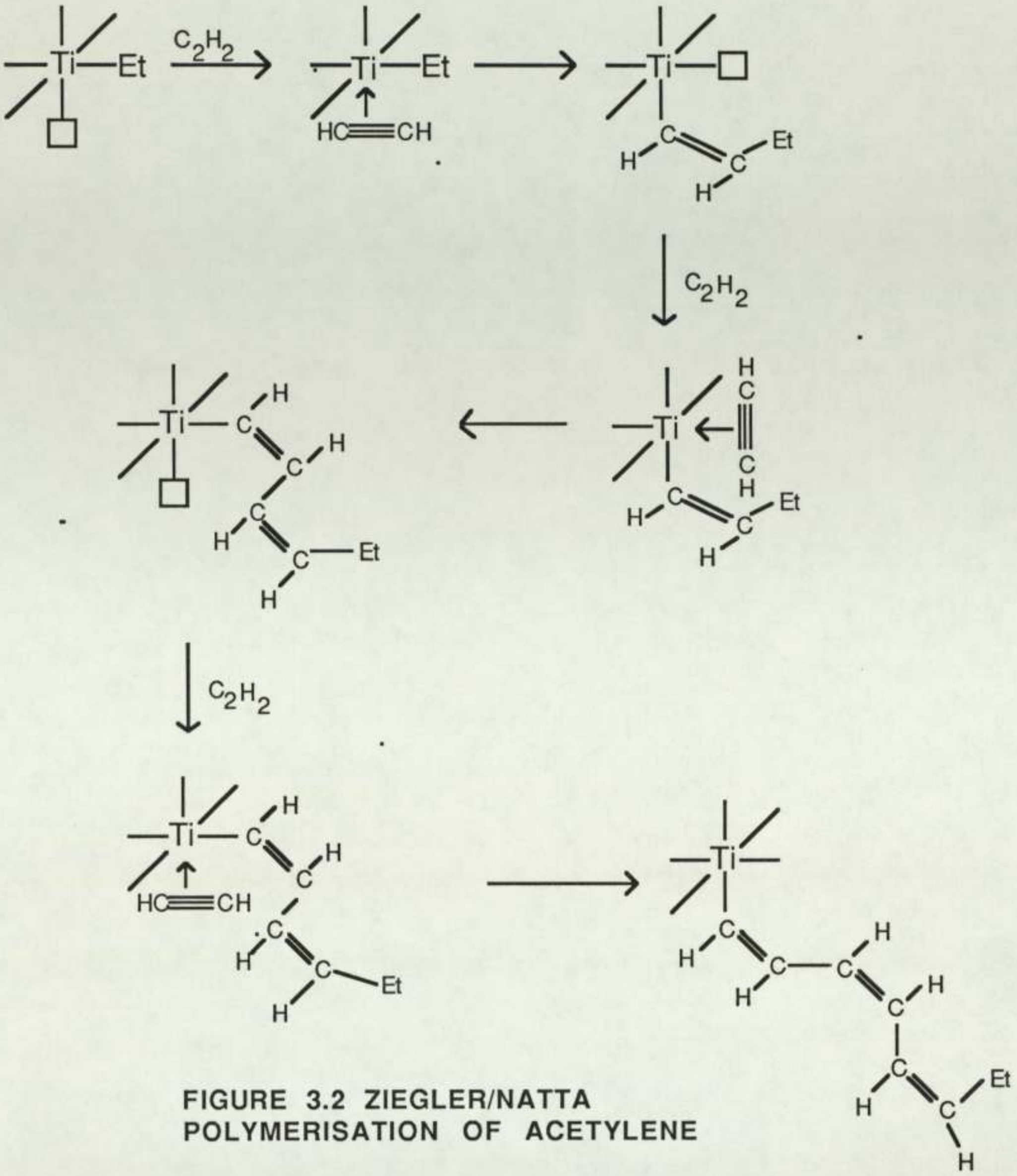


FIGURE 3.2 ZIEGLER/NATTA POLYMERISATION OF ACETYLENE

The propagation scheme shown in figure 3.2 is for the growth of a single polyacetylene chain on a catalytic species which consists of clusters of Ti and Al atoms bridged by ethyl and butoxyl groups as shown above. Titanium alkoxides are known to exist as trimers and tetramers and Complexation to oligomers of higher molecular weight may occur at low polymerisation temperatures. Furthermore, upon deposition on the wall of the reaction vessel, these oligomers are likely to form larger clusters, resulting in the initiation of a large number of polyacetylene chains in a small area. These large clusters form the nuclei for the crystallisation of polyacetylene. Polymerisation and crystallisation probably occur simultaneously.

Termination of the polymerisation reaction is by reduction of Ti^{3+} to Ti^{2+}, Equ. 3.7, or by means of a chain transfer reaction with the aluminium alkyl[89] equ.3.8,

$$2Ti^{3+}P \rightarrow 2Ti^{2+} + P_{-H} + P_{+H} \qquad \text{equ. 3.7}$$

$$Ti^{3+}(C_2H_2)_nEt + AlEt_3 \rightarrow Ti^{3+}Et + Et_2Al(C_2H_2)_nEt \qquad \text{equ. 3.8}$$

3.3 SYNTHESIS OF LOW MOLECULAR WEIGHT POLYACETYLENES (POLYENES)

The first example of the preparation of polyenes by the method outlined in section 2.5 was reported by Baker and Bates[24]. In the present study polymerisations were performed both in the presence and absence of acetone to examine the effect it had on the polymerisation reaction.

When there is no acetone present in the reaction mixture the reaction produces large quantities of black powdered polyacetylene. However even when a small quantity of acetone ($2cm^3$) is added to the standard reaction mixture (section 2.5.3) the production of the black precipitate is totally suppressed. This inhibition is thought to work in the following manner.

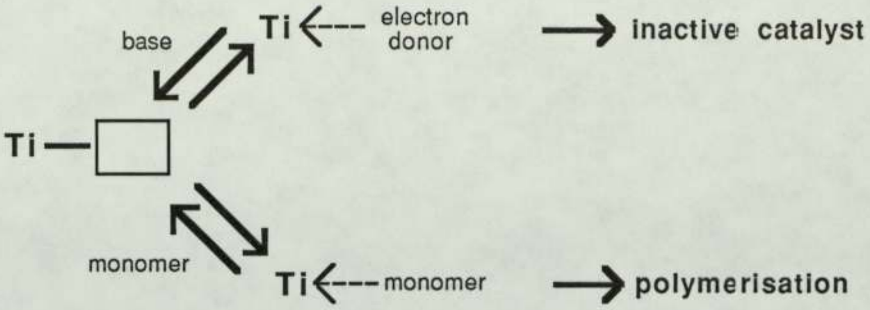


FIGURE 3.3 INHIBITION OF ZIEGLER/NATTA POLYMERISATION OF ACETYLENE

After the titanium has been alkylated, the vacant site may be complexed by either the base (acetone) or the monomer (acetylene). Acetone has a high electron density centred on the oxygen and these electrons are easily donated to the vacant site to form a stable complex. Since the acetone is such a strong electron donor it can render the titanium catalyst site inactive, leading to a great reduction in the quantity of polyacetylene produced.

It is possible that if the acetone were replaced with a weaker electron donor the site would not become completely inactive and the equilibrium (figure 3.3) would become more dynamic and the polymerisation controlled rather than suppressed. It was found that a suitable base to use as the inhibitor was ethyl benzoate.

In the ethyl benzoate molecule the electron pairs associated with the oxygen atoms are delocalised to a greater extent than the electrons associated with the oxygen in acetone. In the ethyl benzoate molecule the benzene ring helps to reduce the electron density on the ester linkage.

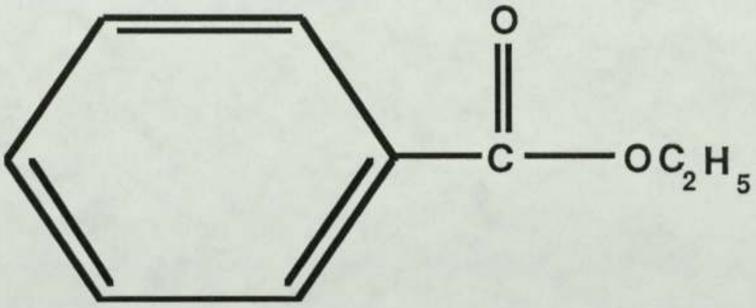


FIGURE 3.4 STRUCTURE OF ETHYL BENZOATE

When ethyl benzoate was introduced into the standard reaction mixture (section 2.5.3) in amounts ranging from 0.8cm^3 to 20cm^3. It was found that even at the highest concentration of inhibitor, polyacetylene was still produced in visible quantities although the precipitate took a great deal longer to appear compared to the uninhibited case. (*i.e.*, Precipitation occurred after the addition of 16cm^3 of the $AlEt_3$ solution rather than after the addition of 2cm^3.)

It was very difficult to obtain any quantitative results pertaining to the quantity of polyene produced in any single preparation. This was because the final yellow product had a heavy smell of ester indicating contamination. This was even the case at the lowest concentration of ethyl benzoate, although with prolonged evaporation on the vacuum line the contamination could be reduced. Great care had to be taken when undertaking this reduction as there was was some danger of losing the product in carrying out this operation.

3.3.1 INFRA-RED ANALYSIS OF THE POLYENE MIXTURE

The infra-red absorption spectrum of a sample of the polyene mixture in carbon tetrachloride is shown in figure 3.5 . This particular sample was prepared in the absence of any inhibitor in the reaction system, to reduce the number of possible impurities and side reactions. The reference sample was freshly distilled carbon tetrachloride.

The sharp band at 1225 cm^{-1} and the broad band at 1000-1100 cm^{-1} can be discounted in the polyene analysis as they are due to silicone grease which was found to be present in small amounts in all samples. This contamination could only be reduced slightly even when the greatest of care was exercised.

The group of absorptions around 3000 cm^{-1} are due to the C-H stretching modes in various environments contained within the polyene. The weak adsorption at about 3020 cm^{-1} is due to the =C-H stretch. The remaining three absorptions at 2960, 2920 and 2860 cm^{-1} are due to -C-H stretching and are associated with the end groups of the polyenes. The difference in frequency is due to the different degrees of conjugation associated with individual end groups. The conjugation lowers the frequency and therefore the wavenumber of the absorbtion.

The broad band centered on 800 cm^{-1} is due to the out of plane C-H bend in the C=C-H group; while the weak absorption at 1600 cm^{-1} can be attributed to conjugated carbon-carbon double bonds. The five absorptions from 1350 to 1500 cm^{-1} are due to the C-H bending and deformation modes connected with

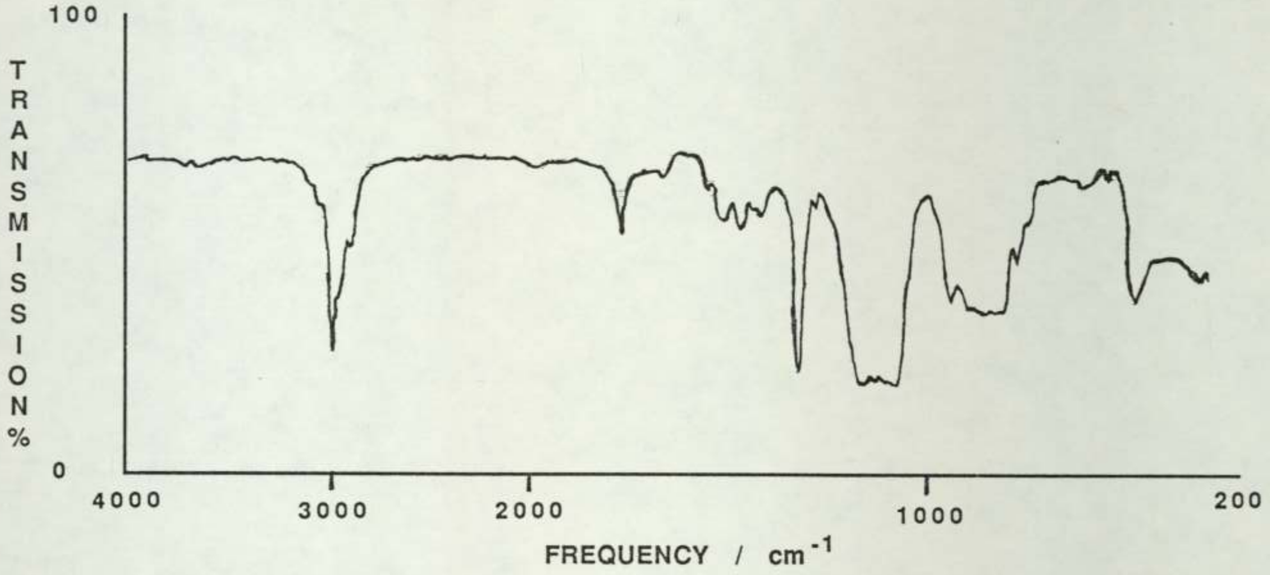


FIGURE 3.5. INFRARED SPECTRUM OF POLYENE MIXTURE

such groups as $-CH_2-$ and $-C{=}CH_2$, *i.e.*, end groups or saturation brought about by radical attack.

The sharp absorption at 1720 cm^{-1} may be attributable to a ketonic carbonyl stretch. Carbonyl groups are introduced into the polyene by oxidation caused by radical attack in the carbon tetrachloride which contains dissolved oxygen[90,91].

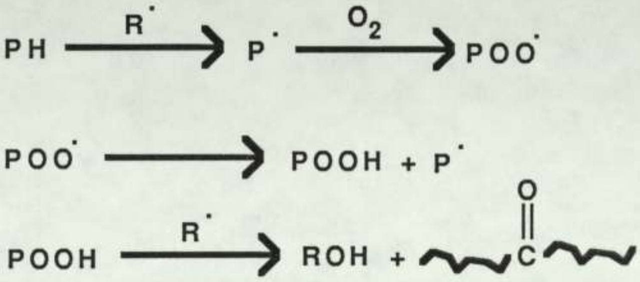


FIGURE 3.6 OXIDATION OF POLYENES

As is the case with many other polymers the oxidation of the polyenes can be followed by the growth of the C=O absorption band.

3.3.2 U.V./VISIBLE SPECTRUM OF THE POLYENES

The U.V./Visible spectrum of a sample of the polyene mixture is shown in figures 3.7 and 3.8 . Again this sample was prepared in the absence of an inhibitor to reduce the frequency of possible side reactions and formation of impurities.

Individual polyenes exhibit a distinctive four peak electronic absorption

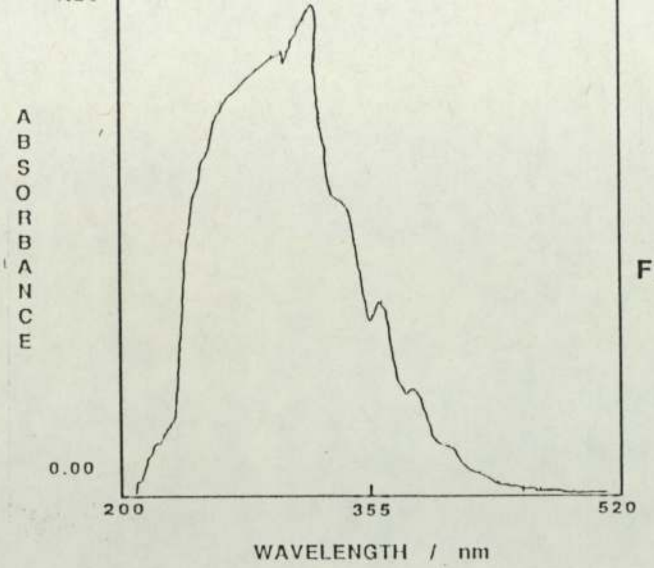


FIGURE 3.7. U.V./VISIBLE SPECTRUM OF POLYENE MIXTURE

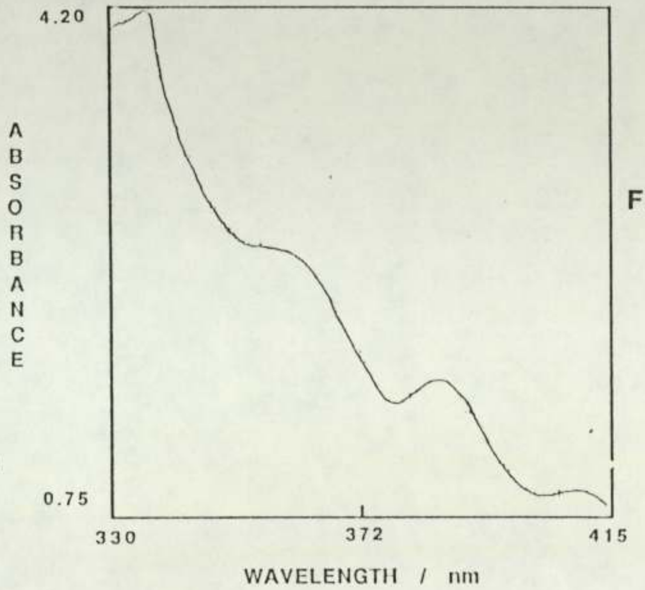


FIGURE 3.8. U.V./VISIBLE SPECTRUM OF POLYENE MIXTURE 330-415 nm

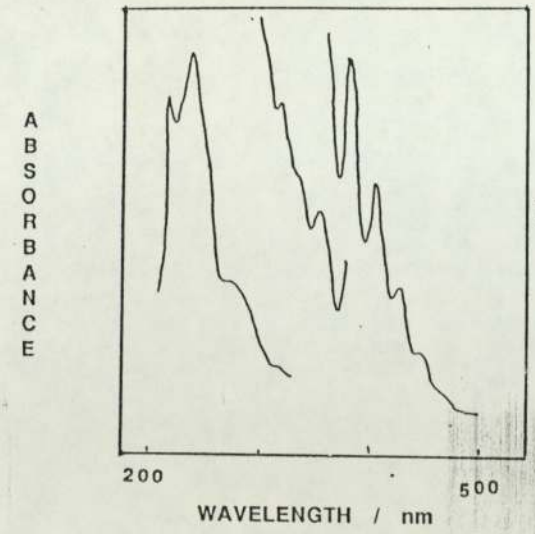


FIGURE 3.9. U.V./VISIBLE SPECTRUM OF POLYENE MIXTURE AS PREPARED BY BAKER AND BATES

envelope[92,93] and as the number of conjugated double bonds increases, the wavelength of the absorption encroaches on the visible region. In long chain polyenes a change from cis- to trans- configuration at one or more double bonds lowers both the wavelength and the intensity of the absorption maximum.

The results presented here are in very good agreement with those of Baker and Bates [24] . They reported peaks in the U.V./Visible spectrum at 318, 334, 353, 380, 404, 426, 448, and 468 (figure 3.9). In the work reported here peaks occur at 314, 336, 355, 386, 410 and 432 nm. The U.V./Visible spectrum of the isolated product shows a broad absorption envelope with a periodic fine structure, which is to be expected for a mixture of polyenes because of the nature of the absorption of the individual components.

The separation of this complex mixture into the individual components would enable a study of the end group structure to be made. This may yield information on the initiation of acetylene polymerisation as well as the termination step. A knowledge of the end group structure would also be of help in the interpretation of the mass spectra . (see below)

3.3.3 GAS CHROMATAGRAPHY / MASS SPECTROSCOPY OF THE POLYENE MIXTURE

A sample of the polyene mixture (synthesised in the presence of acetone since the presence of ethyl benzoate leads to the masking of some peaks in the gas chromatagraph). Initially a concentrated sample of the polyenes was injected in to the column. This resulted in the spectrum shown in figure 3.10. This gas

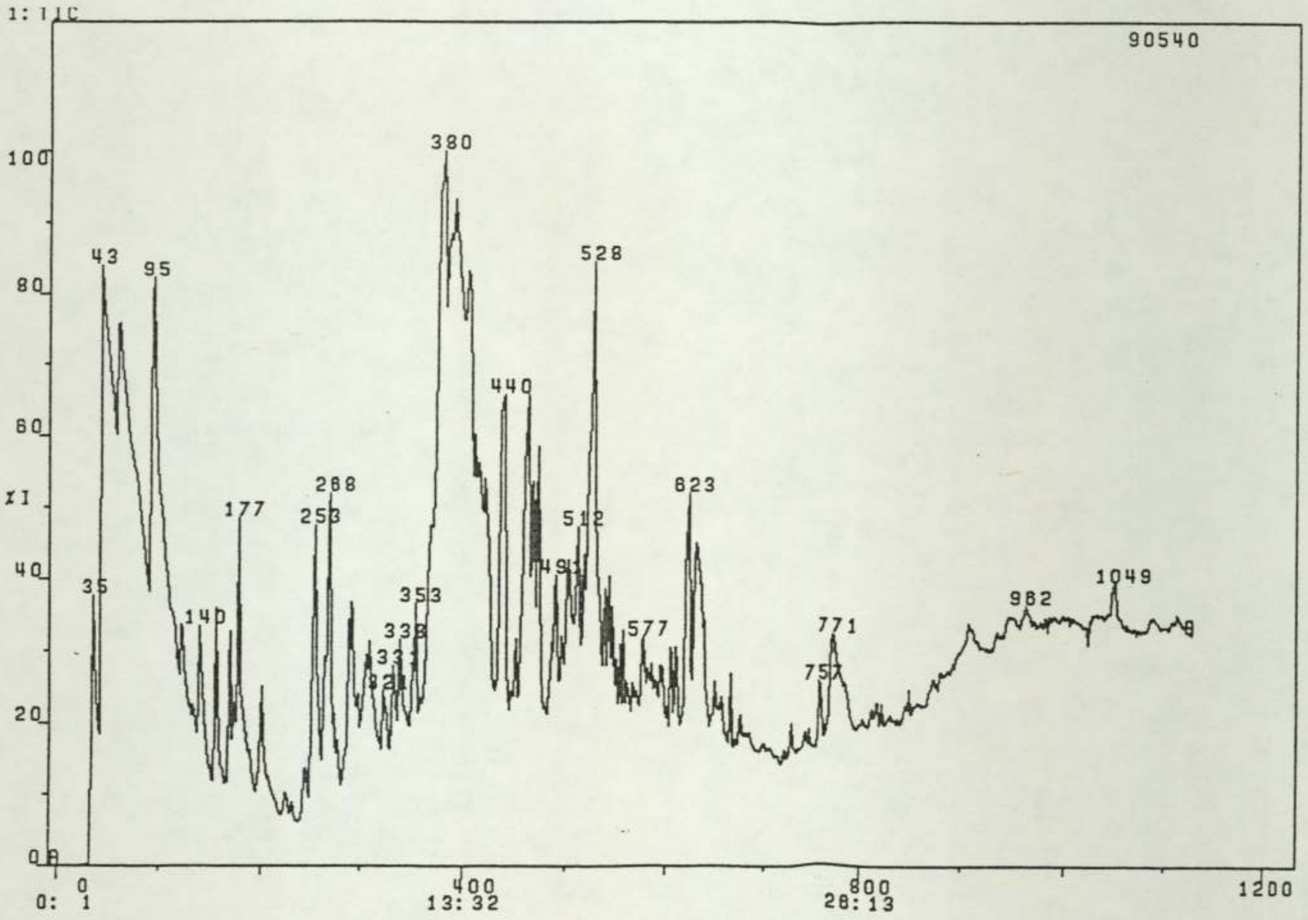


FIGURE 3.10. G.C.M.S. OF CONCENTRATED POLYENE MIXTURE

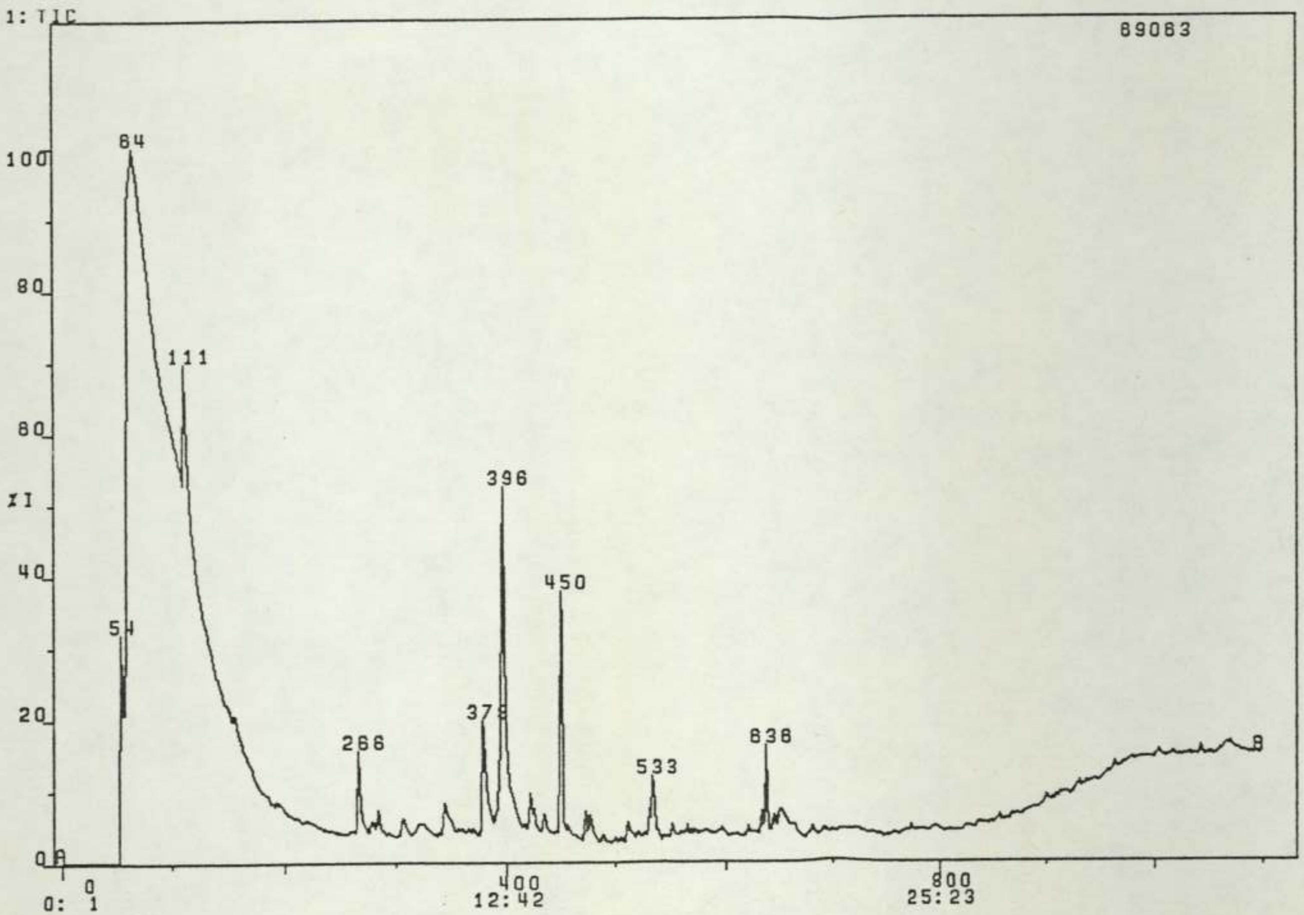


FIGURE 3.11. G.C.M.S. OF DILUTE POLYENE MIXTURE

chromatagram is very complex and shows signs of overloading the chromatagraphic column. The sample was diluted approximately 10 fold and then reanalysed to give the simplified spectrum shown in figure 3.11.

The mass spectrum of the major peaks may now be examined in detail. The solvent peak (scan Nº 64) is followed by a secondary peak at scan Nº 111 whose mass spectrum is characteristic of toluene. (confirmed by library spectrum)

The peak (scan Nº 266) has a high mass of 128 amu but there appears to be no distinctive pattern within the spectrum. The peak (scan Nº 378) has a high mass of 141 amu and within the spectrum peaks at 98, 83, 55 and 43 are indicative of 3-hexene-2-one, which could be an end group of the polyene chain.

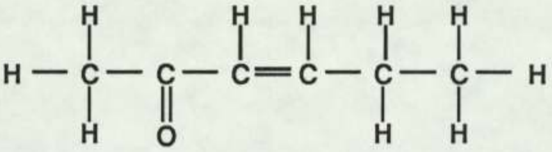
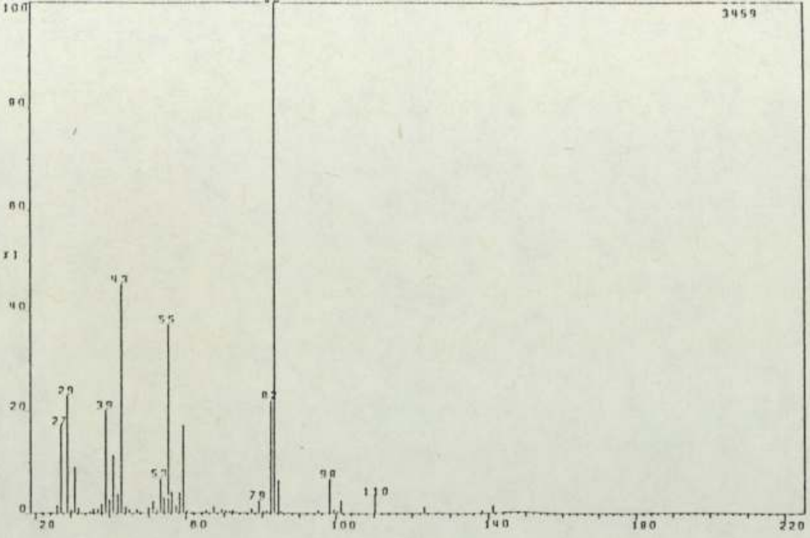
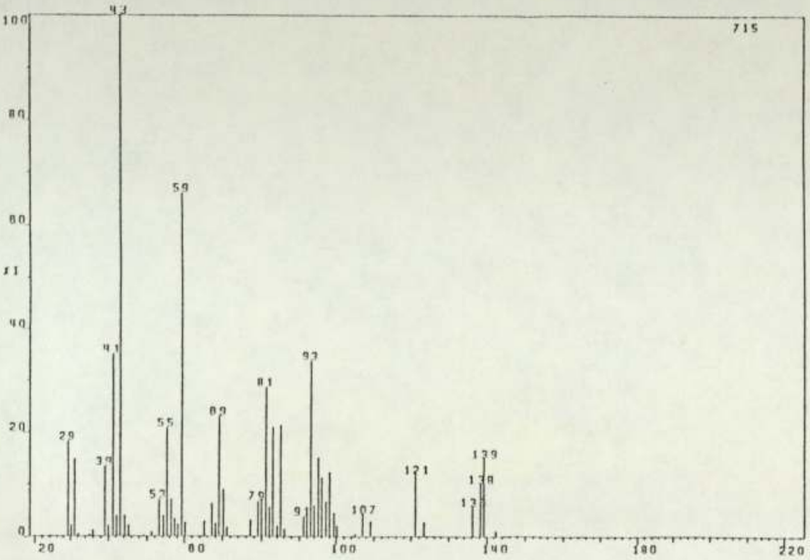


FIGURE 3.12 STRUCTURE OF 3-HEXENE-2-ONE

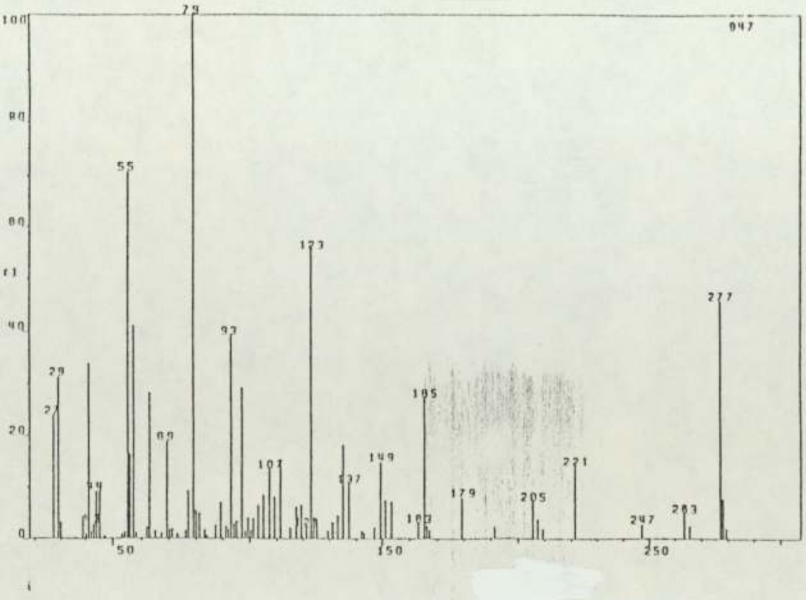
The peak (scan Nº 396) has a high mass of 154 amu and the mass spectrum contains about 60 peaks , the majority of which are below M/e = 100, meaning that there is a very complex fragmentation pattern. The peak centered on scan Nº 450 has a high mass of 160 amu but again there is a very complex fragmentation pattern. This can also be said for the peak at scan Nº 533. (between M/e = 80 and M/e = 100 there is a peak at every value of M/e) The



a) peak number 378



b) peak number 533



c) peak number 636

FIGURE 3.13. MASS SPECTRA OF SELECTED PEAKS IN G.C.M.S.

peak at scan Nº 636 has a high mass of 279 amu meaning that the parent molecule may contain 10 acetylene monomer units. Here again the vast majority of the peaks in the mass spectrum are below 150 amu. Some examples of the very complex mass spectra are shown in figure 3.13.

These complex mass spectra are very difficult to interpret, and additional difficulties arise due to overlapping peaks in the gas chromatagraph. A degree of simplification could possibly be achieved if another technique e.g. G.P.C., were employed before analysis by G.C.-M.S.in order to fractionate the sample into single components or simple mixtures . These individual fractions could be then examined using G C -M S

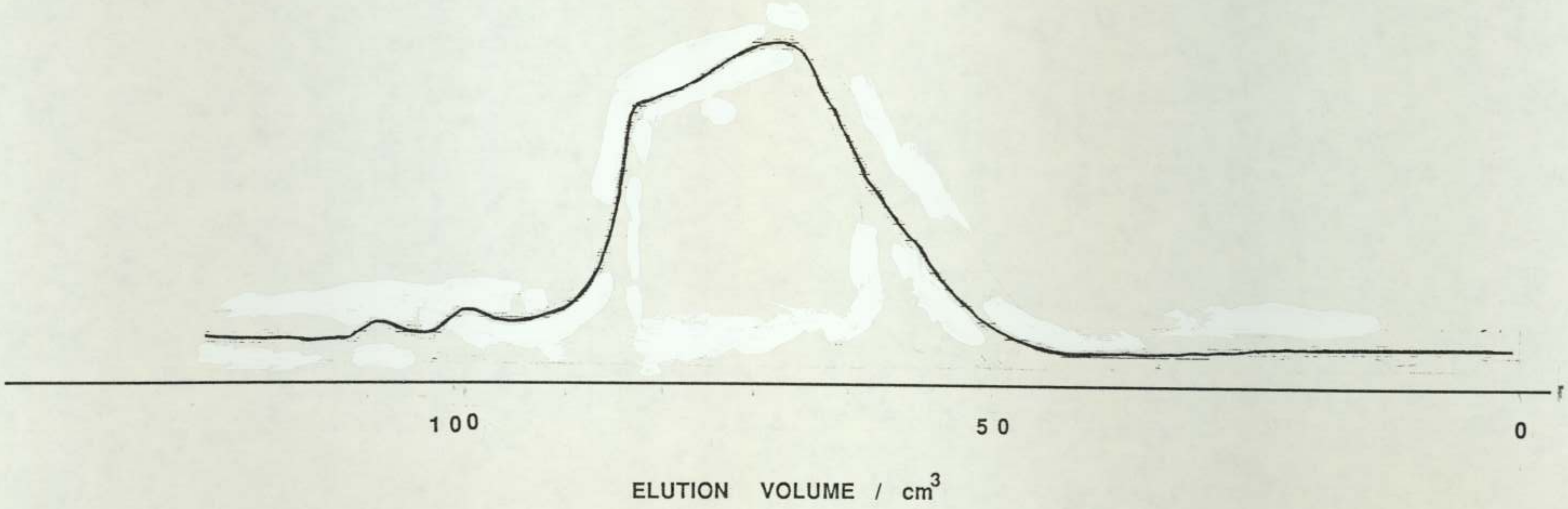
3.3.4 GEL PERMEATION CHROMATOGRAPHY

In an exploratory attempt to separate the polyene mixture into simple fractions gel permeation chromatography was used. The trace shown in figure 3.14 merely indicates that the mixture can be separated into fractions which if collected and analysed by G.C.-M.S. may produce a simpler spectrum. It should also be possible to separate the ethyl benzoate from the polyene which would allow for easier characterisation.

3.4 METATHESIS POLYMERISATION OF ACETYLENE

Since Banks and Bailey[94] first reported their discovery of a catalytic disproportionation reaction many mechanisms have been proposed for the metathetic polymerisation of olefins[95,96]. In olefin metathesis, scission of the

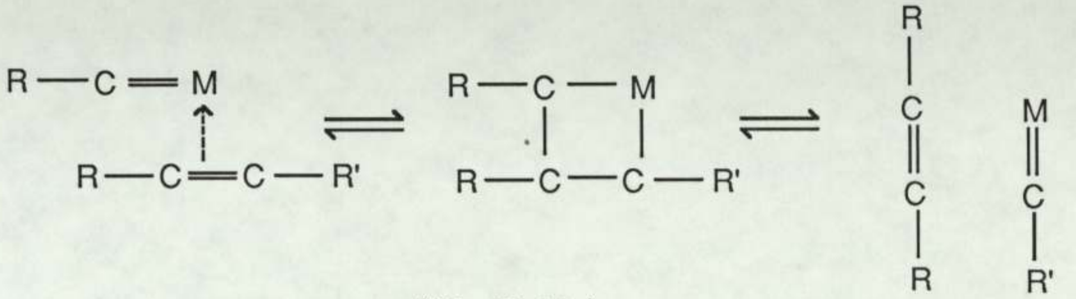
FIGURE 3.14. G.P.C. TRACE OF POLYENE MIXTURE



C=C bond takes place, meaning that an olefin having two substituents R and R', can be converted to two olefins, one with only R groups the other with only R' groups.

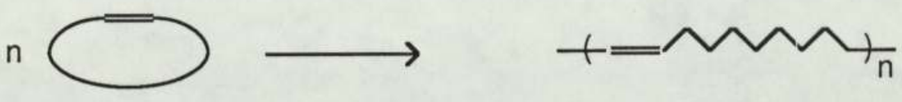
$$2\,R-C=C-R' \rightleftharpoons R-C=C-R + R'-C=C-R'$$

The reaction mechanism shown below is now generally accepted.

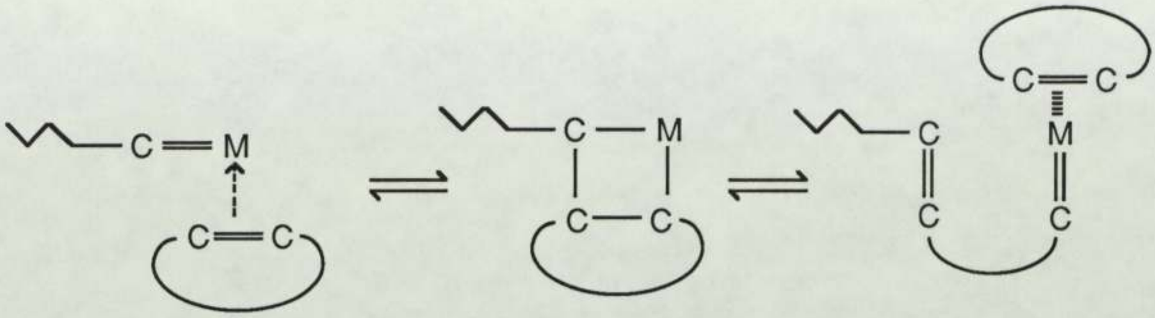


(M = W, Mo)

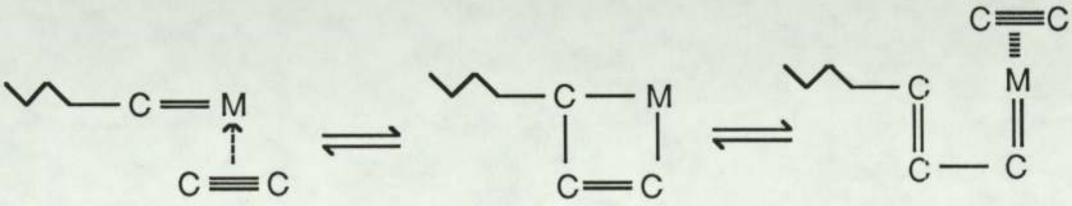
The active species is thought to be a complex having a metal to carbon double bond (C = M) , which is called a metalla carbene[97,98] . When a cyclo-olefin is employed rather than an olefin, then a polymer is obtained.



and a similar reaction mechanism is valid.



The metal carbene mechanism can also be applied to the polymerisation of acetylene.



It is possible to do this because; (i) There are many catalysts which effect both olefin metathesis (including the polymerisation of cyclo-olefins) and the polymerisation of substituted acetylenes (WCl_6 and $MoCl_5$ with co-catalyst)[66,73]. (ii) Acetylene can be regarded as an extreme member of the cyclo-olefins, in other words a two membered ring in which the normal aliphatic chain is replaced by a single carbon to carbon bond. Katz has demonstrated that the polymerisation of various substituted acetylenes is initiated by metal carbenes[99-101] these facts indicate that both olefin metathesis and the polymerisation of acetylenes proceed via the metal carbene mechanism.

3.4.1 YIELD AND ELEMENTAL ANALYSIS OF METATHETICALLY PRODUCED POLYACETYLENE

Table 2. shows the dependence of the yield of polyacetylene on the mole ratio of W / Al in the reactions.

The yields of polymer quoted in table 2 are not by any means high, but this may be a reflection on the nature of the W/Al catalyst system, since in other metathesis reactions this catalyst system is known to be notoriously inefficient and furthermore the active site for polymerisation is occluded in the polymer particle.

TABLE 2. POLYMERISATION OF ACETYLENE USING WCl_6 /$AlEt_3$

$[WCl_6] \times 10^4$ Mol. dm^3	$[AlEt_3] \times 10^4$ Mol. dm^3	Yield gms	Ratio C:H
3.5	6.8	0.18	0.91 : 1
3.5	13.8	0.20	0.83 : 1
3.5	20.3	0.16	0.61 : 1
6.8	6.8	0.26	0.82 : 1

(a) Temp: 20 °C :polymerisation time 48h.

3.4.2. N.M.R. SPECTRUM OF METATHETICALLY PRODUCED POLYACETYLENE

The powdered polyacetylene was examined by solid state nuclear magnetic resonance spectroscopy. Natural abundance ^{13}C NMR spectra have been obtained with cross polarisation and magic angle spinning. A typical solid-state spectrum is shown in figure 3.15 . The major resonance occurs at 136 ppm, upfield from TMS, which is in very good agreement with the values obtained by other workers; Sohma et al 136 ppm[102] and Gibson et al 137.3 ± 0.4 ppm[103] .The chemical shift is believed to be purely of chemical origin and not from paramagnetic effects.

3.4.3 INFRA-RED SPECTRUM OF METATHETICALLY PRODUCED POLYACETYLENE

The infra-red spectrum of a sample of the metathetically produced polyacetylene is shown in figure 3.16. There was great practical difficulty in obtaining any infra-red spectrum of the powdered samples using the KBr disc technique. The spectrum obtained had to be greatly expanded in order to show up the salient features.

In the infra-red spectrum of a trans rich polyacetylene film the characteristic peaks [104] are at 3013 cm^{-1}, which is attributable to C-H stretching and 1292cm^{-1}, which can be asigned to C-H in plane deformation. The most prominent peak

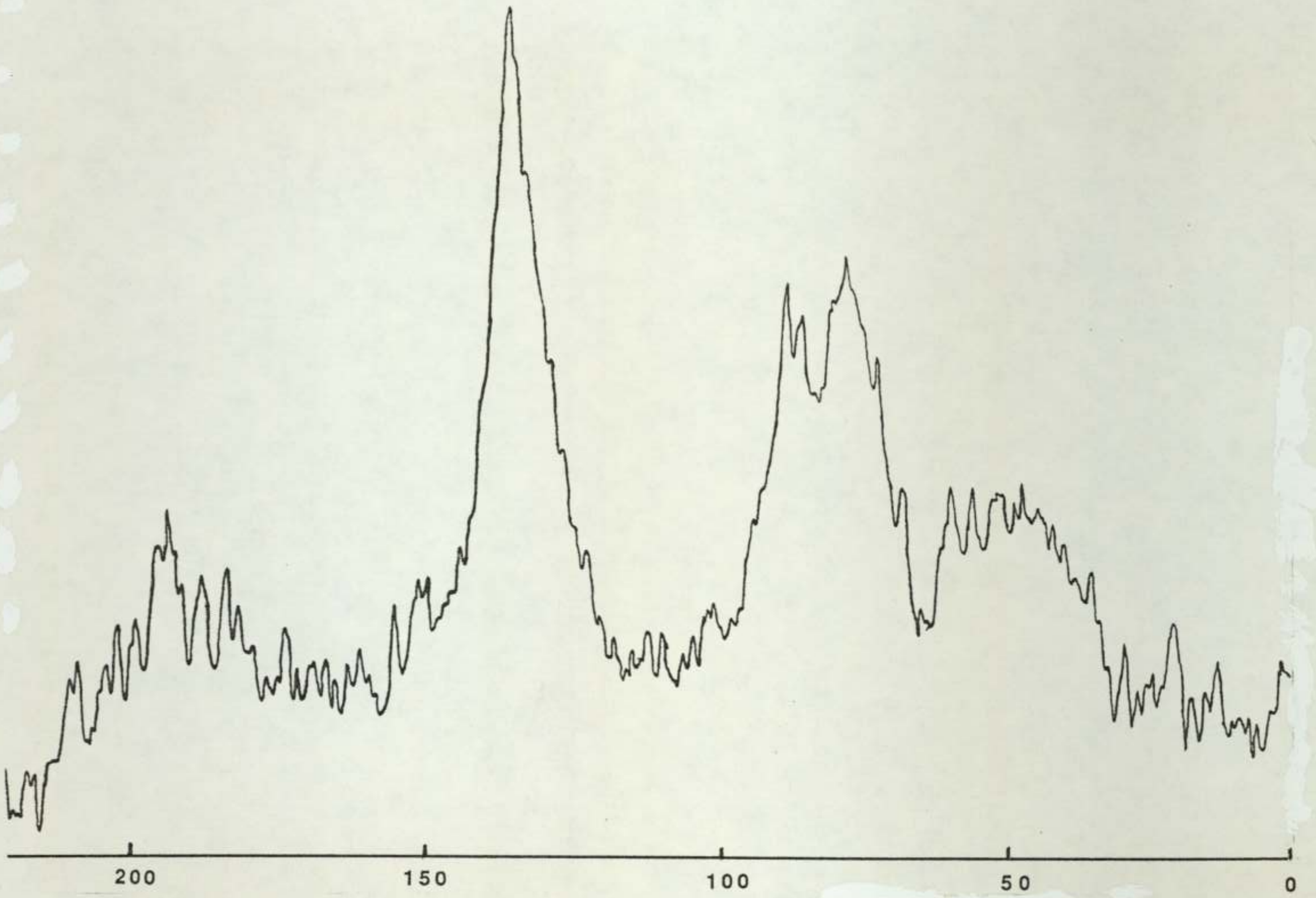


FIGURE 3.15. N.M.R. SPECTRUM OF METATHETICALLY PRODUCED POLYACETYLENE

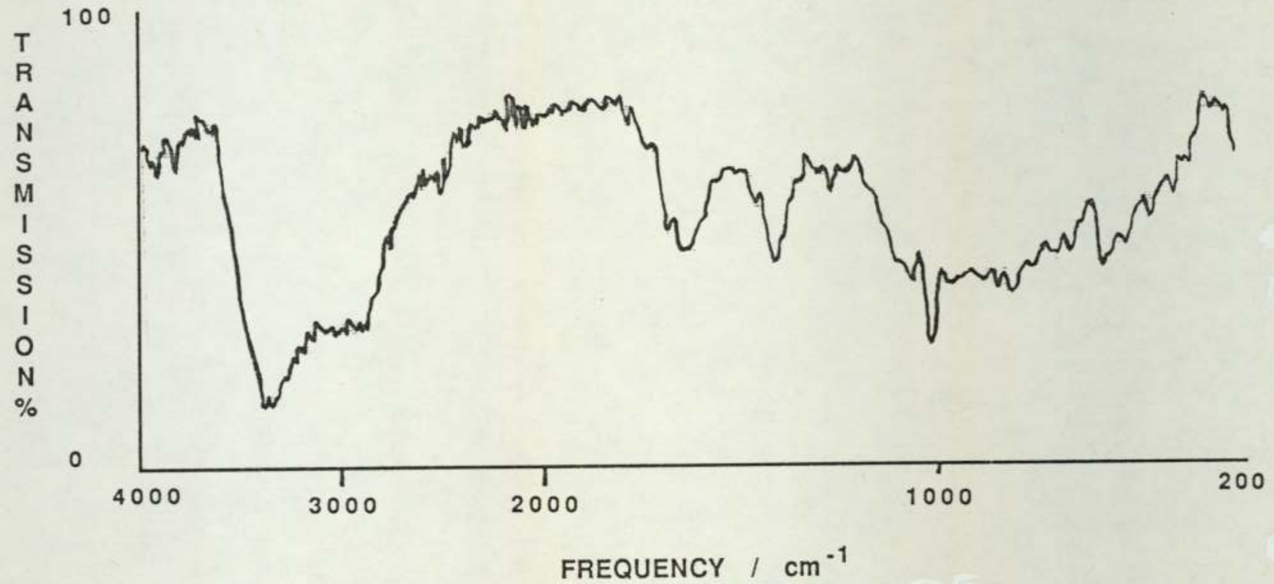


FIGURE 3.16. INFRARED SPECTRUM OF METATHETICALLY PRODUCED POLYACETYLENE

was at 1015 cm^{-1} which is attributable to C-H out of plane deformation in trans polyacetylene. The spectrum in figure 3.16. does show evidence of a peak at 1015 cm^{-1} but the other two weaker absorbances, at 3013 cm^{-1} and 1292cm^{-1}, cannot be detected. The spectrum is very similar to that of a sample of coal[105], which is not surprising since both substances are alike structurally. both contain large amounts of carbon and hydrogen with a large degree of conjugated unsaturation.

3.4.4 SCANNING ELECTRON MICROSCOPY

The crystal structure and morphology of polyacetylene is of great importance since it is directly related to its conductive properties. The general gross morphology is independent of preparative technique, form or cis- trans- content, and is reported to be an extended chain form consisting of an irregular matted web of highly crystalline smooth fibrils forming a loose sponge-like network.[14,106-109]

Plate 1 and 2. show the surface morphology of samples of metathetically prepared polyacetylene. Clearly visible is the fibrillar nature of the polyacetylene. The fibrils appear to have widths ranging from 10 μm to 15μm. These dimensions may be compared to widths of 12μm obtained for polyacetylene made with a WCl_6-Ph_4Sn catalyst.[73]

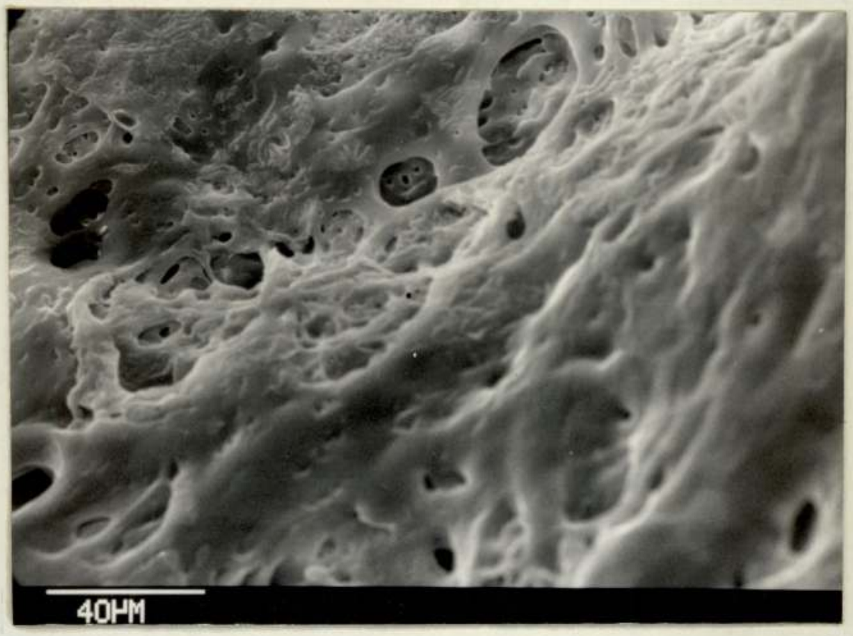


PLATE 1. SURFACE MORPHOLOGY OF METATHETICALLY PREPARED POLYACETYLENE (x 500)

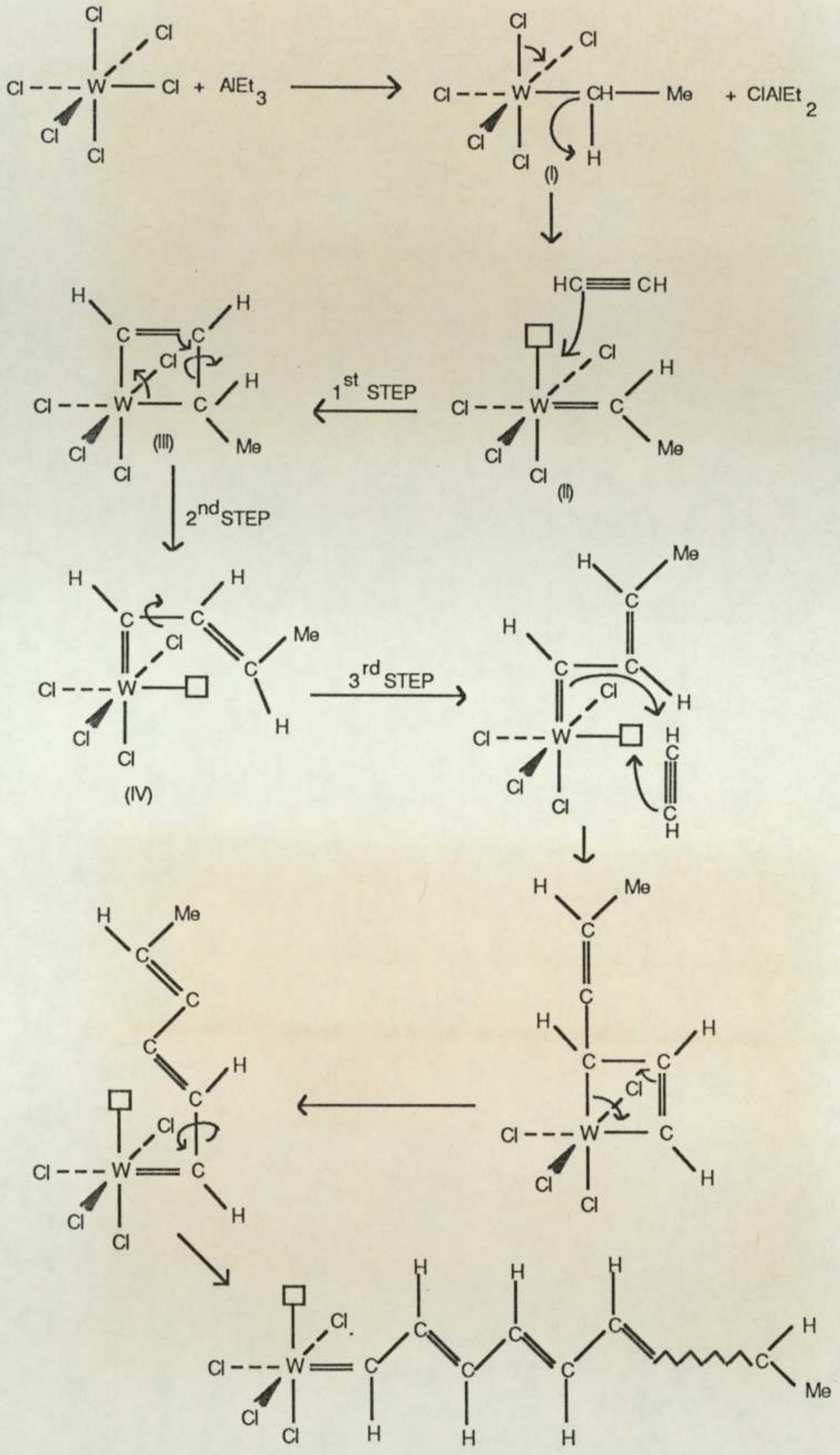
PLATE 2. SURFACE MORPHOLOGY OF METATHETICALLY PREPARED POLYACETYLENE (x 1000)

3.5 MECHANISM OF THE METATHESIS POLYMERISATION OF POLYACETYLENE

It is now possible to try and expand upon the mechanism shown in figure 3.17 and propose a mechanism for the metathesis polymerisation of acetylene, based upon information in the literature[97,98,110-112], using WCl_6-$AlEt_3$ as a catalyst.

The mechanism involves the direct substitution of an ethyl group from the aluminium triethyl for a chlorine atom in the WCl_6. The result is a tungsten alkyl (i) which can easily eliminate HCl to generate an active carbene (ii). This is the species which serves as the initiator for the polymerisation of acetylene. The final product will contain ethane as an end group. The second phase of the mechanism occurs when the metallacyclobutene intermediate (iii) undergoes ring scission, (cleavage of the C_3 to metal linkage) , during which time the C_3 to C_2 bond rotates about its axis to form a coplanar double bond. Katz has postulated [101] that the conformation of the polymer is determined by the direction of this rotation. The bond between C_3 and C_2 should rotate in such a way as to minimise the steric interaction between the coordinating metal and the substituent alkyl chain.In the third phase the bond between C_1 and C_2 rotates about its axis due to the steric interaction between the WCl_4 and the end group, This allows the insertion of a second acetylene molecule into the carbene bond.

FIGURE 3.15 METATHESIS POLYMERISATION OF ACETYLENE



CHAPTER 4

CHARACTERISATION OF POLY(ACETYLENE-CO-STYRENE) COPOLYMERS

4.1 INTRODUCTION

With the development of a new catalyst system for the polymerisation of acetylene it was thought that it may be possible to incorporate this catalyst into a transformation reaction which could be used to produce block copolymers containing polyacetylene segments.

The general procedure for transformation reactions has often been used to synthesise block copolymers, particularly for monomers that cannot be adapted to simple sequential anionic polymerisation. Polymerisation of one monomer (e.g. styrene) by an initial mechanism can lead to a polymer that is capable of being reacted with a simple substrate in order to change the structure of the end group to form part of another catalyst system suitable for the polymerisation of a different monomer (e.g. acetylene).

The most common catalysts for metathesis and ring opening polymerisation of olefins contain WCl_6 as the primary catalyst and a metal alkyl as the co-catalyst [113]. Butyl-lithium may be used in this role[114], as the co-catalyst, but it is by no means a common occurrence. This means that it is feasible that polystyryl-lithium could be used as a cocatalyst [115,116] leading to the formation of block copolymers.

4.2 COMPOSITION OF THE COPOLYMER

The results of a typical polymerisation using polystyryl-lithium and WCl_6 as a metathesis catalyst are shown in Table 3.

TABLE 3. POLYMERISATION OF ACETYLENE WITH A TUNGSTEN HEXACHLORIDE- POLYSTYRYL-LITHIUM CATALYST AT CONSTANT W/Li RATIO (a)

Sample number	Mol. Wt. of the polystyrene block	Time of acetylene polymerisation in h.	C:H ratio
1	3100	20	0.98:1
2	3100	5	1.10:1
3	61000	24	0.83:1
4	61000	160	0.85:1

(a) Temp. 20 °C , W/Li ratio 1:4

The carbon to hydrogen ratios of the copolymers are shown in table 3. The theoretical carbon to hydrogen ratio (C:H ratio) for the corresponding homopolymers is also 1:1. It follows therefore that the copolymer, whatever its block composition, will have a C:H ratio of 1:1. samples 1 and 2 come very close to this ideal value . The deviation of the C:H ratio from 1:1 in samples 3 and 4 is probably due to increased polyacetylene content. Polyacetylene has proved very difficult to analyse by this method because of its reluctance to ash fully which in many cases is further complicated by the presence of catalyst residues in the material, especially when the catalytically active site becomes occluded in the polymer.

Table 4 shows the effect on the carbon to hydrogen ratio of changing the tungsten to lithium ratio in the reaction mixture. The results in the table are inconclusive and this appears to be caused by the difficulty in obtaining total combustion of the polyacetylene segment. More information could be extracted from this part of the study if it was possible to determine the number of active sites in the system at any one W:Li ratio since the changes in the colour of the system with W:Li suggests that a great deal of difference exists between the different ratios.

TABLE 4. POLYMERISATION OF ACETYLENE WITH A TUNGSTEN HEXACHLORIDE POLYSTYRYL-LITHIUM CATALYST AT VARIOUS W/LI RATIOS (b)

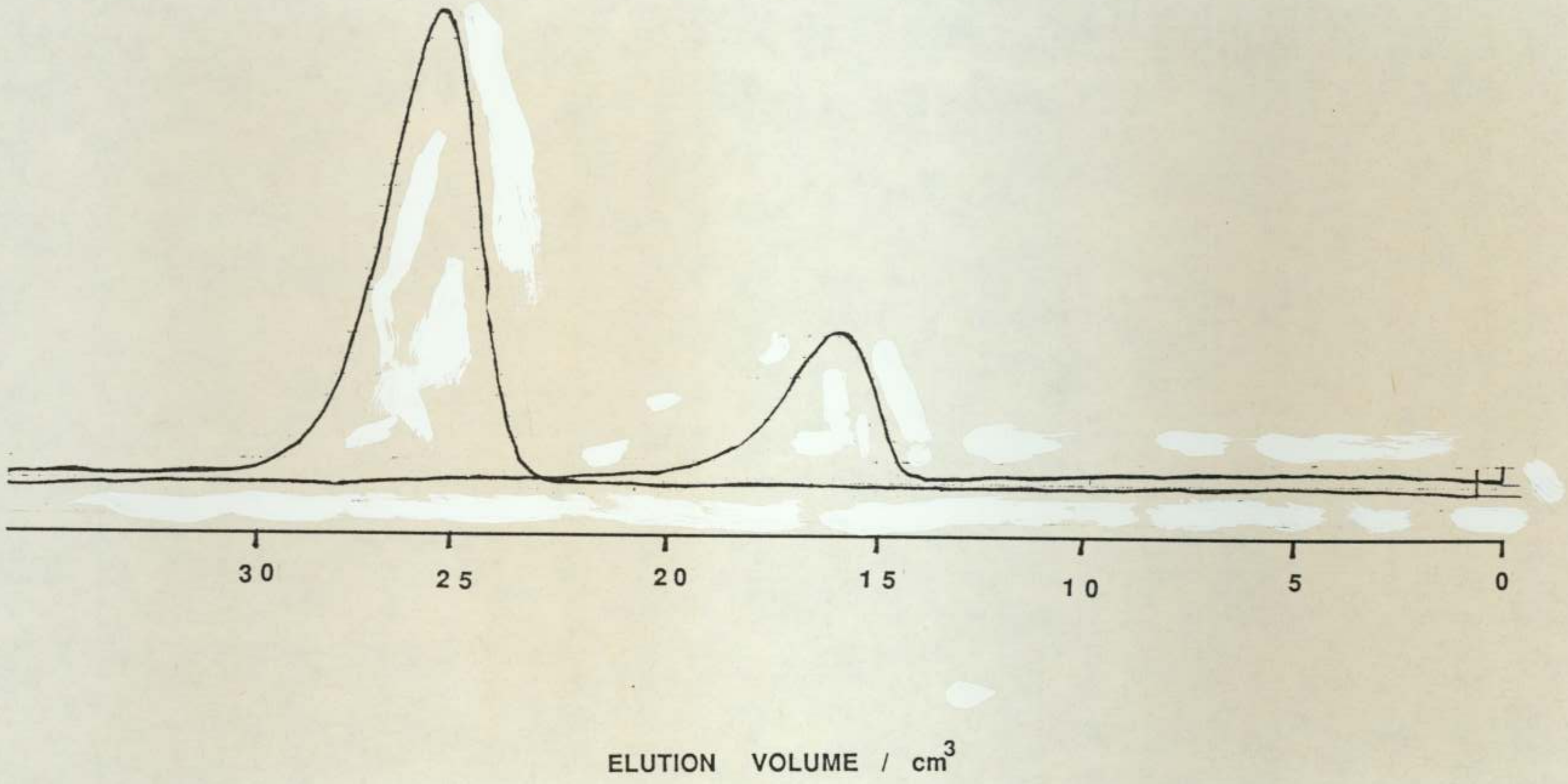
Sample number	W:Li Ratio	Time of acetylene polymerisation in h.	C:H ratio
5	1:4.0	24	0.83:1
6	1:4.0	168	0.94:1
7	1:1.6	1	0.87:1
8	1:1.6	10	0.83:1
9	1:1.6	24	0.87:1
10	1:1.0	24	0.90:1

(b) Temp. 20 °C , Mol. Wt. polystyryl lithium 61000

4.3 GEL PERMEATION CHROMATOGRAPHY

In the early stages of this study an attempt was made to dissolve the dried copolymer in THF. Dissolution was found to be impossible and only suspensions of very fine particles of the copolymer in the solvent were obtained. These particles could be removed from the solvent by filtration and as a consequence these samples could not be analysed using G.P.C. since all the material was removed by the filtering pre-column. These observations are at odds with the fact that during the polymerisation the copolymer appears to be in

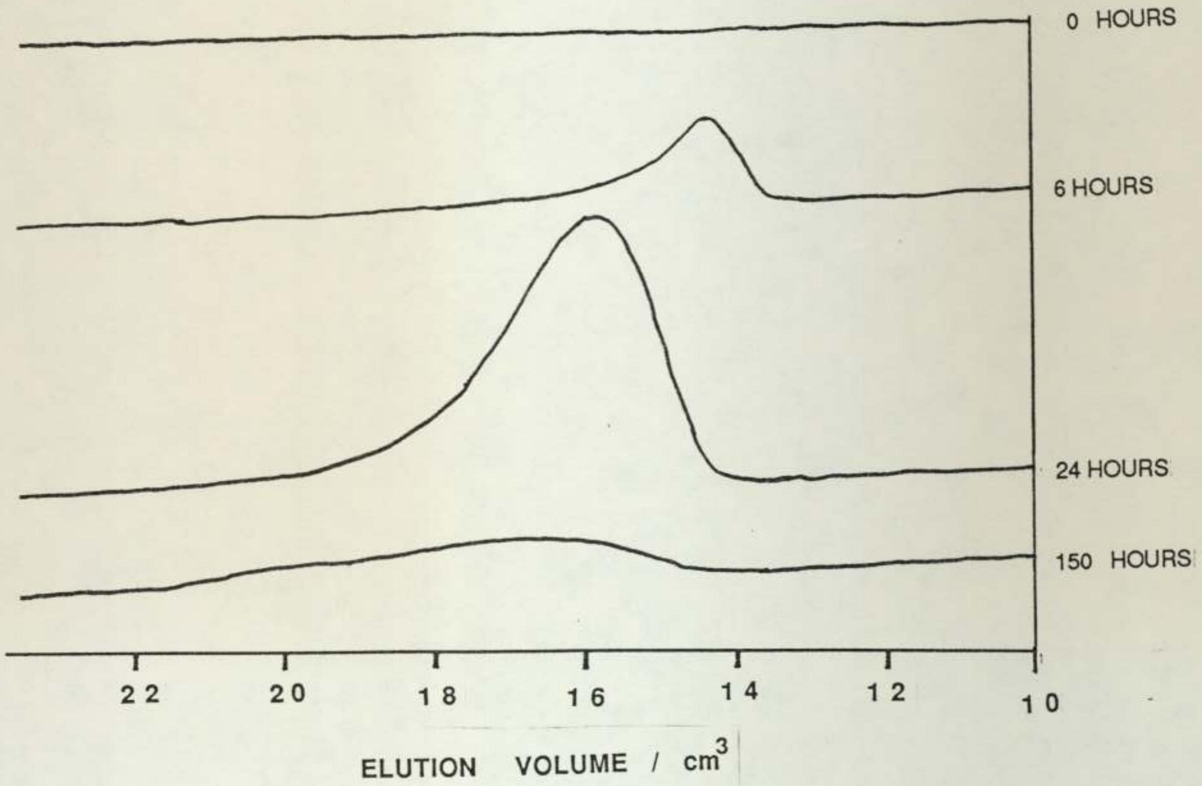
FIGURE 4.1. TYPICAL G.P.C. TRACE OF POLY(STYRENE-CO ACETYLENE)



solution. This was demonstrated by removing a sample of the reaction mixture while the reaction was in progress. The sample, without prior filtration, was introduced directly into the injection loop of the G.P.C. and injected into the system. If the UV detector is set at 430 nm it will detect any polyene type structures in solution. The chromatagraph in figure 4.1 shows that there is an absorbance detected at an elution volume of between 14.5 cm^3 and 17 cm^3 which corresponds to an equivalent polystyrene molecular weight of between 2 and 6 million.

If samples of the reaction mixture are removed at various times during the reaction the series of traces shown in figure 4.2 are obtained. For the starting material of polystyryl-lithium there is no detector response, this is because polystyryl-lithium has no significant absorption at 430 nm. After 6 hours of polymerisation some polyene is detected in solution; this exhibits a retention volume corresponding to a molecular weight of between 2 - 6 million polystyrene equivalents. The situation appears to change little during the first 48 hours of polymerisation. After this time the absorbance seems to indicate a broadening of the molecular weight distribution, which should be expected for a system containing a number of active sites of possibly different structure and activity producing polymers of different molecular weights. The intensity of the absorption also appears to decrease with time and this behaviour can be explained by gradual precipitation of the copolymer in the reaction vessel thereby reducing the concentration of the copolymer in solution. The formation of such apparently high molecular weights from starting materials whose molecular weights were all below 100,000 seems to indicate that there appears to be aggregation of the copolymer molecules in the reaction medium leading to

FIGURE 4.2. EFFECT OF REACTION TIME ON G.P.C. TRACE OF POLY(STYRENE-CO ACETYLENE)



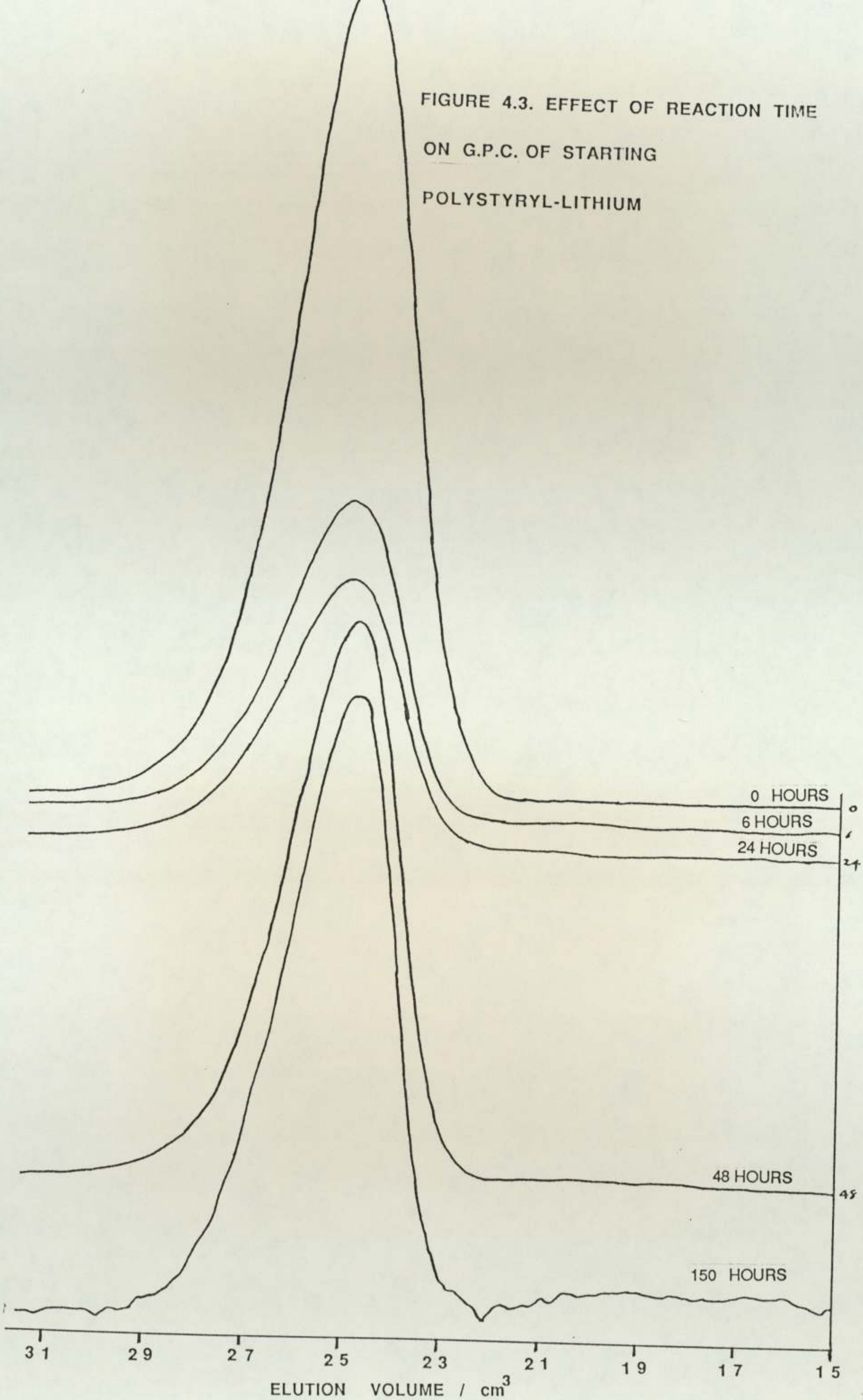


FIGURE 4.3. EFFECT OF REACTION TIME ON G.P.C. OF STARTING POLYSTYRYL-LITHIUM

the illusion of very high molecular weight polymers.

Further evidence of aggregation in solution was provided by photon correlation spectroscopy work carried out at RSRE Malvern.This initial study showed that the average radius of particles in the system was approximately 1 μm with the maximum radius being of the order of 3μm

It has been postulated by Thorn-Csanyi[117] that when polystyryl-lithium or oligostyryl-lithium are used as metathesis catalysts in conjunction with WCl_6, the styrene portion of the catalyst forms dimers and these dimers constitute the major portion of the products produced by this system, even when a comonomer is introduced. The series of G.P.C. traces shown in figure 4.3 show the refractive index detector responses for a number of samples taken from the reaction mixture at various times during the polymerisation. Comparison of the unreacted polystyryl-lithium remaining in the reaction mixture at any time during the reaction with the initial polystyryl-lithium shows that there is no dimerisation and the only product that is detectable using this technique is the copolymer.

4.4 U.V. / VISIBLE SPECTRUM OF THE COPOLYMER

Samples of the reaction mixture were removed from the reaction vessel and the U.V / visible absorption spectrum was produced. Figure 4.4 shows a typical U.V / visible absorption spectrum of a sample of the reaction mixture. It can be seen that there is a large absorption envelope extending from 340 nm to about 700 nm with the maximum absorbance occurring in the range 552 nm to 542 nm. This is consistent with there being short polyene chains in solution. The back

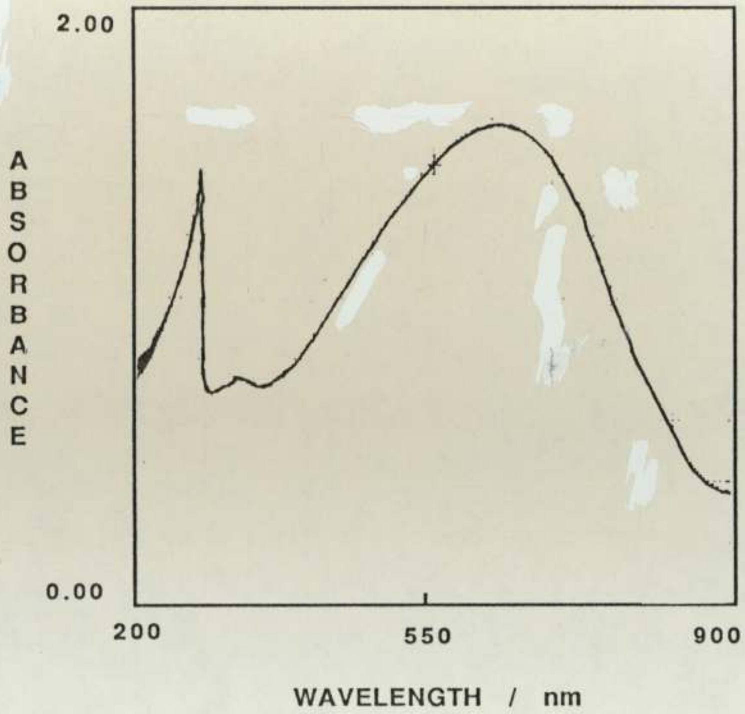


FIGURE 4.4. U.V./VISIBLE SPECTRUM OF POLY(STYRENE-CO ACETYLENE)

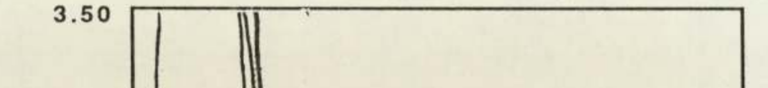


FIGURE 4.5. EFFECT OF REACTION TIME ON U.V./VISIBLE SPECTRUM OF POLY(STYRENE-CO ACETYLENE)

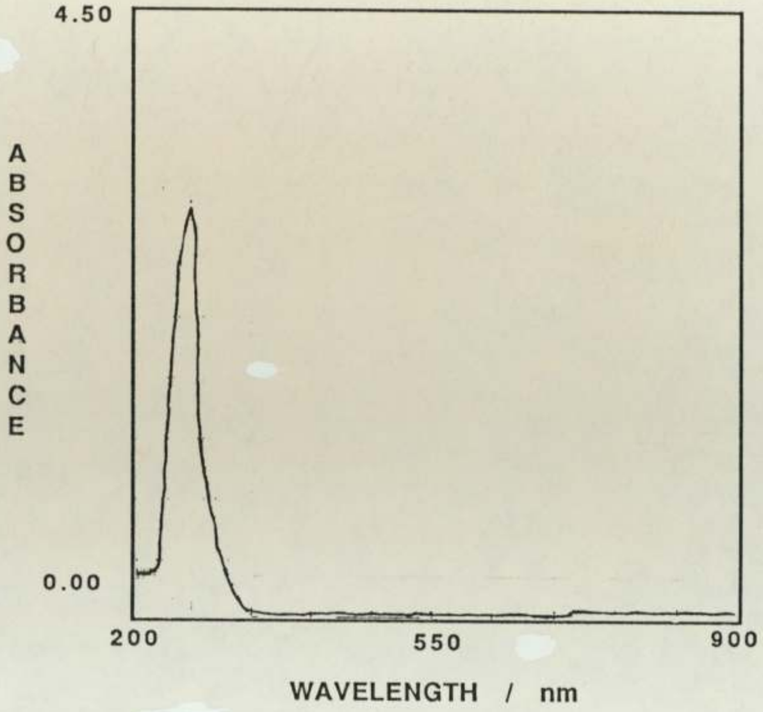


FIGURE 4.6. U.V./VISIBLE SPECTRUM OF WCl_6/POLYSTYRYL-LITHIUM MIXTURE

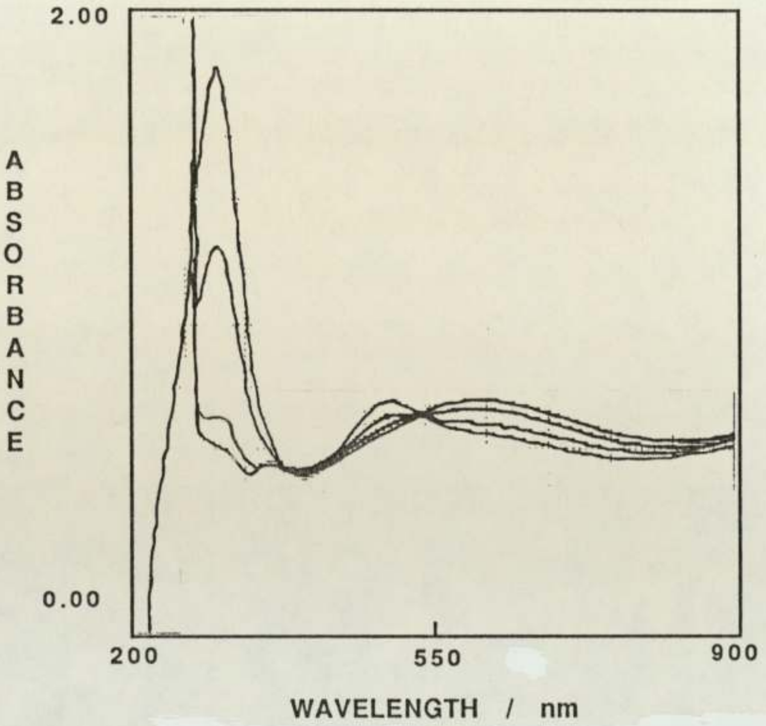


FIGURE 4.7. EFFECT OF IODINE ON THE U.V./VISIBLE SPECTRUM OF POLY(STYRENE-CO ACETYLENE)

ground scan was that of freshly distilled toluene which means that the majority of the polystyrene absorbance is masked; that which remains can be seen as the sharp peak centred on about 270 nm. In order to prevent any precipitation in the solution prior to the spectrum being obtained the sample was subjected to ultrasonics in order to inhibit or prevent aggregation.

Samples (1 cm^3) were removed from the reaction mixture and made up to the mark in the cuvett (ensuring constant dilution). It can be seen in figure 4.5 that the absorption builds up with time. In this case the absorption envelope is not as pronounced because the sample is very much more dilute.

The absorption band that is due solely to the polystyryl-lithium and WCl_6 can be seen in figure 4.6. There is no absorbtion in the region corresponding to that attributed to the polyene chains in solution (*i.e.*, 340nm-700 nm).

In order to attempt to prove that the absorption centered around 600 nm is due to conjugated chains in solution, iodine was added to a dilute sample of the reaction mixture. Figure 4.7 shows the effect of the addition of iodine on the absorption at 600 nm. The absorption is reduced by the addition of iodine and moves to a lower wavelength. This shift in absorption maximum coincides with the appearance of two new absorbances at 500 nm and 300 nm, but these two peaks can be attributed to free iodine in solution. The reduction in the absorption at around 600 nm is believed to be caused by iodine complexing with the conjugated double bonds and breaking up the conjugation.

4.5 INFRA-RED SPECTRUM

The infra-red spectrum shown in figure 4.8 is typical of polystyrene synthesised by normal anionic means and figure 4.9 shows a typical infra-red spectrum of polystyrene / polyacetylene block copolymer synthesised by anionic to metathesis polymerisation at room temperature.

The copolymer spectrum includes the bands at 1015 cm^{-1} and 450 cm^{-1}, which are characteristic of both trans- and cis- polyacetylene. The spectrum of the copolymer contains bands from both polyacetylene and polystyrene. The intensity of the band at 740 cm^{-1} is commonly used[14,104] to evaluate the cis-polyacetylene content in polymers. In this particular case this band overlaps a band from the polystyrene which is attributable to C-H out of plane deformation, and thus makes an estimate of the cis to trans ratio by this technique very difficult.

4.6 NMR. SPECTRUM OF THE COPOLYMER

Although there are several reports in the literature of "soluble polyacetylene" [38,43,46] there have been no reports of solution NMR results of copolymers containing polyene units. The nature of the copolyrners produced in this study makes them ideal candidates for investigation by cross polarisation - magic angle spinning NMR (CP-MAS NMR). Figure 4.10 shows a CP - MAS ^{13}C NMR spectrum of a sample of anionically prepared polystyrene and figure 4.11 shows a CP - MAS ^{13}C NMR spectrum of a sample of the corresponding copolymer.

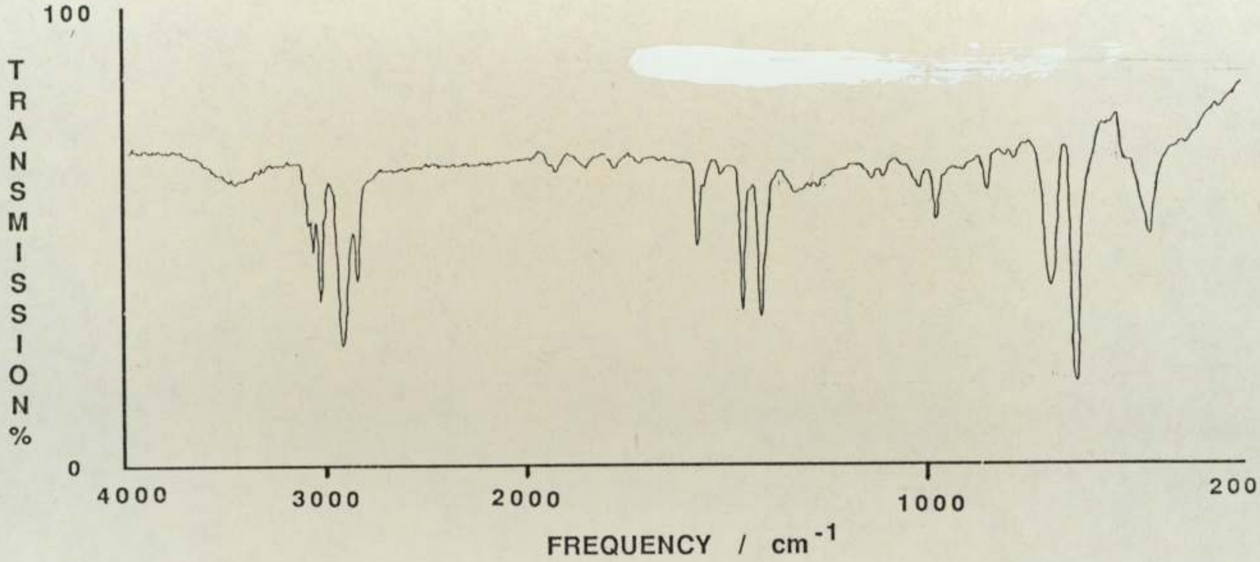


FIGURE 4.8. INFRARED SPECTRUM OF POLYSTYRENE

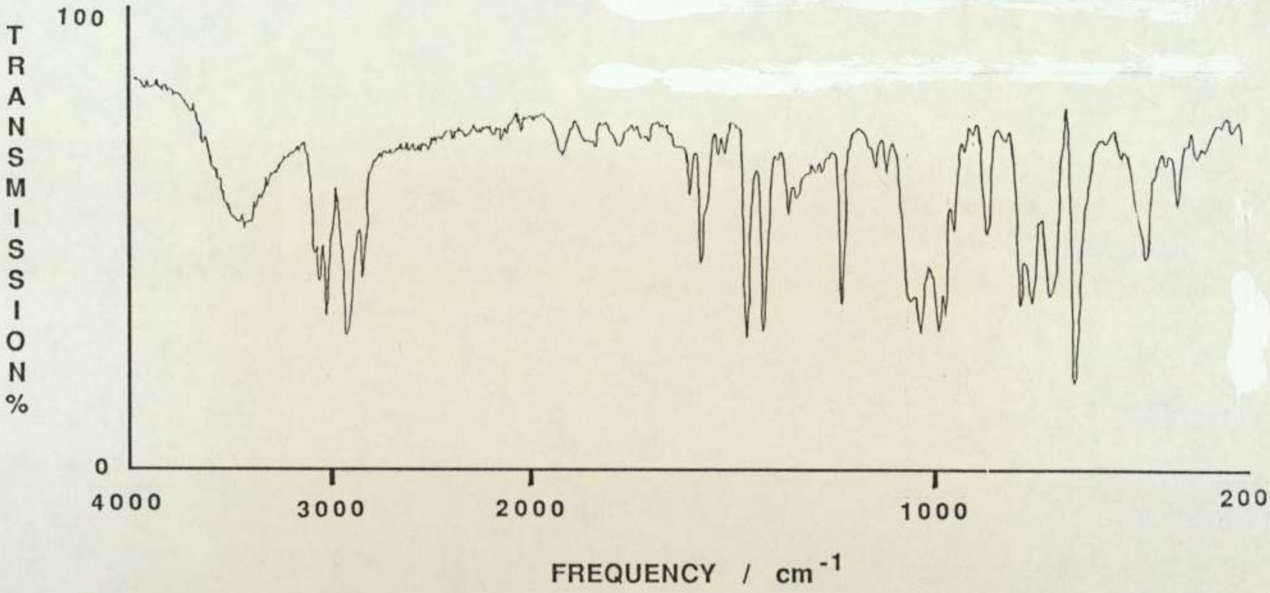


FIGURE 4.9. INFRARED SPECTRUM OF POLY(STYRENE-CO ACETYLENE)

In the earlier section 3.4.2 it was noted that homopolyacetylene had a resonance centered on 136 ppm with respect to (wrt) TMS. The nature of the structure of polystyrene (cyclic conjugation) produces an NMR spectrum very similar to that of polyacetylene. The polystyrene spectrum shows a resonance centred on 126 ppm. Since the band widths are broad this makes any interpretation of the CP-MAS ^{13}C NMR spectrum of the copolymer very difficult. The spectrum shows a resonance centered on 128-129 ppm wrt TMS, *i.e.,* a down field shift from pristine trans- polyacetylene and an upfield shift from polystyrene.

The only other report on the ^{13}C NMR spectrum of polyacetylene copolymers was that of Baker and Bates [22,23] . The narrow NMR line widths of a doublet observed at 129 ppm were used to support their argument that the copolymers were actually present as dissolved rather than suspended species. However in a later correction[118] it was reported that the doublet was in fact due to toluene. When dried samples of 100% ^{13}C-labeled solubilised polyacetylene were examined by magic angle spinning techniques, a signal attributable to trans-polyacetylene was observed at 138 ppm wrt TMS in addition to the spectrum of the carrier polymer. Due to 100% ^{13}C enrichment the trans-polyacetylene resonance was broadened to 1-2 KHz by dipole-dipole interaction of the ^{13}C nuclei. These are the only reported studies on the NMR of copolymers containing polyacetylene segments.

From the NMR spectrum shown in figure 4.11 very little can be deduced about the structure of the copolymer because of the overlap of the resonances. In order to facilitate a more detailed NMR-based investigation into the copolymer

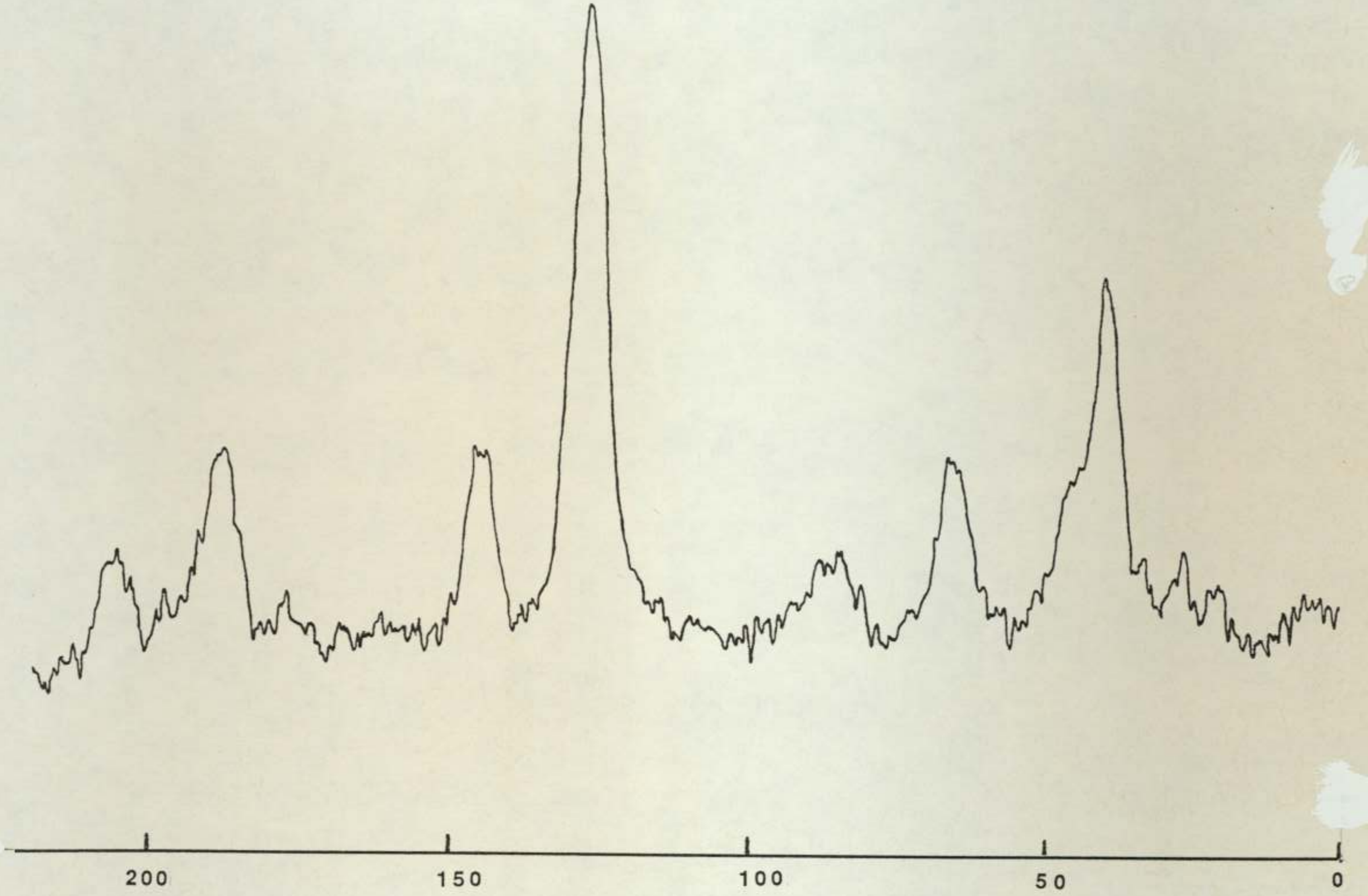


FIGURE 4.10. N.M.R. SPECTRUM OF POLYSTYRENE

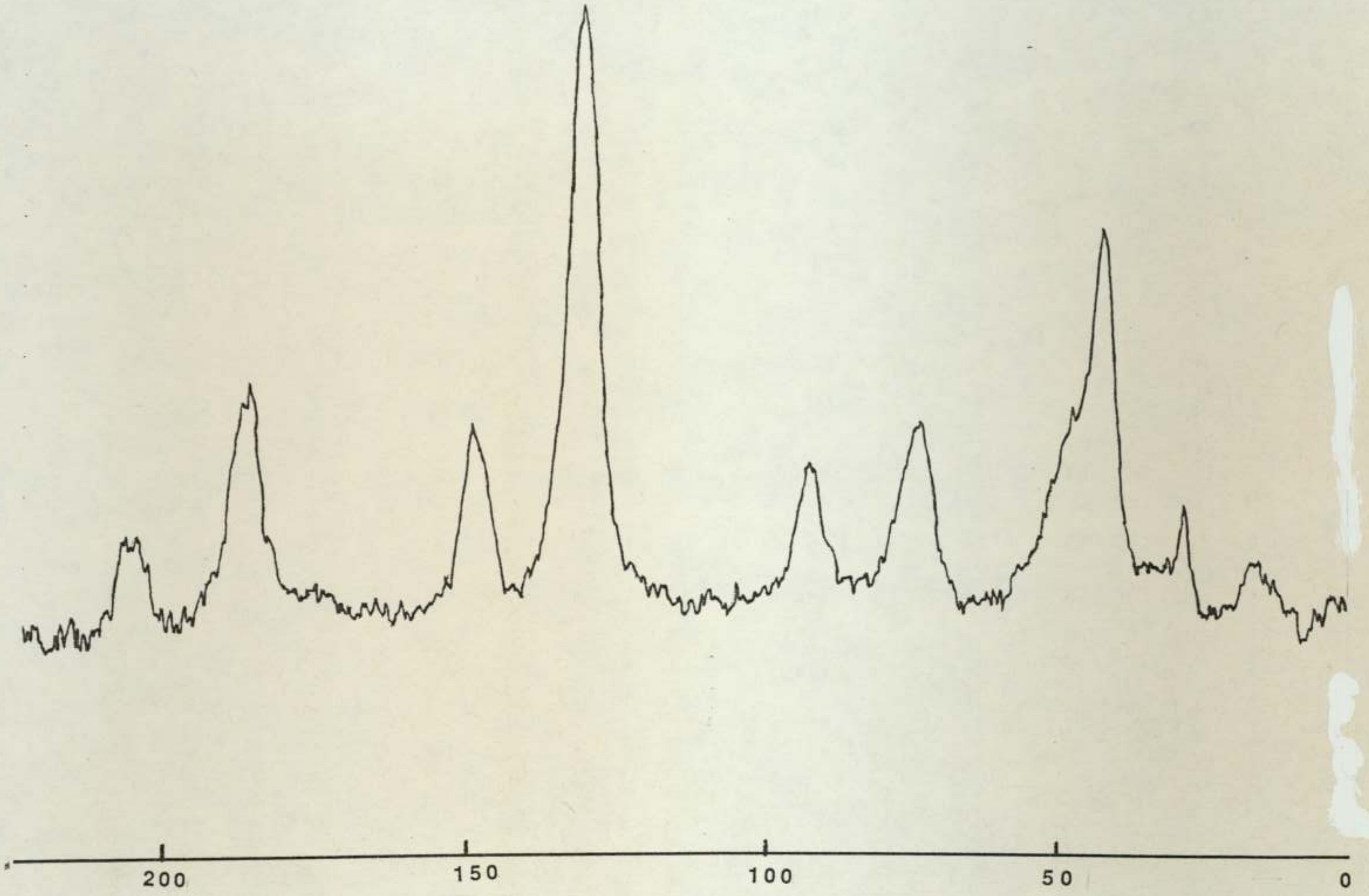


FIGURE 4.11. N.M.R. SPECTRUM OF POLY(STYRENE-CO ACETYLENE)

the polyacetylene block would have to be produced with a 100% ^{13}C enrichment which would make it much easier to observe the polyacetylene resonance.

4.7 SCANNING ELECTRON MICROSCOPY

Plate 3 shows the surface morphology of a sample of dried polystyrene. It shows the glassey morphology that is normally associated with polystyrene which has been precipitated in methanol. Plate 4 shows the surface morphology of a sample of the copolymer. The fibrillar morphology of pure polyacetylene as studied by scanning electron microscopy is altered by the copolymerisation process. It can be seen that the characteristic fibrils of polyacetylene have been affected by the presence of the flexible polystyrene chains in the structure. Coupled with the modification of the fibrillar structure, the void space that exists in pure polyacetylene has almost completely disappeared leading to a homogeneous non-fibrillar structure. The surface of the copolymer is seen to be uneven and pitted with a number of small holes 1-5 μm in diameter. This type of behaviour has also been observed by Aldissi [39,40]

Plates 5, 6, 7 and 8. are a series of photographs showing a particular feature on the surface of a sample of the copolymer. Plates 5 and 6 show the general nature of the feature. The surface of the copolymer appears to "criss-crossed" by areas which appear to be of a different composition and morphology to the remainder of the bulk polymer. A closer look at the edge of the feature (plates 7 and 8) shows that these areas are made up of what appears to be aligned fibrils lying just under the surface of the bulk. This type of morphology has been

PLATE 3. SURFACE MORPHOLOGY OF POLYSTYRENE (X 1000)

PLATE 4. SURFACE MORPHOLOGY OF POLY(ACETYLENE-CO-STYRENE) (X 1000)

PLATE 5. MORPHOLOGY OF A SURFACE FEATURE ON POLY(ACETYLENE-CO-STYRENE) (X 200)

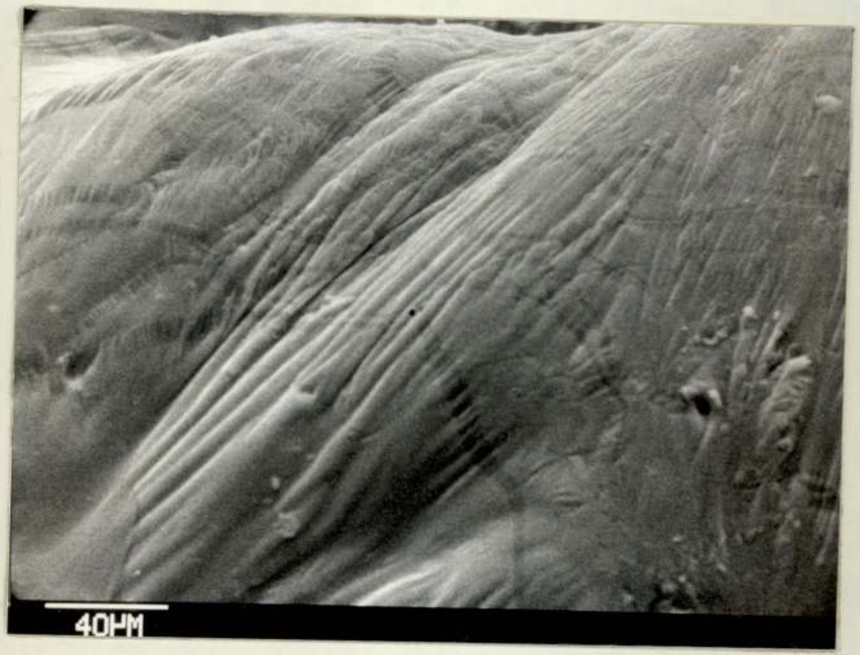


PLATE 6. MORPHOLOGY OF A SURFACE FEATURE ON POLY(ACETYLENE-CO-STYRENE) (X 500)

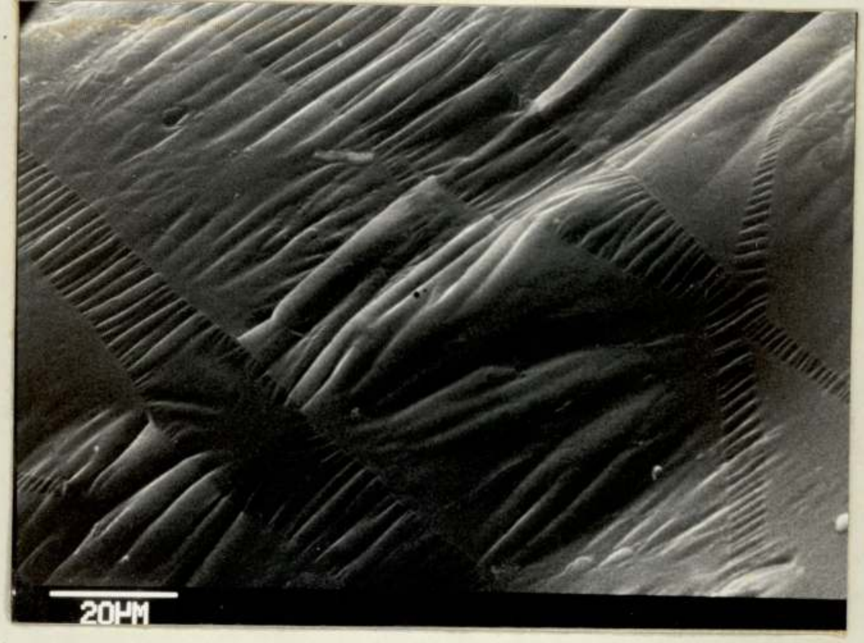


PLATE 7. MORPHOLOGY OF A SURFACE FEATURE ON POLY(ACETYLENE-CO-STYRENE) (X 1000)

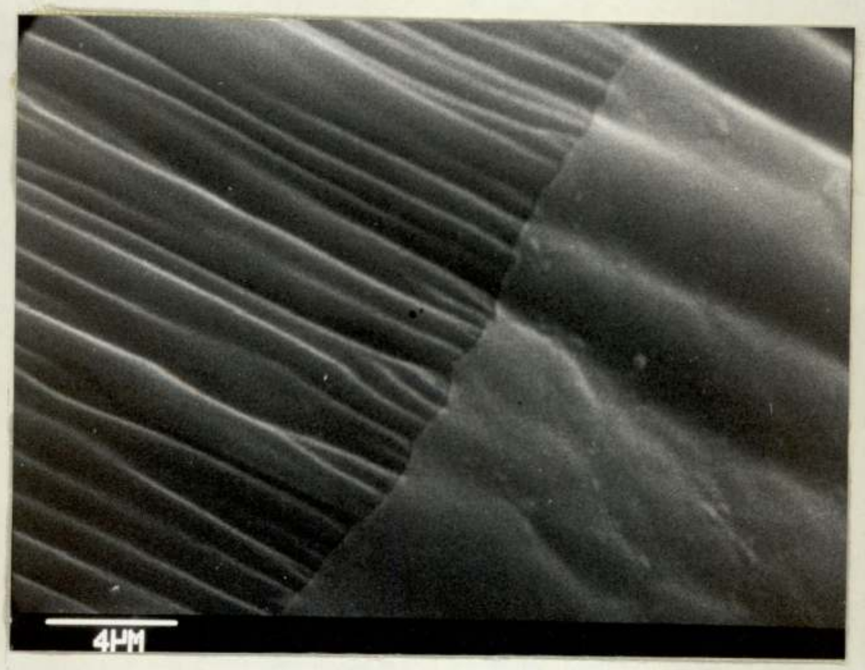


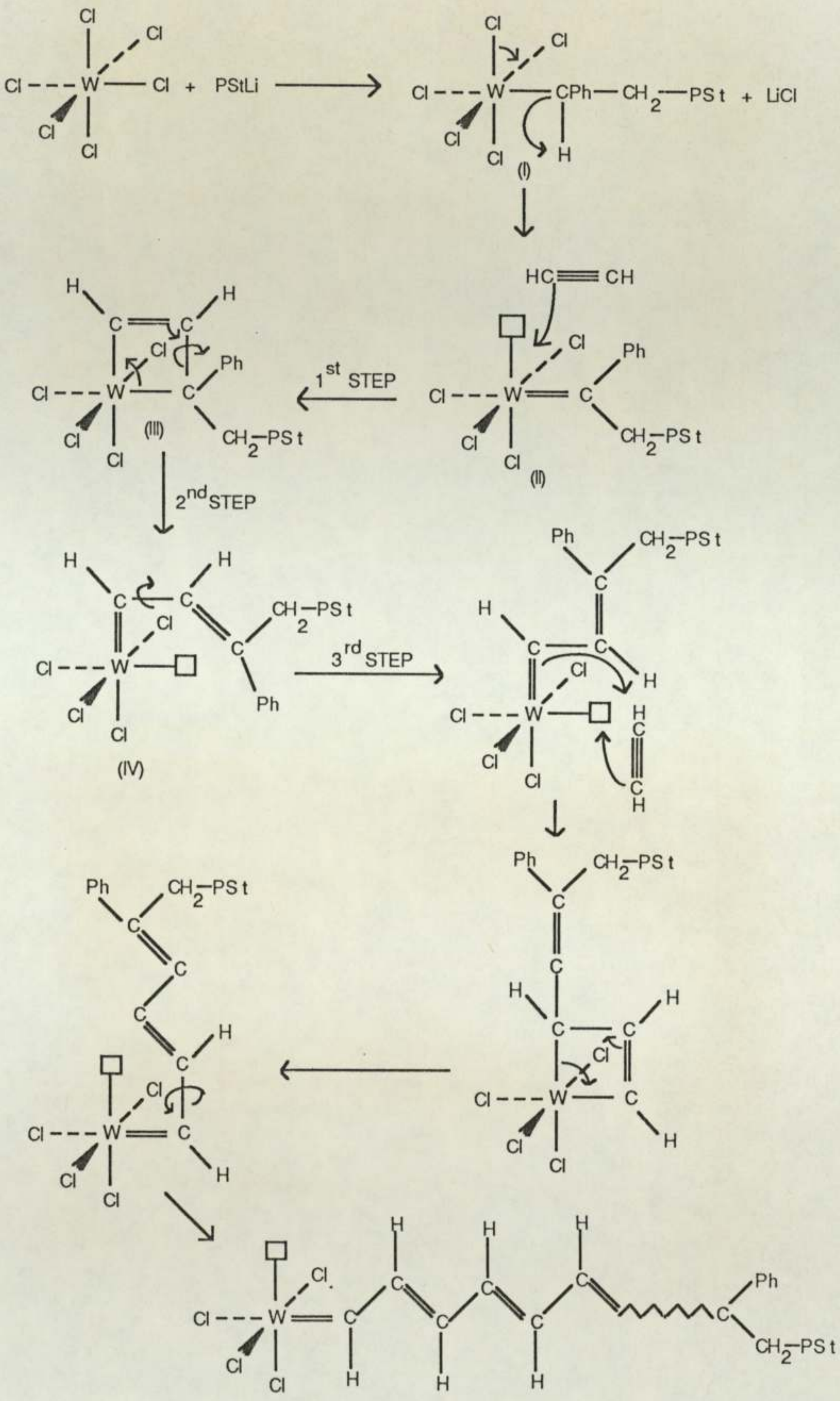
PLATE 8. MORPHOLOGY OF A SURFACE FEATURE ON POLY(ACETYLENE-CO-STYRENE) (X 5000)

observed with homo polyacetylene[119] which has been polymerised directly on to an electron microscope grid. If this is done at high monomer pressure the product is a smooth film . This can be attributed to the fusion of the fibrils by the liberated heat of polymerisation because there is no dilutent to act as a heat sink. This only occurs at the surface however, since when the film is fractured the usual fibrillar morphology is revealed. In the case of the copolymer the fibrils may be revealed, when on drying, the outer layer of the sample shrinks and splits revealing the aggregated polyacetylene fibrils below

4.8 MECHANISM OF COPOLYMER FORMATION

It is now possible to postulate that the mechanism for the production of poly(styrene-co-acetylene) could follow the the mechanism shown in figure 4.12. The mechanism is identical to that shown in figure 3.15 only in this case the "end-group" attached to the polyacetylene block will be a polystyrene block.

FIG. **4.12** FORMATION OF POLY(STYRENE-CO-ACETYLENE)



CHAPTER 5

THEORY ASSOCIATED WITH THE ELECTRICAL CONDUCTIVITY OF POLYMERS

5.1 INTRODUCTION

Polymers with conjugated π-electron backbones display unusual electronic properties such as low energy optical transitions, low ionisation potentials and high electron affinities. The result is a class of polymers which can be oxidised or reduced more easily and more reversibly than conventional polymers. Charge transfer agents (dopants) effect this oxidation or reduction and in doing so convert an insulating polymer to a conducting polymer that may possess near metallic conductivity, in many cases.

Two key developments in the early stages of research on conducting polymers were the discovery [14]of a synthetic route to free standing , high quality films of polyacetylene and the observation that these films could be doped by electron donors or acceptors to conductivity levels of 10^3 $(\Omega \text{ cm})^{-1}$; a value approaching the conductivity of some metals[15] . The conductivity of doped polyacetylene is comparable to the highest values achieved in an organic system, *i.e.,* those of highly ordered organic charge transfer crystals. This comparison is important since it indicates that the high degree of disorder that is present in homopolyacetylene and most other polymers does not necessarily exclude the possibility of good conductivity. Interest in polyacetylene, both theoretical and experimental has generated a prolific amount of data, both in respect of effective dopants[120] and conductivity mechanisms[5]. The theoretical understanding of the electronic structure of the undoped polymer is now at a fairly high level, though there are many areas of disagreement.

Conjugated organic polymers in the pure undoped state are best described as electrical insulators. The conductivity of cis- polyacetylene is detectable at about 10^{-9} $(\Omega\ \mathrm{cm})^{-1}$ and increases to about 10^{-5} $(\Omega\ \mathrm{cm})^{-1}$ on isomerisation to trans-polyacetylene[121] , but these conductivities are not intrinsic to the polymer and instead are attributable to defects and impurities[122]. Other systems such as poly (p-phenylene) and poly (p-phenylene sulphide) have conductivities in their undoped state which are similar to conventional polymers ($< 10^{-12}$ $(\Omega\ \mathrm{cm})^{-1}$)[123-125].

The conductivity, σ, is proportional to the product of the free-carrier concentration, n, and the carrier mobility, μ .

$$\sigma = e\, n\, \mu \qquad \text{equ. 5.1}$$

where e is the unit of electronic charge (1.6×10^{-19} C). The doping of conjugated polymers generates high conductivities primarily by increasing the charge carrier concentration. This is accomplished by oxidation or reduction with electron acceptors or donors, respectively. For example a polymer may be oxidised by the acceptor removing an electron, thereby producing a radical cation (or hole) associated with the chain. If the hole can overcome the coulombic binding energy to the acceptor anion with either thermal energy or, at high dopant concentration, via screening of the coulombic charge of the anions, it moves through the polymer and contributes to the conductivity (providing a path exists to the electrode). Dopant concentrations are extremely high compared to those commonly encountered in doped inorganic semi-conductors, which contain dopant concentrations in the parts per million range.

In some cases the dopant constitutes 50% of the final weight of the conducting polymer composition. Thus the system would be more appropriately described as a conducting charge transfer complex than a doped polymer.

5.2 DOPING

Polyacetylene has been p-doped by a large variety of compounds and n-doped by a smaller number of ions[126]. When either cis or trans polyacetylene films are exposed to the vapour of electron attracting substances (p-type dopants) such as Br_2, I_2 and AsF_5 they become "doped" with these materials and their electrical properties change markedly. With many dopants the conductivity increases rapidly through the semi-conducting regime to the metallic regime. The concentrations of the dopants shown in table 5[126,127] are generally the maximum or close to the maximum value obtainable. Doping can be terminated at any level of lower doping, with the corresponding decrease in conductivity.

Polyacetylene is usually doped by exposing the pristine layers of the polymer to the dopant, which may be either gaseous or dissolved in an inert solvent. Toluene for example, is used as the solvent in the case of $AgClO_4$, iodine as a dopant is usually applied from the gas phase at a pre-defined partial pressure. Arsenic pentafluoride is a very powerful dopant; it is not easy to dope polyacetylene with AsF_5 to a desired concentration and conductivity. This rapid doping tends to result in an inhomogeneously doped material and probably causes the wide range of results reported for the conductivity of polyacetylene doped with AsF_5

Undoubtedly one of the most elegant methods of doping, and one of the simplest, is the electrochemical oxidation of polyacetylene in the presence of a suitable supporting electrolyte[128]. This is an important development since it opens up a method of doping which can introduce, in a readily controlled manner, a wide variety of species which cannot be introduced by conventional chemical means. For this purpose an electrolysis cell was set up in which a polyacetylene film (1 × 3 × 0.01 cm) could be used as the anode in the electrolysis of aqueous 0.5M KI solution. At a potential of 9 volts the initial current was only 1mA because of the low conductivity of the pristine polymer. As the polymer becomes doped its conductivity increased. In 30 minutes the current increased to 43 mA and the polymer was doped to the metallic state with a composition corresponding to $(CHI_{0.07})_x$ and a conductivity, σ_{RT}, equal to 9.7 $(\Omega\ cm)^{-1}$

The reduction of polyacetylene to a conductive derivative can also be accomplished by treating the polymer with alkali metals or, even better, with sodium or potassium naphthalide in THF[129].

$$(CH)_x + 0.21_x Na^+NPth^- \rightarrow [Na_{0.21}(CH)]_x + 0.21xNPth \qquad \text{equ. 5.2}$$

A very large increase in conductivity is observed but it is not as great as that observed with most p-type dopants.

TABLE 5. ELECTRICAL CONDUCTIVITY OF DOPED POLYACETYLENE

	$(\Omega \mathrm{cm})^{-1}$ 25 °C
pure polyacetylene	
cis-$(CH)_x$	1.7×10^{-9}
trans-$(CH)_x$	4.4×10^{-5}
p type polyacetylene	
trans-$[CH(HBr)_{0.04}]_x$ *	7.0×10^{-4}
trans-$[CHCl_{0.02}]_x$ *	1.0×10^{-4}
trans-$[CHBr_{0.23}]_x$	4.0×10^{-1}
cis-$[CH(ICl)_{0.14}]_x$	5.0×10^{1}
cis-$[CHI_{0.3}]_x$	5.5×10^{2}
trans-$[CHI_{0.2}]_x$	1.6×10^{2}
cis-$[CH(IBr)_{0.15}]_x$	4.0×10^{2}
cis-$[CH(AsF_5)_{0.1}]_x$ *	1.2×10^{3}
trans-$[CH(AsF_5)_{0.1}]_x$	4.0×10^{2}
cis-$[CH(SbF_6)_{0.05}]_x$	4.0×10^{2}
cis-$[CH(SbCl_6)_{0.009}]_x$	1.0×10^{-1}
cis-$[CH(BF_2)_{0.09}]_x$	1.0×10^{2}
cis-$[CH(ClO_4)_{0.0645}]_x$	9.7×10^{2}
cis-$[CH(AsF_4)_{0.077}]_x$	2.0×10^{2}
n type polyacetylene	
cis-$[Li_{0.3}(CH)]_x$	2.0×10^{2}
cis-$[Na_{0.21}(CH)]_x$	2.5×10^{1}
cis-$[K_{0.16}(CH)]_x$	5.0×10^{1}
trans-$[Na_{0.28}(CH)]_x$	8.0×10^{1}

Cis or trans refers to the principal isomeric composition before doping
Composition by elemental analysis except * composition by weight uptake

In this study iodine was used as a dopant since it is easy to handle and fairly easy to introduce into the polymers. As a consequence it is this dopant that will be discussed in further detail.

5.3 THE NATURE OF IODINE IN DOPED POLYACETYLENE

Doping is carried out in the vapour of the halogen. Initially [130] the structure of the highly conducting polyacetylene was suggested to be a charge transfer π-complex, a stable intermediate of the electrophilic addition with the formula,

$$[\,(CH=CH)_n - (CH=CH - - - - - I^+)\, I_3^- - -]_m$$

Raman and photoelectron spectroscopic studies of Hsu et al[131] and Raman spectroscopic studies by Lefrant et al[132] indicate, however, that the halogen in doped polyacetylene is in a negatively charged complex ion form with most of the dopant in the form of the tri-iodide, I_3^- , and a smaller part existing as the penta-iodide, I_5^-. The I_3^- ions are situated between close-packed planes of polyacetylene chains forming an intercalated compound[131,133].

Analysis of structural data suggests that the following chemical reactions take place between the polyacetylene and the iodine.

$$2(CH)_x + 3I_2 \rightarrow 2(CH)_x^{+}I_3^{-} \qquad \text{equ 5.3}$$

$$(CH)_x^{+}I_3^{-} + I_2 \rightarrow (CH)_x^{+}I_5^{-} \qquad \text{equ 5.4}$$

The detailed mechanism of these reactions has not yet been determined. The iodine concentration of fully doped polyacetylene is $y = 0.31 - 0.33$. If the iodine in polyacetylene existed totally in the I_3^- form, the degree of charge transfer would be about 0.1. The presence of I_5^- ions lowers the degree of charge transfer. According to the Mossbaüer spectroscopic studies of Kaindle et al[134] at high concentrations of I_2, doped polyacetylene contains predominantly I_5^- ions; thus the charge transfer of the fully doped material may be only 0.07. Further evidence for the presence of I_3^- and I_5^- ions came from the mass spectroscopy study of Allen et al[135]. Trans -polyacetylene was saturated with iodine and a sample injected directly into the source of a mass spectrometer. Two peaks were observed indicating the presence of two iodine species. The results were consistent with the following equilibrium.

$$[CH(I_5^-)_y]_x \leftrightarrow [CH(I_3^-)_y]_x + yxI_2 \qquad \text{equ. 5.5}$$

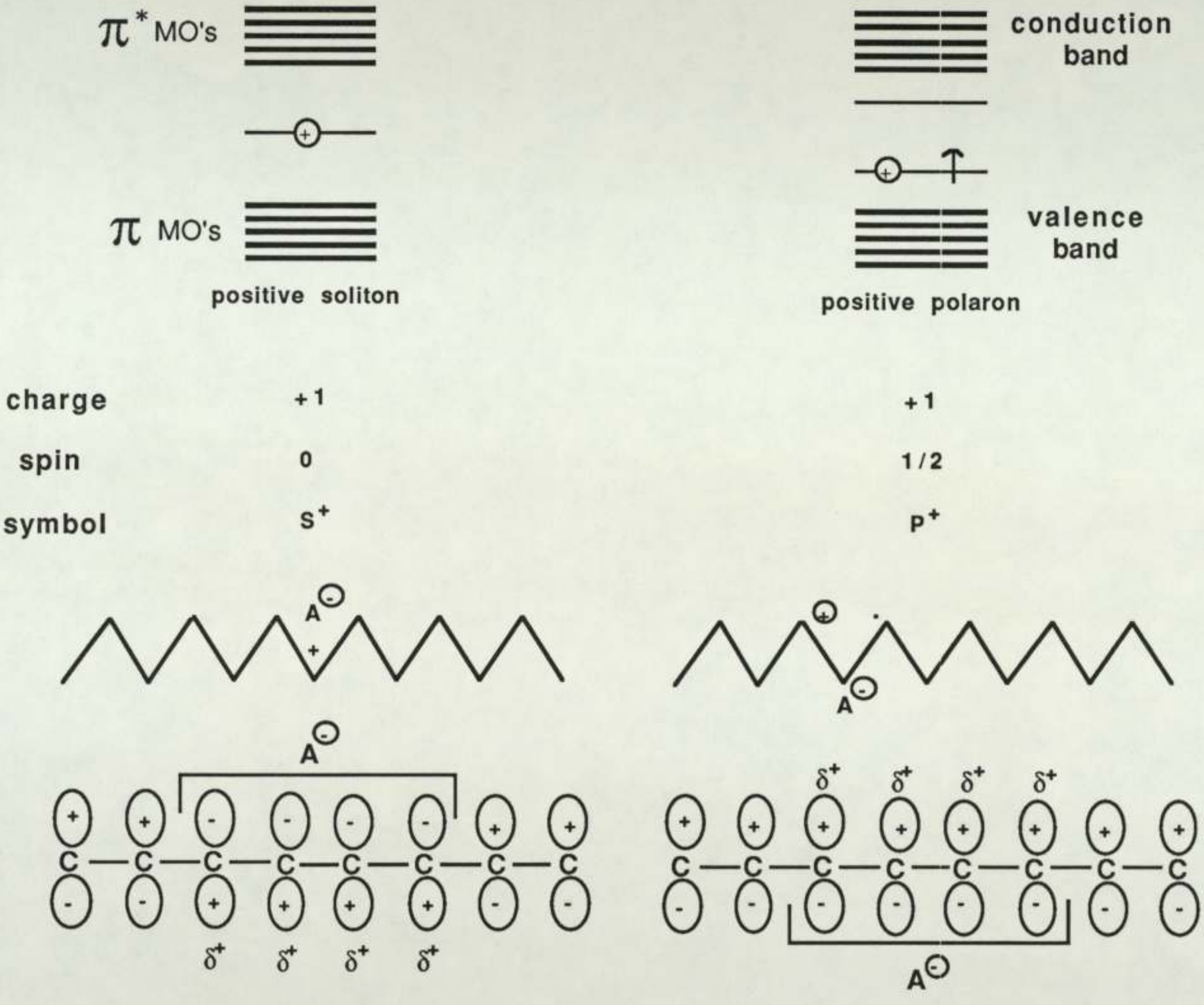
At higher temperatures the I_3^- ions are eliminated. Similar results have been observed with the other halogens.

The decomposition of iodine doped polyacetylene at room temperature takes place very slowly. Pron et al.[136] studied the process at elevated temperatures and reported two processes; a reversible removal of iodine which had been observed [137] even at low temperatures and low pressures and an irreversible chemical reaction resulting in a σ-bonded cross-linked material.

5.4 DOPING MECHANISM

Since iodine is much larger than the repeat unit, its addition is not just a minor perturbation of the structure, as occurs in doped silicon but, a major reorganisation.

FIGURE 5.1 SCHEMATIC DIAGRAM OF A POSITIVE SOLITON AND A POSITIVE POLARON



In the case of the doping of polyacetylene with iodine the doping reaction is that of an oxidising agent with a long chain polyene. As has been seen, this interaction leads to a negative iodine species (I_3^- and I_5^-) and a carbo-cation. Since it has been shown by various experiments (Seebeck effect and Hall effect) that the majority of the charge carriers in doped polyacetylene are in fact positively charged, the nature of the carbo-cation should be investigated. In undoped polyacetylene there is bond alternation. There are therefore two types of bonds between the carbon atoms. When a positive charge is introduced into the chain it is delocalised over a portion of the chain. This means that the electron density over this portion of the chain varies and so the bond order will effectively change causing a shift in the infra-red spectrum.[138,139] The charge carrier is thought to be a delocalised cation known as a positive soliton (negative solitons are produced during n-type doping). The presence of this charge carrier causes a phase inversion in the band alternation. It is thought that p-type doping converts a neutral soliton to a positive soliton.

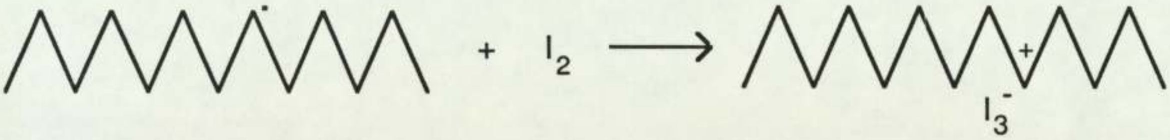


FIGURE 5.2 SOLITON PRODUCTION

A second mechanism of doping is the direct oxidation of polyacetylene by a p-type dopant resulting in the formation of a positive polaron, P^+, or a delocalised radical cation. It comprises a neutral defect and a charge defect.

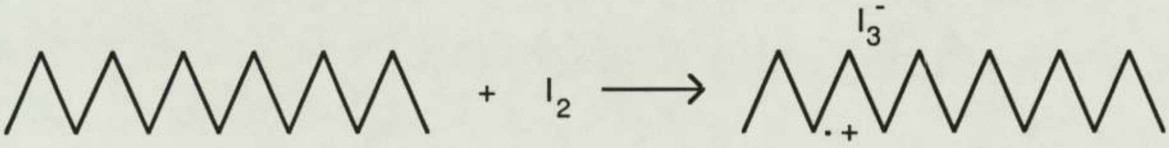


FIGURE 5.3 POLARON PRODUCTION

5.5 MECHANISM OF CONDUCTION IN POLYACETYLENES.

Many studies have been devoted to the electrical properties of polyacetylene but its mechanisms of conduction are still not resolved.

For lightly doped polyacetylene, (concentrations of dopant lower than 0.01 molecules per carbon atom), an inter-soliton electron hopping mechanism has been proposed by Kivelson[140]. This theory leads to predictions that are in good agreement with most experiments. Other models involving hopping among localised states[141] and polaron hopping[142] have also been proposed and applied to ac conductivity.

At higher dopant levels, (concentrations of 0.01-0.04 dopant molecules per carbon atom), the model of variable range hopping among states near the Fermi-level has been used to explain most of the experimental values[143]. Other models involving the diffusion of charged solitons[144] and bipolar inter-chain hopping[145] have been recently proposed.

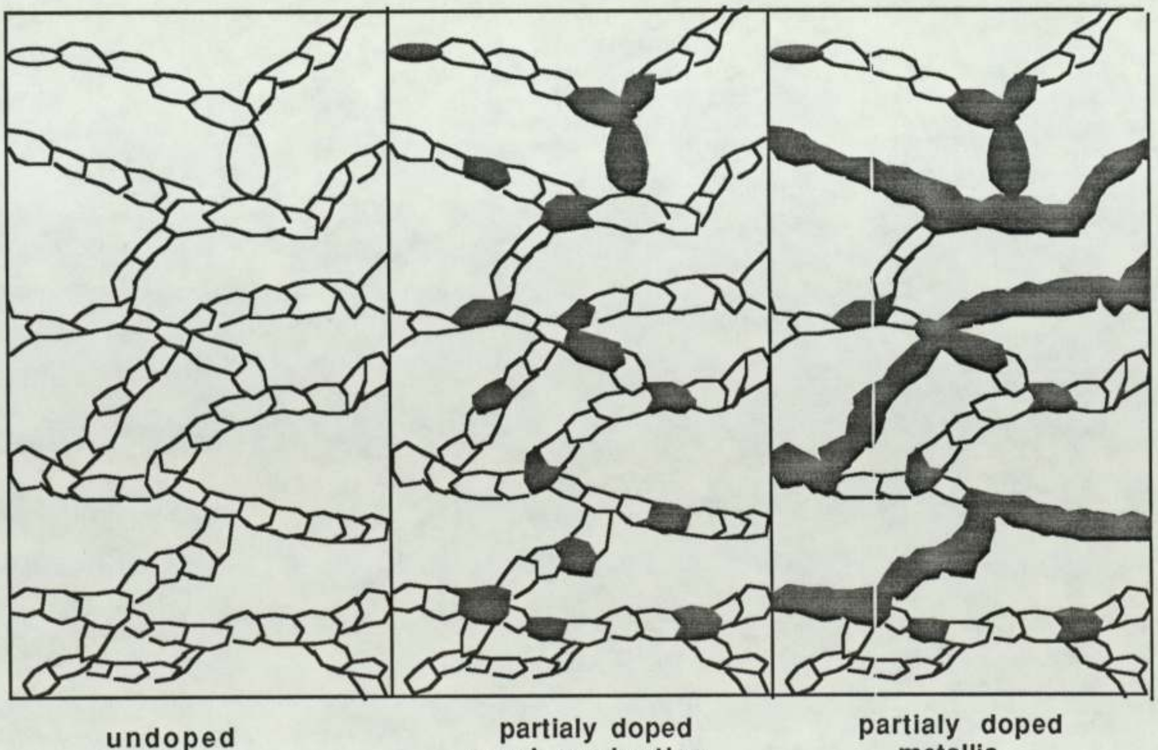
At high dopant concentrations (>0.05 dopant molecules per carbon atom), the density of states increases considerably and the bulk conductivity can be described as that of a disordered metal[146].

The conduction mechanisms mentioned above have one thing in common. They assume that the material is homogeneous and that the localised states, polarons or the charged and neutral solitons are randomly distributed. There is however a conduction mechanism which has been developed from the study of conducting composite materials, *i.e.,* materials consisting of an electrically insulating matrix in which conducting particles are suspended. This theory of conduction appears to be applicable to not only doped polyacetylene but also polyacetylene-polystyrene copolymers.

Polyacetylene because of its fibrillar morphology is not a uniform material, *i.e.,* the fibrils have varying dimensions. Secondly, there is ample evidence to suggest that the doping of polyacetylene can be grossly inhomogeneous, creating tiny metallic domains separated by insulating regions. Even if doping is uniform, the carriers are delocalised and free to move over distances which are very large compared to atomic dimensions.

In the case of polyacetylene-polystyrene block copolymers the conduction of electricity involves a two phase system, only one of which is appreciably conductive.

FIGURE 5.4 PERCOLATION



undoped insulating

partialy doped semi-conducting

partialy doped metallic

The conductivity of such a system is dependent upon the concentration of that phase, *i.e.,* the amount of polyacetylene in the copolymer. For low concentrations of polyacetylene the conducting phases are electrically isolated by the insulating matrix. A d.c. current may flow only if a path exists through the solid and therefore the sample is insulating. As the concentration of the conducting phase increases such a path will be formed and this will manifest itself as a very large increase in the conductivity of the sample. This critical concentration for percolation depends on the structure of the two phase system. With increasing concentration of the conducting phase further pathways would be formed until the equivalent of homopolyacetylene is attained when the saturation value of conductivity is reached.

For both doped polyacetylene and the doped block copolymer of polyacetylene and polystyrene the electrical conductivity may be dominated by carrier transfer between conducting segments rather than hopping between localised states. The premise is that the carriers tend to tunnel between conducting regions at the points of their closest approach; the relevant tunnel junctions are small in size and are subject to thermally activated voltage fluctuations across the junction. The voltage fluctuations modulate the potential barrier and introduce a temperature dependence to the tunneling probability. This fluctuation-induced tunneling mechanism has been developed by Sheng and coworkers[147-149].

5.6 FLUCTUATION INDUCED TUNNELING

When the concentration of polyacetylene or doped regions of the polymer is sufficiently low there are no continuous conduction pathways across the sample and conduction is dominated by electron tunneling across small barriers separating large conducting regions. Tunneling can be regarded essentially as taking place between two bulk conductors.

If it is assumed that the conducting domains are irregular in shape, the tunneling takes place in the area of closest approach of these domains. Such a tunnel junction can be approximated to a parallel-plate capacitor with area A, separation w, and capacitance $C = A/4\pi w$. C is only a small part of the total capacitance C_o between the two large conducting segments. A direct consequence of the large surface area of the conducting regions is that C_o is large and therefore the charging energy, $e^2/2C_o$, required to transfer an electron, of charge e, from one neutral conducting region to its neighbour is negligible.

Owing to the random thermal motion of the electrons in the conducting region, there can be a transient excess or deficit of charges on the tunnel junction surfaces, resulting in voltage fluctuations across the junction. The average square of the thermal fluctuation voltage across the junction $\langle V^2{}_T\rangle$ is;

$$\langle V_T^2 \rangle = \frac{k_B T}{C} \qquad \text{equ. } 5.7$$

Where k_B is the Boltzman constant and T the temperature.

The tunneling mechanism gives a field and fluctuation-induced conductivity.

$$\sigma = \sigma_o \exp\left[-\frac{T_1}{T}(\varepsilon^*)^2 - \frac{T_1}{T_o}\varphi(\varepsilon^*) \right] \qquad \text{equ. } 5.8$$

Where the parameter T_1 represents the temperature below which the conductivity becomes temperature independent, (corresponding to a pure elastic tunneling mechanism) and is given by,

$$T_1 = \frac{a\varepsilon_0^2}{k_B} \qquad \text{equ. } 5.9$$

Where a is a measure of the junction volume.

T_o is the temperature above which the conduction mechanism across the junctions is purely thermally activated and is given by,

$$T_0 = \frac{T_1}{2\chi w\, \xi(0)} \qquad \text{equ. } 5.10$$

The function $\varphi(\varepsilon^*)$ where ε^* is the reduced electric field, a temperature dependent quantity, depending in turn on λ, a dimensionless parameter that governs the shape of the potential energy barrier lying between the two conducting regions. Thus,

$$\lambda = \frac{0.795e^2}{4w\ KV_0} \qquad \text{equ } 5.11$$

where e is the electronic charge and K is the dielectric constant of the insulating barrier.

In equations 5.9 and 5.10 ε_0 is the electric field when the maximum potential is equal to zero.

The efficiency of the tunneling process is described by χ the tunneling constant

$$\chi = \left(\frac{4\pi m V_0}{h^2}\right)^{0.5} \qquad \text{equ. } 5.12$$

In terms of, m the effective mass of the carrier and V_0 the magnitude of the potential energy barrier.

If the intrinsic conductivity, σ_j, of the conducting regions is attributable to the electrical transport in a three-dimensional disordered material is;

$$\sigma_j = \sigma_{jo}\exp[-BT^{-0.25}] \qquad \text{equ. } 5.13$$

then the total resistivity R(T) can be written as the sum of the resistance of the bulk conducting region, $R_i(T)$ and the tunneling resistance, $R_j(T)$,

$$R(T) = R_i(T) + R_j(T) \qquad \text{equ. } 5.14$$

At sufficiently low fields and at concentrations of metallic domains below the percolation threshold, the conductivity is dominated by the probability of carrier tunneling between pairs of oppositely charged grains formed by the excitation of a pair of neutral grains. Equation 5.8 may be expressed in a simpler functional form, with the temperature dependence of the conductivity having the form,

$$\sigma \approx \exp[-AT^{-0.5}] \qquad \text{equ. 5.15}$$

At high fields non-Ohmic behaviour is expected for the model.

For highly disordered metallic domains with concentrations above the percolation threshold the conductivity follows a temperature dependence similar to that predicted by the theory of variable range hopping in three dimensions, namely

$$\sigma \approx \exp[-AT^{-0.25}] \qquad \text{equ. 5.16}$$

Even if the concentration of metallic domains is above the percolation threshold, there may still be potential energy barriers between the metallic domains, and as a consequence conduction requires tunneling. Thermal fluctuations can modulate the potential energy barrier to facilitate electron transport and thereby result in a temperature dependence of the form.

$$\sigma = \sigma_0 \exp\left(\frac{-T_1}{T+T_0}\right) \qquad \text{equ. 5.17}$$

At high temperatures, since T_0 is very small, this can be simplified to the form,

$$\sigma \approx \exp[-DT^{-1}] \qquad \text{equ. 5.18}$$

However, since the percolation threshold is dependent on the distribution of the sizes and shapes of the metallic grains it is therefore not suprising that it is difficult to predict a simple relationship between dopant concentration and conductivity.

For the fluctuation-induced tunneling conduction in disordered materials it is predicted that the conductivity will show a dependence on the field resulting from the localisation of a voltage drop across the highly resistive barrier of the insulating matrix. Another consequence of the model is that the frequency dependence of the conductivity, resulting from the capacitive coupling between the highly conductive regions, has the form $\sigma \approx \omega^k$. In addition it has been predicted[150] that the onset of frequency dependence occurs at approximately 100Hz. Overall it has been predicted that the dependence of the conductivity on the electric field should follow the exponential form given in equation 5.8.

CHAPTER 6

ELECTRICAL CONDUCTIVITY OF POLY(STYRENE-CO-ACETYLENE)

6.1 INTRODUCTION

The purpose of this chapter is to present the results obtained from measuring the electrical conductivity of the various polymers produced in this study. The dependency of the measured conductivity on doping , pressure, frequency and temperature is discussed. It is important to realise at this stage that the samples used in this study were all in the powdered form and as a consequence it is very difficult to compare the results obtained in this study with those obtained using different measurement techniques or different sample forms. Most of the information contained within the literature has been obtained using the "four probe technique", where the sample is in the form of a very thin film which has been produced by interfacial polymerisation.

The errors involved in the measurements in this chapter are small. Both the temperature and pressure are tightly controlled as previously described in chapter two. The parallel resistance of the sample is measured ten times and the average automatically taken. Errors are introduced by the inhomogeneity of the copolymer. To overcome this up to four samples of each polymer were studied.

6.2 EFFECT OF DOPING ON CONDUCTIVITY

In this section the effect on the conductivity of doping the polymers with iodine will be discussed.

6.2.1 METATHETICALLY PREPARED POLYACETYLENE

TABLE 6. AC CONDUCTIVITY OF DOPED AND UNDOPED METATHETICALLY PRODUCED POLYACETYLENE, 25°C, 10 KHz

UNDOPED	DOPED
$(2.74 \pm 0.5) \times 10^{-8}$	$(1.12 \pm 0.5) \times 10^{-5}$

The conductivity of both doped and undoped polyacetylene are shown in table 6. The samples were exposed to iodine vapour for two weeks at room temperature and atmospheric pressure.It can be said that the samples have attained their maximum doping level under those conditions.

By measuring the gain in weight due to the uptake of iodine the stoichiometric formula of the complex was determined to be $[CHI_{0.09}]_x$. The addition of iodine to the polyacetylene causes an increase in conductivity of about three orders of magnitude. This compares very well with other preparations of polyacetylene which have been shown to have conductivities in the range 6×10^{-5} $(\Omega\ cm)^{-1}$ to 7×10^{2} $(\Omega\ cm)^{-1}$ when doped with iodine, the exact value depends upon both the preparation technique and the method of measurement[151].

The conductivity of doped polyacetylene, $[CHI_{0.09}]_x$, is somewhat lower than the value published by several other workers. One possible reason for this apparent anomaly is shown in studies on the effect of dopant concentration on conductivity for polyacetylene[152-155]. It was found that for an increase in y, in $[CHI_y]_x$, from $y=10^{-3}$ to $y=0.32$ the conductivity was seen to increase rapidly from 10^{-5} $(\Omega\ cm)^{-1}$ to 10^{2} $(\Omega\ cm)^{-1}$. Any error in the calculation of y produces a large difference in the value of the conductivity.

6.2.2 POLY(STYRENE-CO-ACETYLENE)

TABLE 7. AC CONDUCTIVITY OF DOPED AND UNDOPED POLY(STYRENE-CO-ACETYLENE), 25°C,10 KHz

UNDOPED	DOPED
$(2.51 \pm 0.5) \times 10^{-9}$	$(1.27 \pm 0.5) \times 10^{-8}$

The conductivity of both doped and undoped poly(styrene-co-acetylene) are shown in table 7. The samples were exposed to gaseous iodine, at atmospheric pressure and room temperature, for two weeks to achieve the maximum level of doping under these conditions. The doping causes the conductivity to increase by an order of magnitude. The increase in conductivity of the doped copolymer is much smaller than the increases in conductivity produced by doping pure polyacetylene. This is because the polyacetylene is only a small part of the whole copolymer and polystyrene does not have the electrical properties of the polyacetylene.

From the weight of iodine taken up by the copolymer it is possible to calculate the maximum possible polyacetylene content of the copolymer assuming that the polyacetylene segment in the copolymer takes up all the iodine, and that the polystyrene block remains unchanged. If the polyacetylene regions attain the same level of dopant concentration as the homo-polyacetylene, then it is possible to estimate that the maximum possible quantity of polyacetylene present in the copolymer is 50% by weight. Aldissi[40] has calculated that it is not until the polyacetylene content of a copolymer reaches 60% that the conductivity of the materials begins to increase to any great extent. This could account for the relatively low value obtained for the conductivity of the doped copolymer.

6.3 THE EFFECT OF TEMPERATURE ON CONDUCTIVITY

In this section the effect of temperature on the conductivity of both the doped and undoped polymers will be discussed.

6.3.1 UNDOPED METATHETICALLY PREPARED POLYACETYLENE

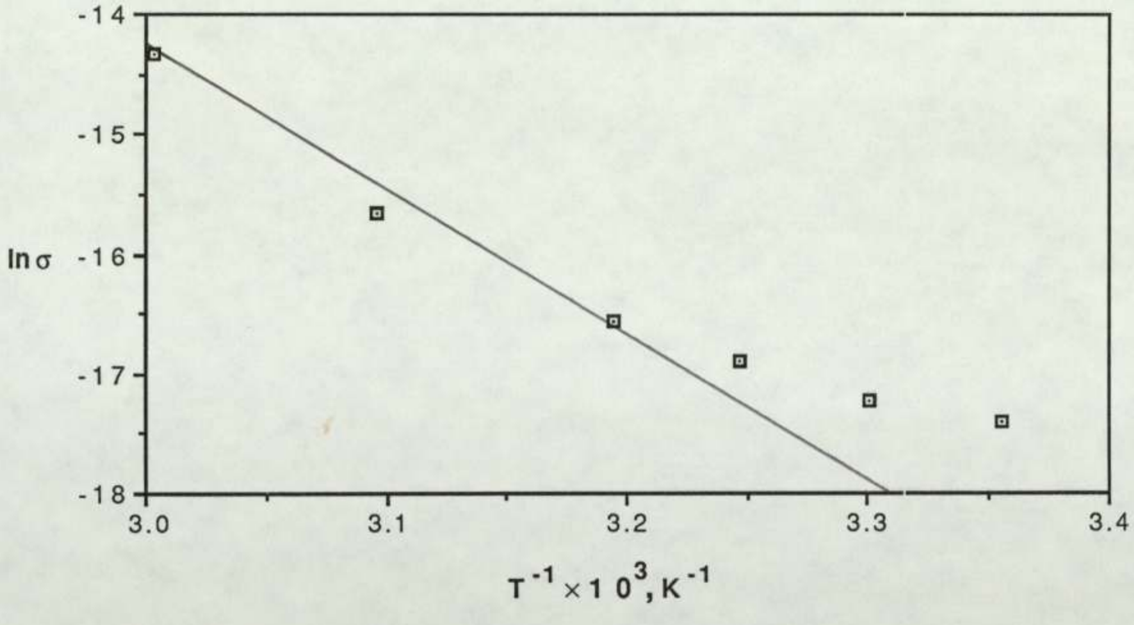


FIGURE 6.1 PLOT OF THE LOG OF THE AC CONDUCTIVITY OF POLYACETYLENE VERSUS T^{-1}

As has been discussed in chapter 5, there are many models that have been used to account for the conductivity of polymers. Figure 6.1 is a plot of the conductivity of undoped polyacetylene versus T^{-1} according to the model of voltage fluctuation induced tunneling above the percolation threshold at high temperatures. The poor fit also rules out the models of hopping conduction involving extended states, band tails and polarons.

The data plotted according to the theory of metallic islands (equation 5.15), figure 6.2 also shows a deviation from the theory. The line was drawn for $\sigma=\sigma_0\exp[-1176T^{-0.5}]$.

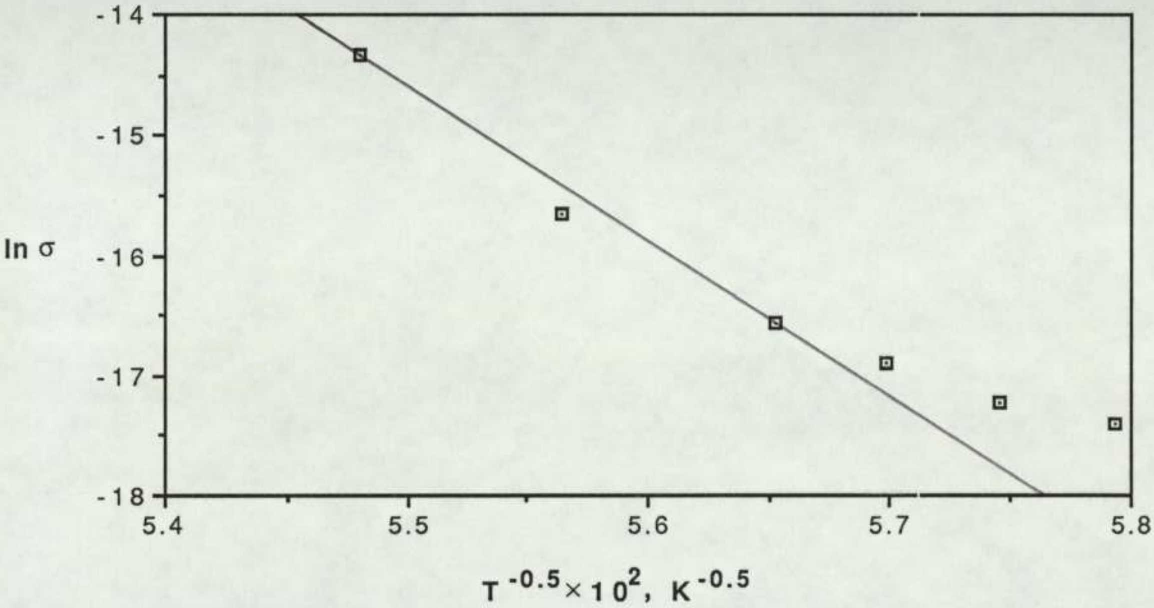


FIGURE 6.2 PLOT OF THE LOG OF THE AC CONDUCTIVITY OF POLYACETYLENE VERSUS $T^{-0.5}$

Figure 6.3 is a plot of the data for concentrations of metallic domains above the percolation threshold, where the temperature has a dependence like that of variable range hopping in three dimensions, equation 5

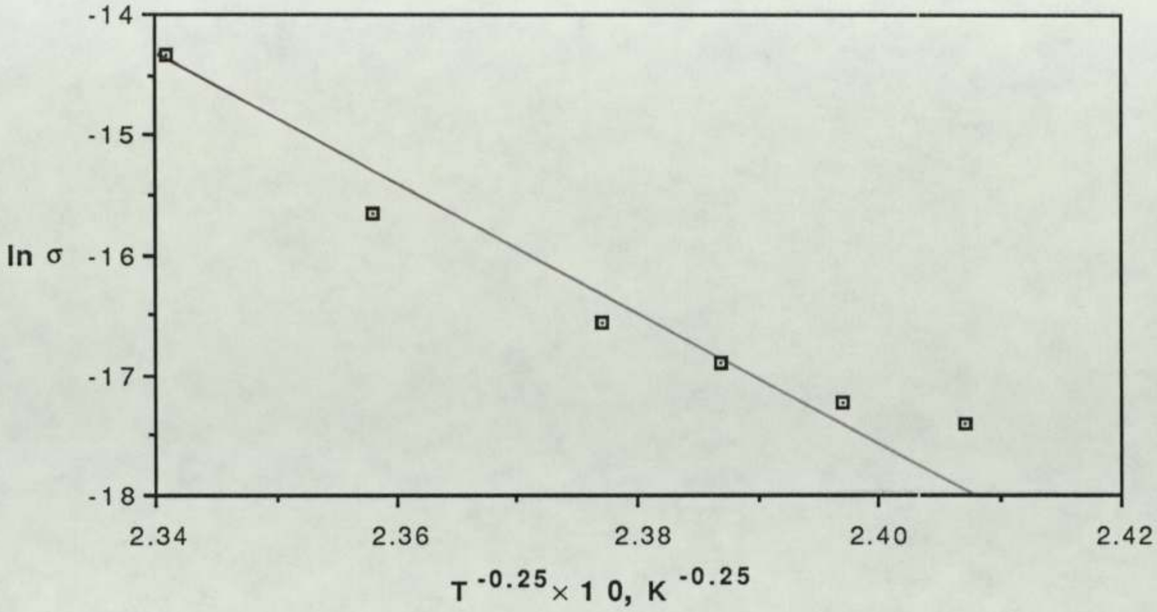


FIGURE 6.3 PLOT OF THE LOG OF THE AC CONDUCTIVITY OF POLYACETYLENE VERSUS $T^{-0.25}$

The line is drawn for $\sigma=\sigma_0\exp[-508T^{-0.25}]$. The data is best fitted to the latter of these three models, but the analysis of temperature dependence of the conductivity of undoped polyacetylene does not shed any light on the probable mechanism of conduction.

6.3.2 DOPED METATHETICALLY PREPARED POLYACETYLENE

At high levels of doping for $(CHI_y)_x$ a linear plot of $\ln [\sigma_{(T)}/\sigma_{(RT)}]$ versus $T^{-0.25}$ can be obtained (figure 6.4) where $\sigma_{(RT)}$ is the conductivity of the doped polyacetylene at room temperature.

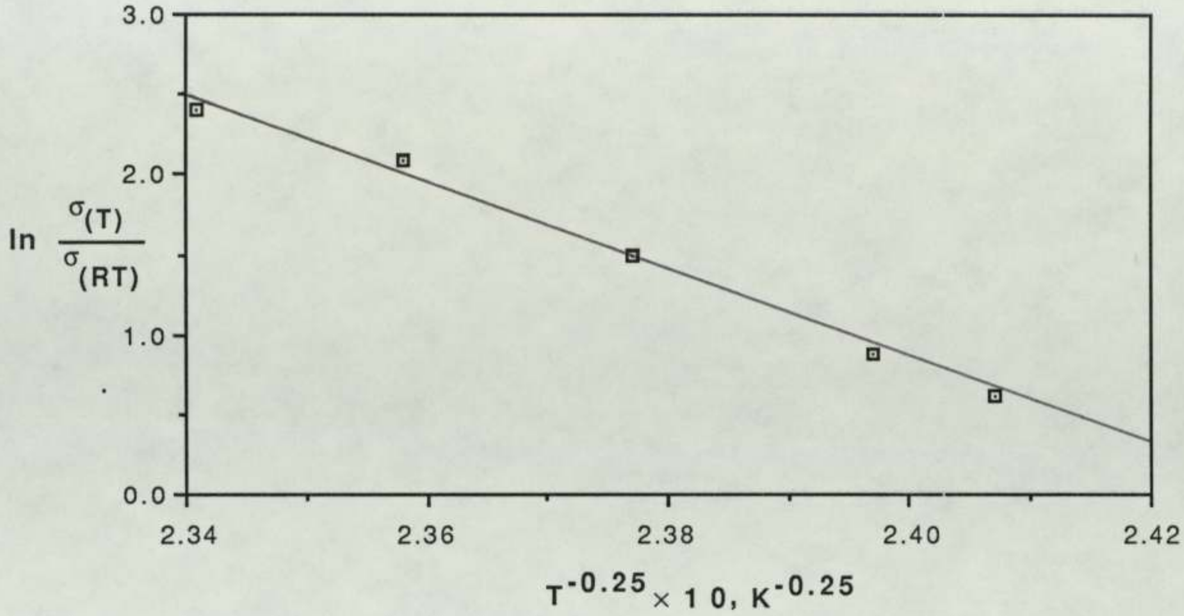


FIGURE 6.4 PLOT OF THE LOG OF THE NORMALISED CONDUCTIVITY OF DOPED POLYACETYLENE VERSUS $T^{-0.25}$

The linear plot may be taken as an indication of conduction by variable-range hopping for the halogen doped polyacetylene.

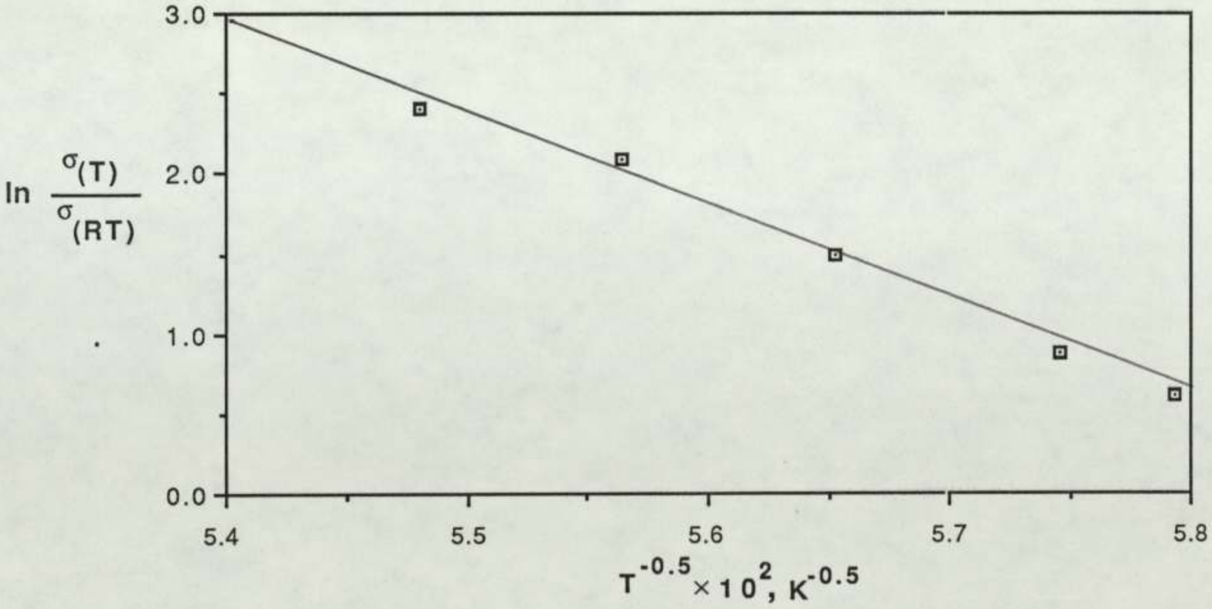


FIGURE 6.5 PLOT OF THE LOG OF THE NORMALISED CONDUCTIVITY OF DOPED POLYACETYLENE VERSUS $T^{-0.5}$

The temperature dependence of conductivity is apparently also consistent with the model of metallic islands figure 6.5. The plot of ln $[\sigma_{(T)}/\sigma_{(RT)}]$ versus $T^{-0.5}$ is linear within experimental error.

The data is also consistent with the model of fluctuation voltage induced tunneling at high temperatures with a good fit with the theory for a plot of ln $[\sigma_{(T)}/\sigma_{(RT)}]$ versus T^{-1} (figure 6.6)

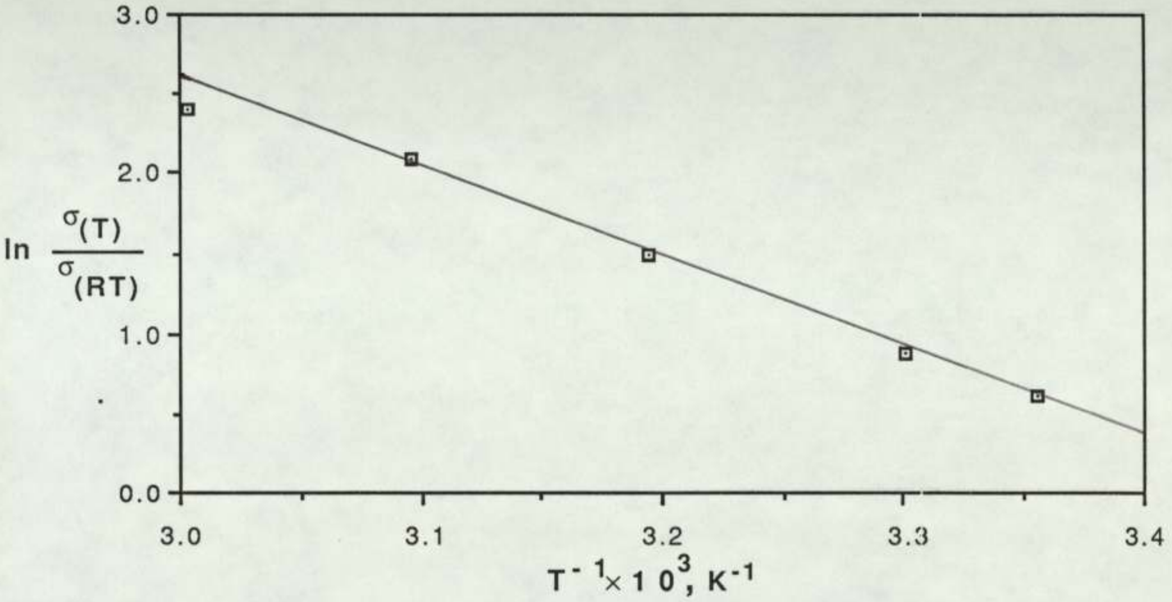


FIGURE 6.6 PLOT OF THE LOG OF THE NORMALISED CONDUCTIVITY OF DOPED POLYACETYLENE VERSUS T^{-1}

This type of behaviour has been observed by Chiang et al[155] Tomkiewicz and coworkers[156] and Sheng[149]. It is quiet clear from the results cited in this section together with those from other reviews[5,157] that the nature of the dopant, the doping procedure and doping level, the initial isomeric content and some other factors affecting the sample quality have strong influences on the functional form of the temperature dependence of the conductivity. As a consequence it is very difficult to draw any conclusions concerning possible conduction mechanisms in polyacetylene (both doped and undoped) based solely upon an analysis of the temperature dependence of electrical conductivity.

6.3.3 UNDOPED POLY(STYRENE-CO-ACETYLENE)

Very little work has been reported on the temperature dependence of the conductivity of copolymers containing polyacetylene segments. Most workers in the field merely quote the maximum value achieved for the conductivity of a particular sample. The major problem with the copolymers is that the characterisation of these materials has been very problematic. Since the conductivities depend to a very large degree upon the composition and structure of the copolymers it is very difficult to draw any general conclusions as in almost every case in the literature the composition and structure are different each time. The technique which is used to measure the conductivity also plays an important role.

The temperature dependency of the conductivity for the copolymer has been investigated above room temperature and below room temperature. The two sets of data will be treated separately. This is because different measurement techniques were used to determine the conductivity of the sample in the two temperature ranges.

Figure 6.7 is a plot of the conductivity of the undoped copolymer versus T^{-1} according to the model of voltage fluctuation induced tunneling above the percolation threshold.

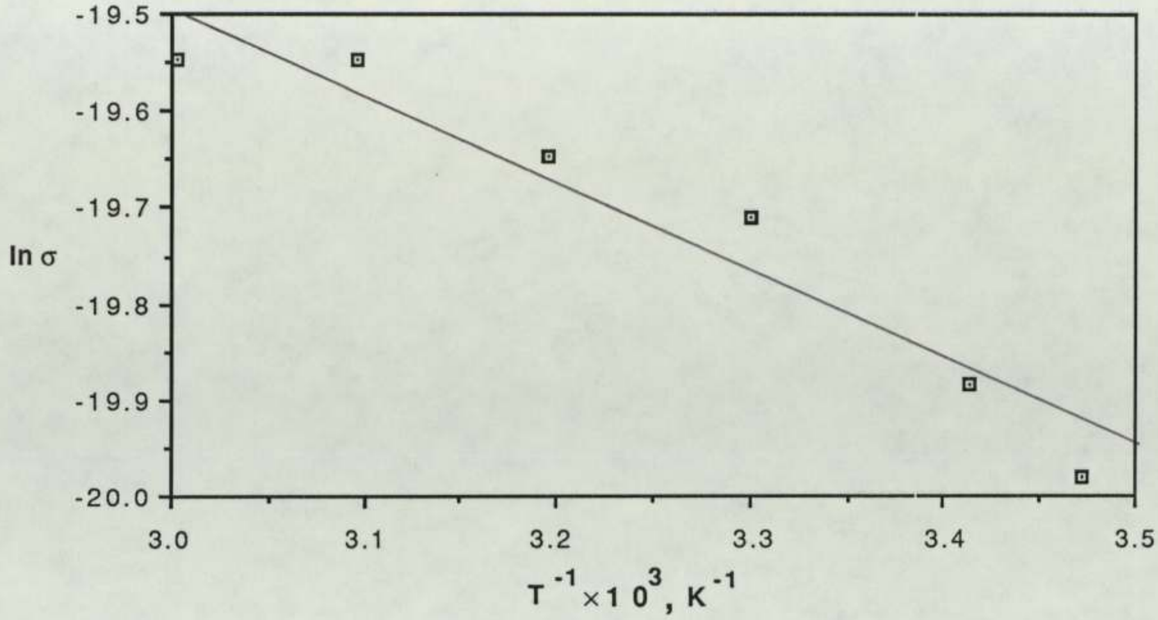


FIGURE 6.7 PLOT OF THE LOG OF THE AC CONDUCTIVITY OF POLY(STYRENE-CO-ACETYLENE) VERSUS T^{-1}

Figure 6.8 shows the data plotted according to the theory of metallic islands.

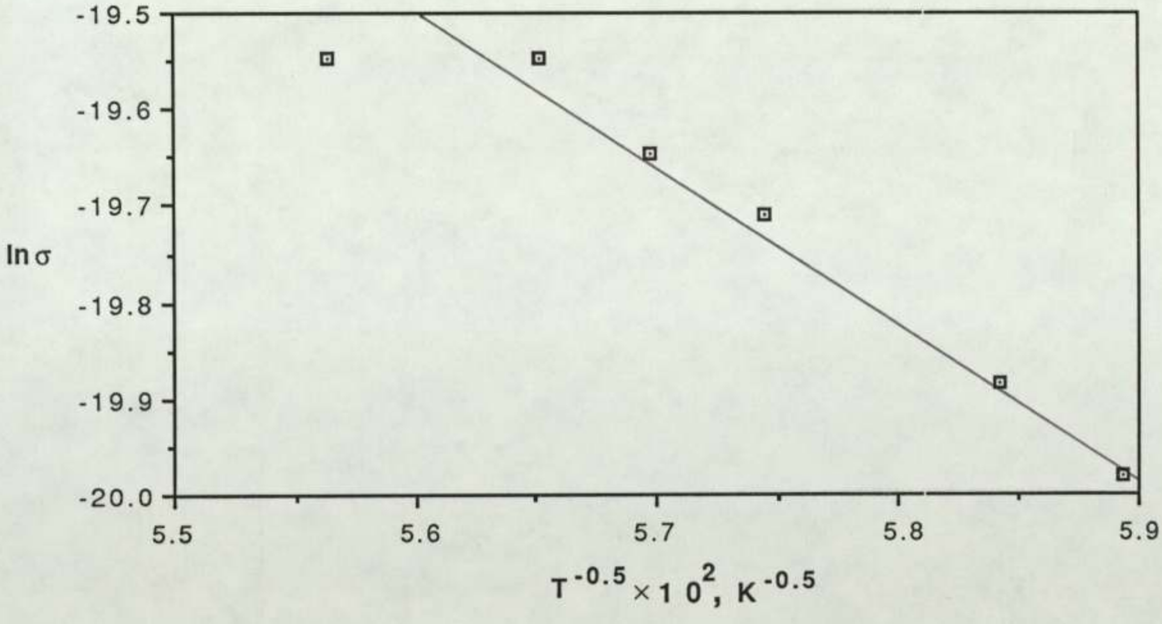


FIGURE 6.8 PLOT OF THE LOG OF THE AC CONDUCTIVITY OF POLY(STYRENE-CO-ACETYLENE) VERSUS $T^{-0.5}$

Figure 6.9 is a plot of the data for concentrations of metallic domains above the percolation threshold, where the temperature dependence is similar to that predicted for variable range hopping in three dimensions.

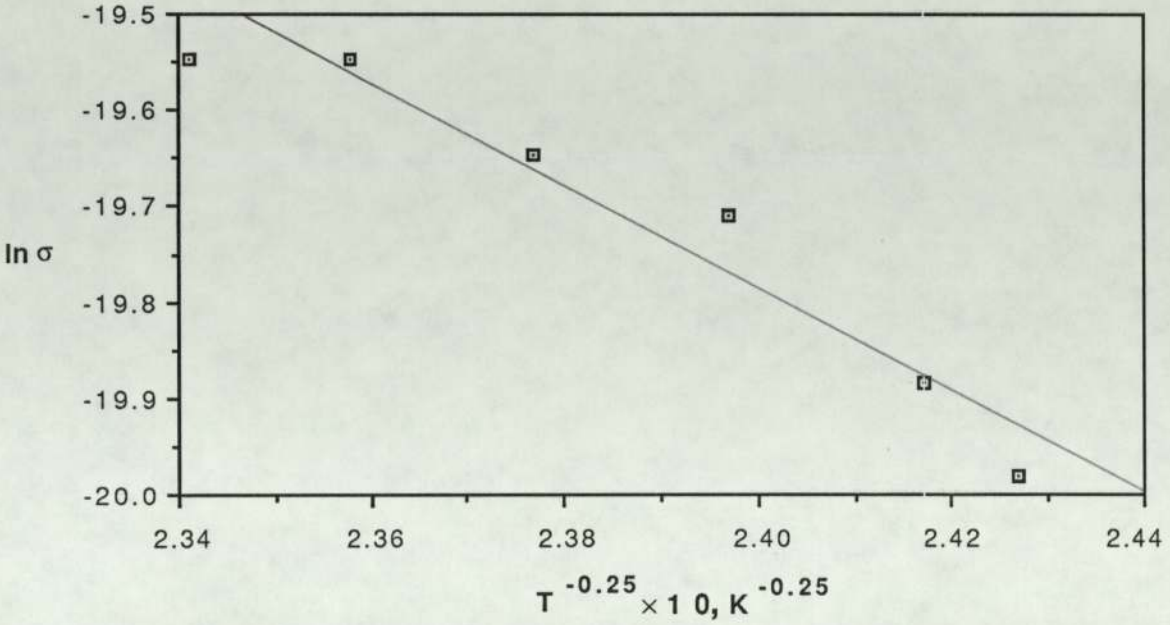


FIGURE 6.9 PLOT OF THE OF LOG OF THE AC CONDUCTIVITY OF POLY(STYRENE-CO-ACETYLENE) VERSUS $T^{-0.25}$

The plots show that the data appears to fit all three versions of the model which is in contrast to the undoped polyacetylene which gave a very poor fit for all three models.The best fit (figure 6.8) is found when the data is plotted according to the situation where the concentration of metallic domains is below the percolation threshold which is what is expected for a material that contains a maximum of 50% by weight of polyacetylene which is the conducting phase.

Below room temperature the data was plotted according to the various models. (figures 6.10, 6.11, and 6.12). Again the data appears to fit all three models although in this case the data does not appear to fit one of the models any better than the other two.

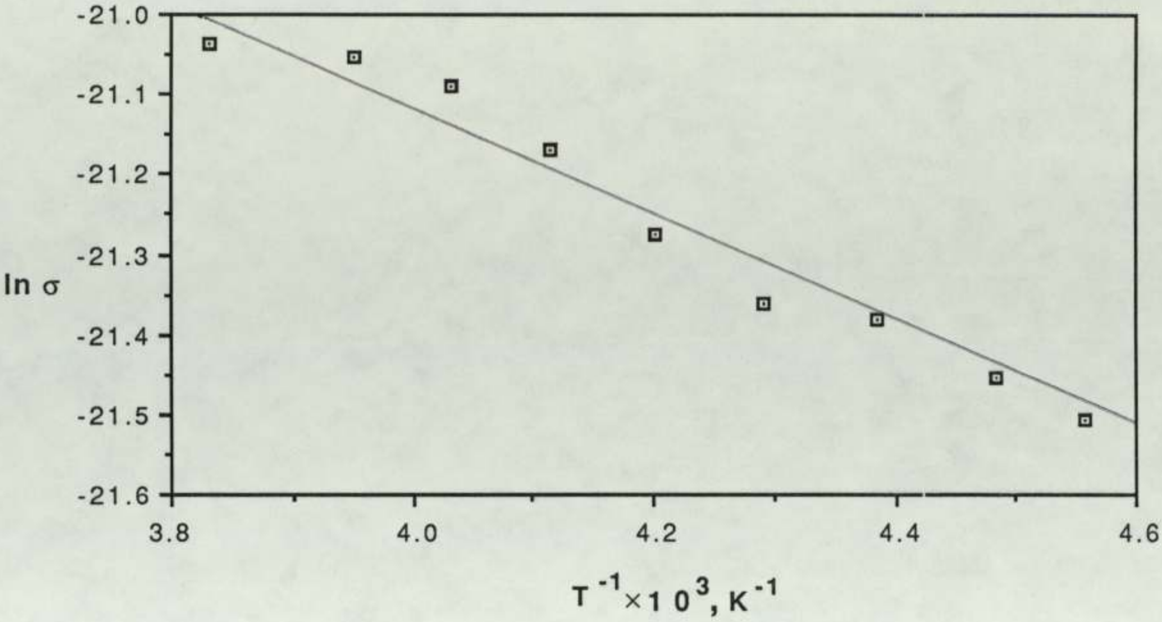


FIGURE 6.10 PLOT OF THE LOG OF THE AC CONDUCTIVITY OF POLY(STYRENE-CO-ACETYLENE) VERSUS T^{-1}

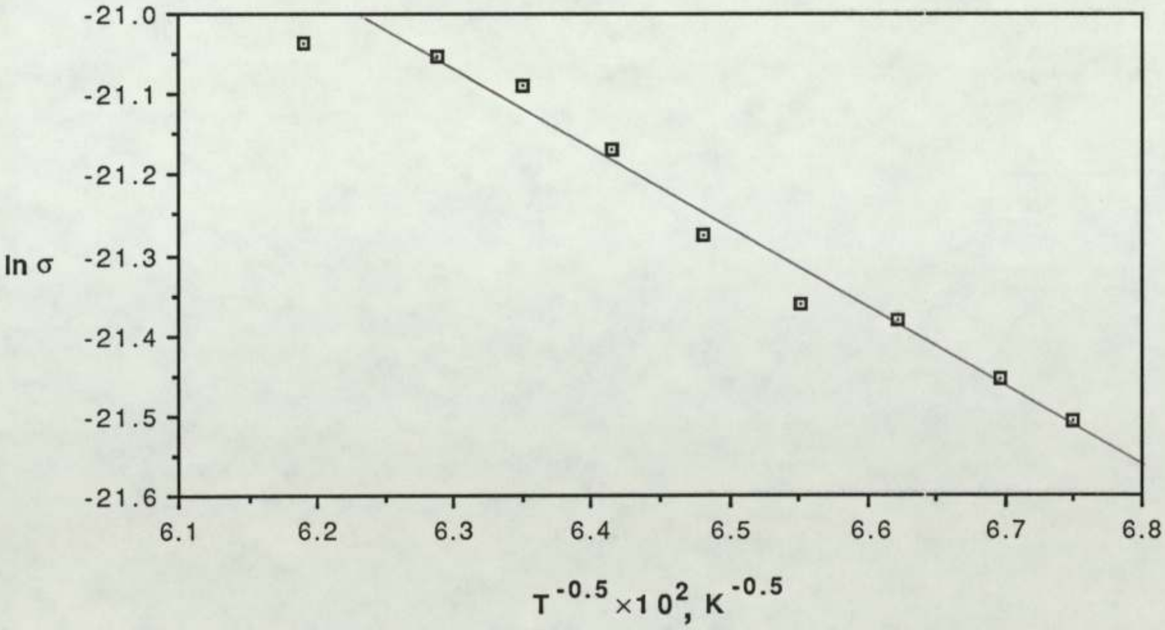


FIGURE 6.11 PLOT OF THE LOG OF THE AC CONDUCTIVITY OF POLY(STYRENE-CO-ACETYLENE) VERSUS $T^{-0.5}$

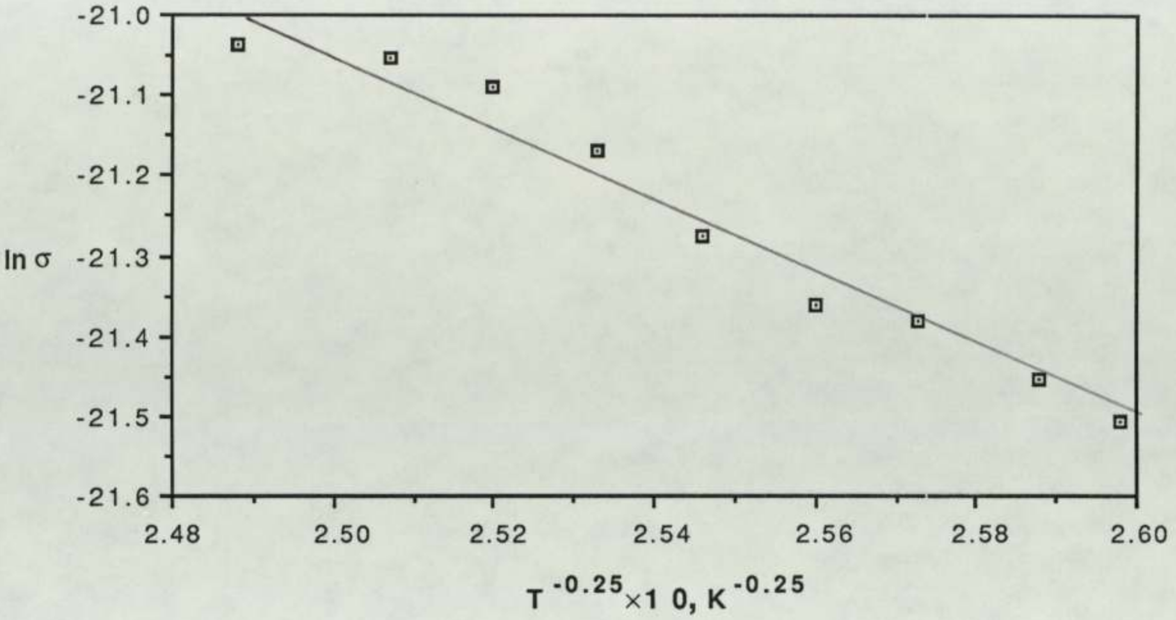


FIGURE 6.12 PLOT OF THE LOG OF THE AC CONDUCTIVITY OF POLY(STYRENE-CO-ACETYLENE) VERSUS $T^{-0.25}$

6.3.4 DOPED POLY(STYRENE-CO-ACETYLENE)

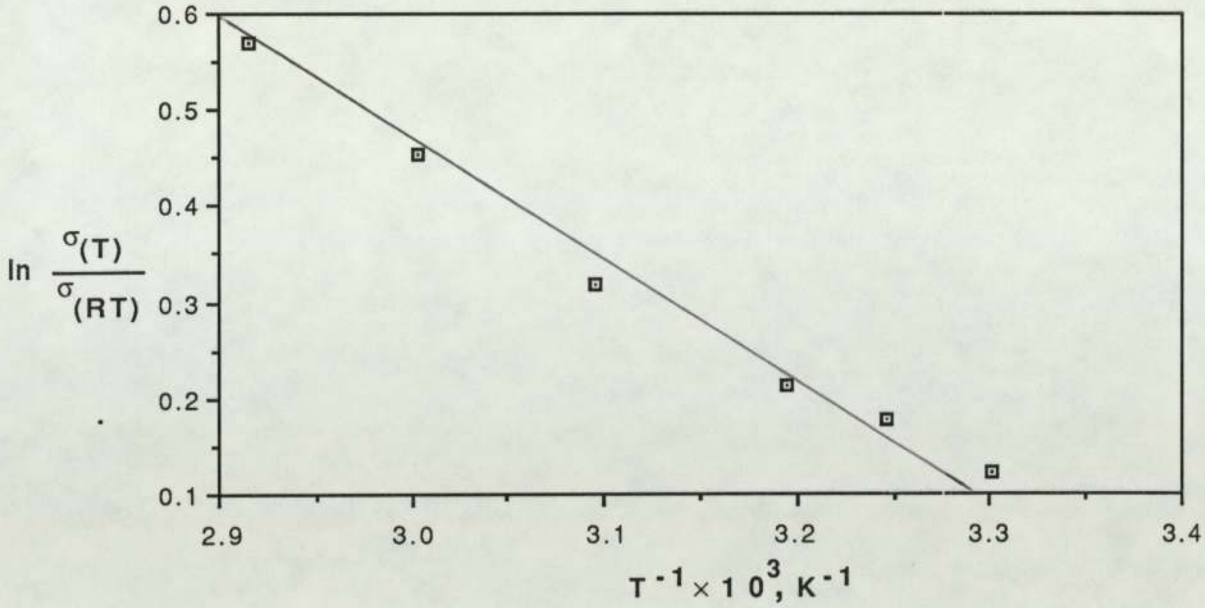


FIGURE 6.13 PLOT OF THE LOG OF THE NORMALISED CONDUCTIVITY OF DOPED POLY(STYRENE-CO-ACETYLENE) VERSUS T^{-1}

The log of the normalised conductivity for the doped copolymer is plotted versus T^{-1}, $T^{-0.5}$, $T^{-0.25}$ according to the various models. (figures 6.13, 6.14 and 6.15)

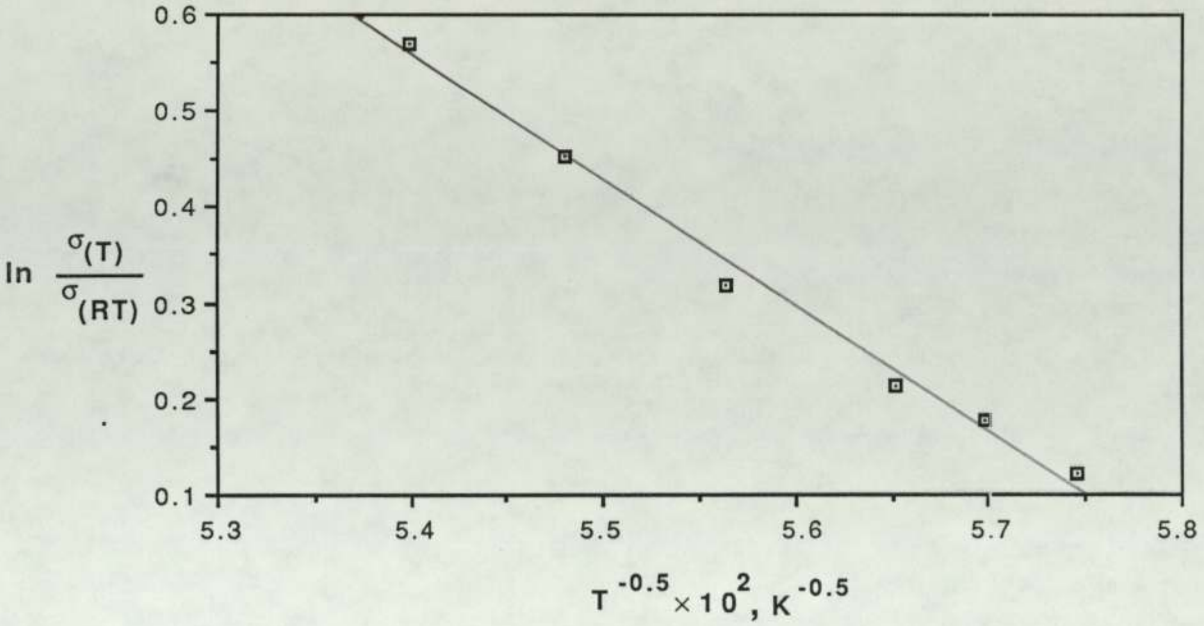


FIGURE 6.14 PLOT OF THE LOG OF THE NORMALISED CONDUCTIVITY OF DOPED POLY(STYRENE-CO-ACETYLENE VERSUS $T^{-0.5}$

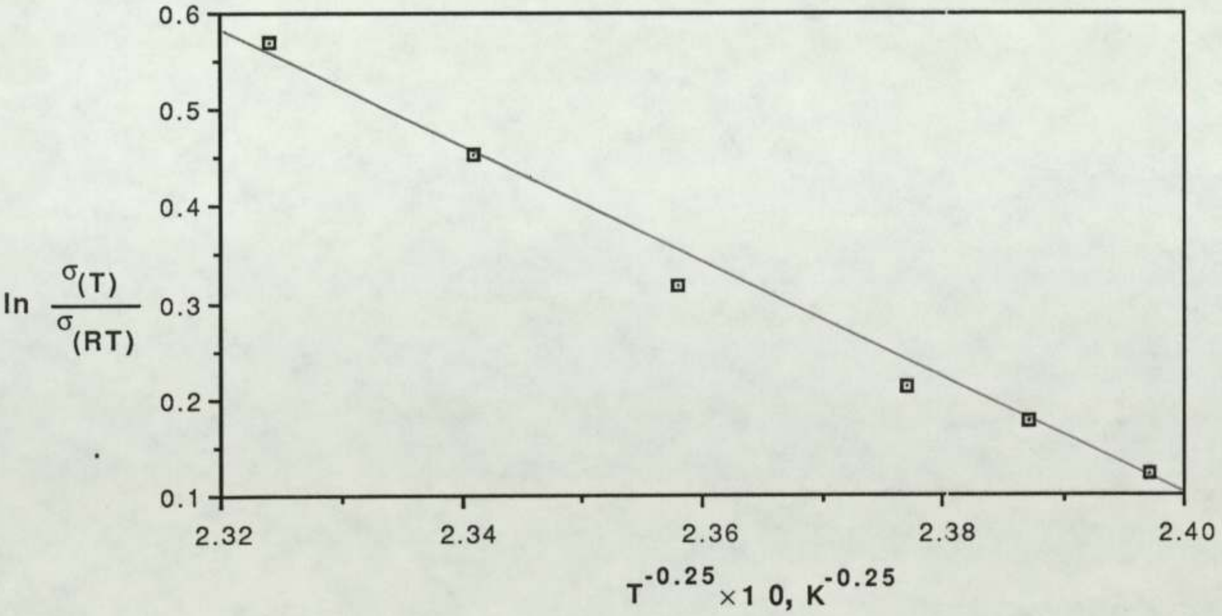


FIGURE 6.15 PLOT OF THE LOG OF THE NORMALISED CONDUCTIVITY OF THE DOPED POLY(STYRENE-CO-ACETYLENE) VERSUS $T^{-0.25}$

Again the data appears to fit all three plots. It is impossible from just looking at the temperature dependency of the conductivity of both the doped and undoped copolymer to gain any knowledge of the conductivity mechanism within the copolymer. There is no similar work in the literature with which to compare these results.

6.4 EFFECT OF FREQUENCY ON THE CONDUCTIVITY

In this section the effect of frequency on the conductivity of the polymers will be discussed.

6.4.1 METATHETICALLY PREPARED POLYACETYLENE

The conductivity of undoped polyacetylene shows a very marked frequency dependence.

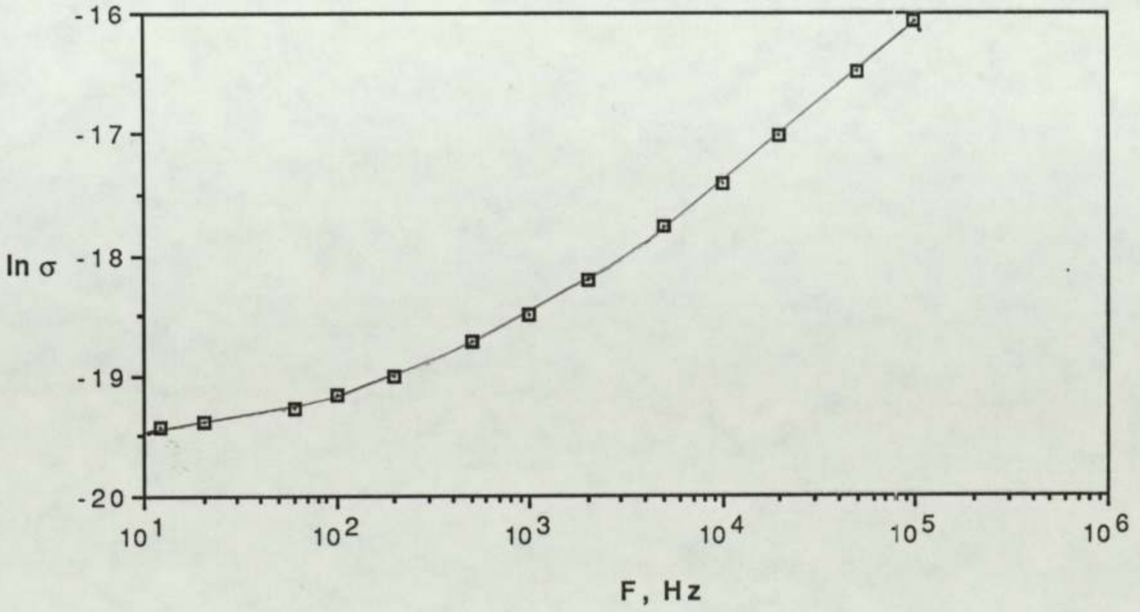


FIGURE 6.16 PLOT OF THE LOG OF THE AC CONDUCTIVITY OF POLYACETYLENE VERSUS FREQUENCY

Figure 6.16 is a plot of the log of the conductivity versus frequency. Other workers have observed a similar frequency dependence[158]. The conductivity of heavily doped polyacetylene shows a much smaller frequency dependence, figure 6.17. Epstein et al[5] reported the conductivity of heavily doped polyacetylene to be frequency independent. This frequency independence is inconsistent with any of the conductivity models.

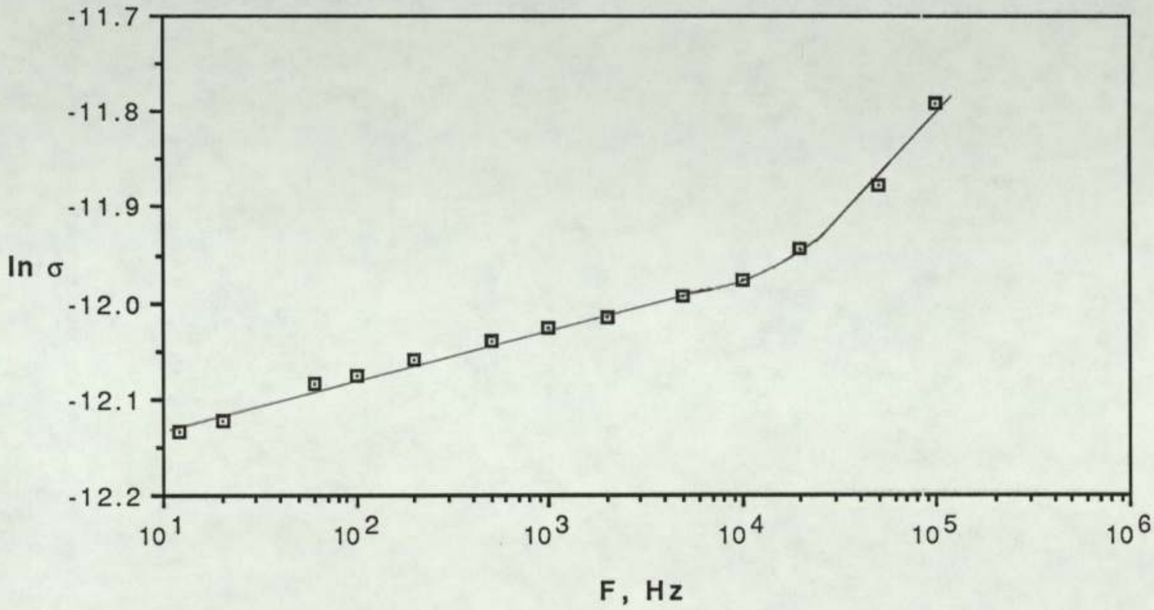


FIGURE 6.17 PLOT OF THE LOG OF THE AC CONDUCTIVITY OF DOPED POLYACETYLENE VERSUS FREQUENCY

6.4.2 POLY(STYRENE-CO-ACETYLENE)

For both doped and undoped forms of the copolymer the conductivity depends markedly on frequency, figures 6.18 and 6.19

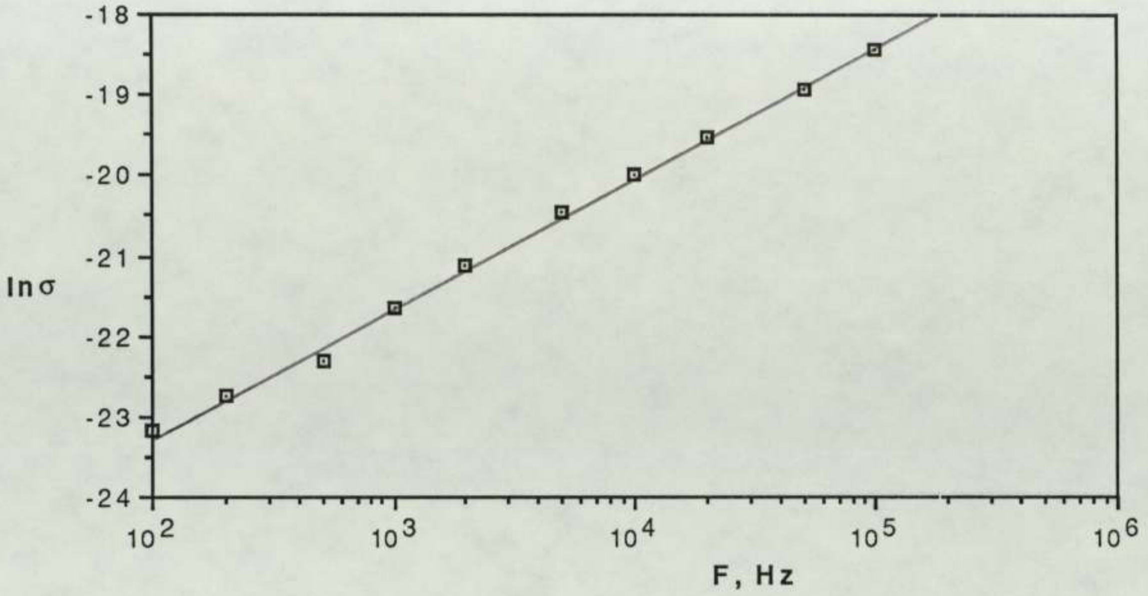


FIGURE 6.18 PLOT OF THE LOG OF THE AC CONDUCTIVITY OF UNDOPED POLY(STYRENE-CO-ACETYLENE VERSUS FREQUENCY

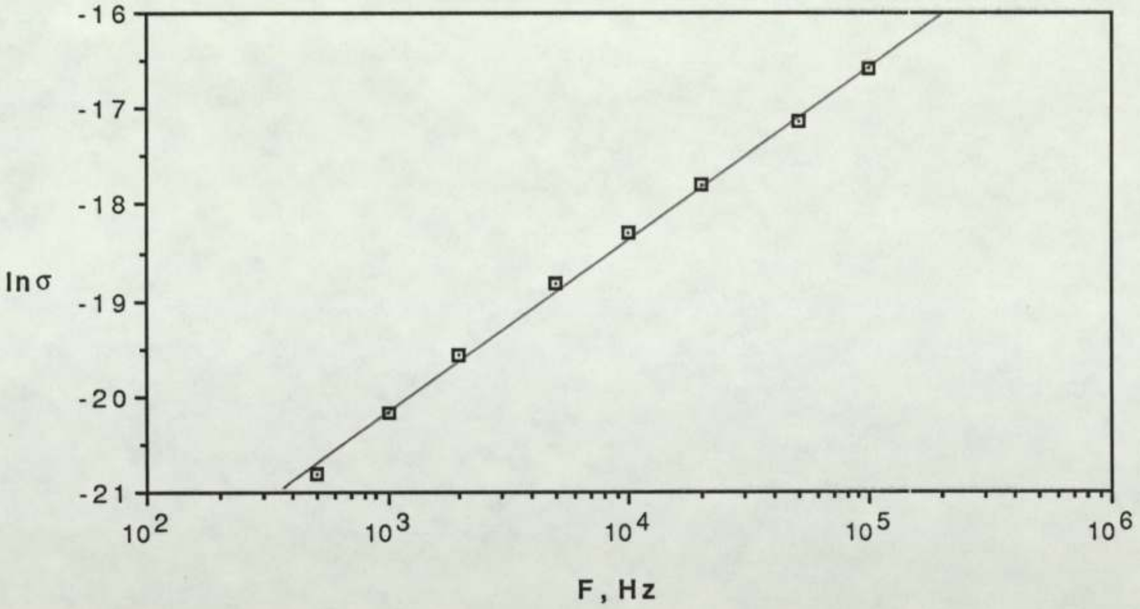


FIGURE 6.19 PLOT OF THE LOG OF THE AC CONDUCTIVITY OF DOPED POLY(STYRENE-CO-ACETYLENE) VERSUS FREQUENCY

The marked frequency dependence of the conductivity of the copolymer in both the doped and undoped phase could possible be derived from the interaction with the polystyrene portion of the copolymer.

6.5 THE EFFECT OF PRESSURE ON THE CONDUCTIVITY

In this section the effect of pressure on the conductivity of the polymers will be discussed.

6.5.1 POLYACETYLENE

The effect of pressure on the conductivity of undoped polyacetylene is shown in figure 6.20. The polyacetylene shows an approximate two fold increase in conductivity for an increase in pressure of 7 tons[1].

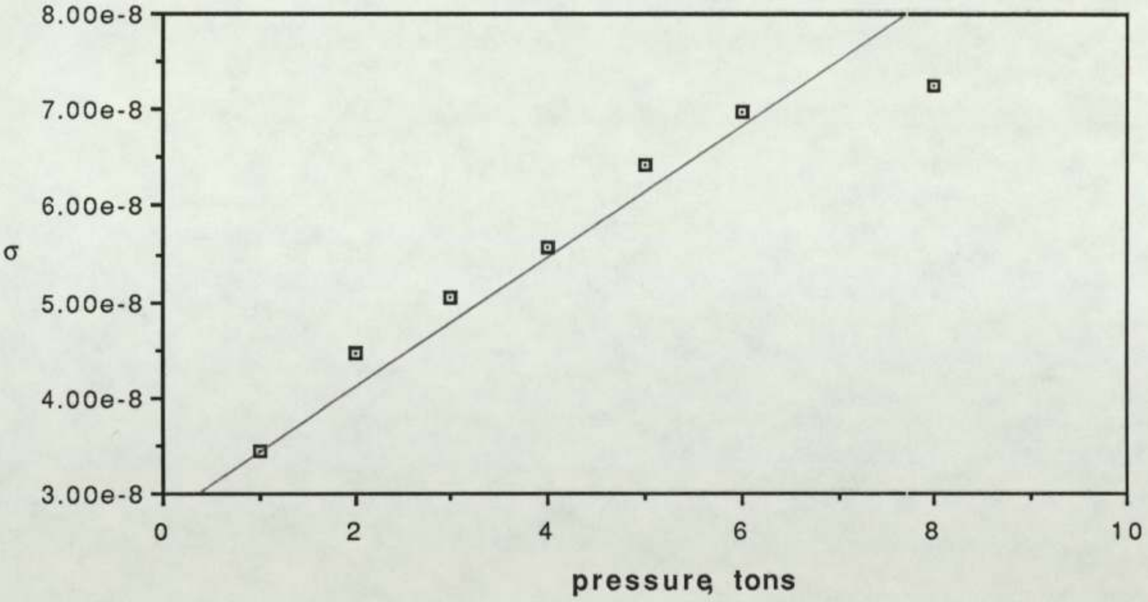


FIGURE 6.20 PLOT OF THE AC CONDUCTIVITY OF POLYACETYLENE VERSUS PRESSURE

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[1] Pressure quoted is in Imperial tons measured directly from the hydraulic press.

$$1 \text{ ton} = 5.63 \times 10^7 \text{ NM}^{-2}$$

Similar results for polyacetylene were obtained by Moses et al[159]

6.5.2 POLY(STYRENE-CO-ACETYLENE)

The effect of pressure on the conductivity of undoped poly(styrene-co-acetylene) is shown in figure 6.21. Again there is approximately a two fold increase in conductivity as the pressure is increased. In both cases the effect of the pressure is believed to decrease the void volume within the polymer but not to influence the intrachain transport processes. The increase in the conductivity of the copolymer can be attributed to an increase in the density of conducting regions per unit volume.

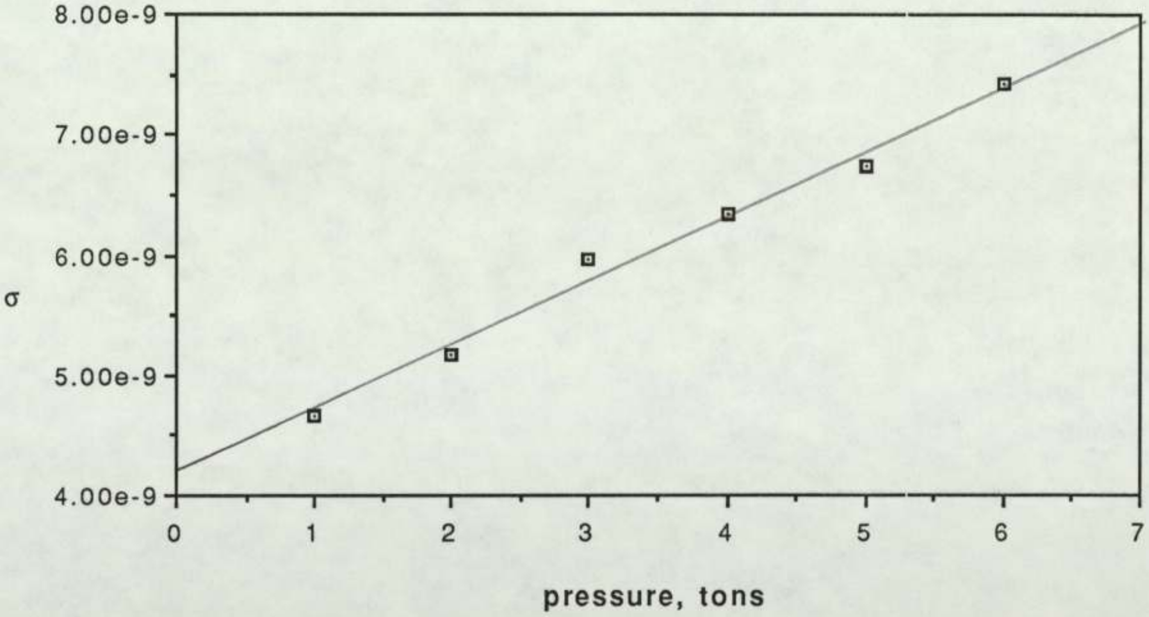

FIGURE 6.21 PLOT OF THE AC CONDUCTIVITY OF POLY(STYRENE-CO-ACETYLENE)VERSUS PRESSURE

CHAPTER 7

CONCLUSIONS AND FURTHER WORK

7.1 INTRODUCTION

It is the purpose of this chapter to bring together and discuss the salient points that have been made during the course of this work. It should then be possible to suggest areas of the study in which further work should be carried out in order to develop these ideas further.

7.2 DISCUSSION AND CONCLUSIONS

This thesis is the first report of the metathetical production of polyacetylene using the catalyst system $WCl_6/AlEt_3$. Until recently it is only substituted acetylenes that have been polymerised using metathesis catalysts of this type. The metathesis catalyst system was incorporated into an anionic-to-metathesis transformation reaction which provides a novel route for the synthesis of poly(styrene-co-acetylene)

The polymer was characterised using a variety of physical techniques. The only analytical technique used in the study that gives definite proof of copolymer formation rather than a mixture of the polymers is gel permeation chromatography. However the remaining physical techniques do confirm the presence of polyacetylene in the bulk copolymer. The increase in molecular weight from 61000 to over 6 million can only be accounted for by the formation of block copolymers followed by aggregation in solution. In common with many other studies of this type of material the characterisation of the copolymer has proved to be very difficult. This is thought to be due in the main to the intractability of the polyacetylene segments.

The scanning electron microscopy provided some interesting photographs of the surface morphology of the copolymer. Plates 5, 6, 7 and 8 indicate that some form of self ordering is occurring within the polymer. This type of behaviour has not been observed in any other of the surface studies that have been carried out on these polymers containing polyacetylene, though these studies can in no way be described as extensive.The full reason for this self-ordering is as yet unknown although the method of preparation and the effect of heat treatment are both areas which could be investigated.

The electrical properties of the poly(styrene-co-acetylene) as discussed in the main text show good general agreement with results previously published in the literature. The generally lower conductivity values for the copolymer as compared to other published results can be attributed to two things, firstly the polymer only contains, at a maximum, 50% by weight of polyacetylene which is below the value needed to produce conductivities that are substantially greater than polystyrene itself. Secondly, as previously mentioned in the text, the method used in this study to measure the conductivity is unusual and the effect on the overall conductivity is unkown.

The study of the temperature dependence of the conductivity in polymeric materials is very common and has been reported widely in the literature. After many years of extensive study by this technique the mechanism of conduction in these materials is still not clear. This present study, in common with other studies, has shown that the data acquired from the conductivity studies can be seen to give good agreement with the predictions of several of the theories postulated to account for the electrical conductivity of polymers. With particular regard to copolymers containing polyacetylene there has been relatively little work on the conductivity dependence on such things as temperature and frequency. The main thrust of the research effort, connected with the copolymers, has been to produce materials which can achieve conductivities that are comparable to that possessed by pristine polyacetylene, with most workers only reporting the maximum conductivity attained for each system produced in the doped and undoped phase. The hesitancy of workers to tackle the conductivity dependencies of the copolymers may be overcome once the mechanism of conduction in homo-polyacetylene is finally elucidated. With no comparable studies published in the literature it makes it very difficult to put the present work into context.

With regard to the synthesis of polyacetylene the novel metathesis catalyst system described in this thesis provides a means to synthesise polyacetylene in a controlled fashion as opposed to the synthesis by the normal Shirakawa catalyst system were the polymerisation proceeds very rapidly. The use of this novel catalyst system used in conjunction with a "comonomer" consisting of a living polymer could provide the means to sythesise many more copolymers containing polyacetylene as well as other novel monomers. The selection of the comonomer plays a vital role in the final electrical properties of any polyacetylene containing copolymer.

The synthesis of polyacetylene oligomers (polyenes) using a modified $AlEt_3/Ti(OBu)_4$ catalyst system proved to be very difficult. Small amounts of a mixture of polyenes was produced but not in sufficient quantities required to make the synthesis worthwhile. If extensive purification of the products could be achieved then some indication of the mechanism of Ziegler/Natta polymerisations could be achieved, especially if detailed structural analysis could be carried out on the isolated products.

7.3 SUGGESTIONS FOR FURTHER WORK

The work reported in this thesis is merely the first stage in a much longer program of work. Much work still remains to be done on the kinetics and mechanism of the reaction. This is mainly because the synthesis involves a metathesis reaction, the mechanism of which is far from being characterised.

The work has demonstrated that an anionic-to-metathesis transformation reaction can be used to produce copolymers containing polyacetylene segments. The electrical properties of the copolymers are dominated by the properties of the monomer used other than acetylene. Until recently workers have concentrated upon employing comonomers that will impart solubility to the copolymer, but this has usually been to the detriment of the electrical properties of the final copolymer. The main reason for this fixation with the solubility problem is that until recently the only simple catalyst system that could be used to polymerise acetylene was the Shirakawa system. The Shirakawa catalyst is a very active system which leads to the very rapid growth of the polyacetylene block in the copolymer. This reaction rapidly results in the production of an insoluble polymer thereby indicating that the solubility of the comonomer is the all important property. With the development of this new more controllable catalyst system the solubility of the comonomer is less important.

The anionic-to-metathesis transformation reaction could be used to initially produce poly(N-vinyl carbazole) via anionic polymerisation followed by a transformation reaction and the subsequent polymerisation of acetylene. This would result in the production of poly(N-vinyl carbazole-co-acetylene). Poly(N-vinyl carbazole) is a well known photoconductive polymer and it could reasonably be hoped that it would impart this property to the copolymer.

The conductivity of poly(styrene-co-acetylene) will never achieve the orders of magnitude of doped polyacetylene but there is still a lot of interesting work that can be done on this novel material. A full characterisation would go a long way towards this goal. Of great interest is the apparent self ordering which is indicated in the SEM studies. The effect of preparation technique on this phenomena and the effect of annealing should give some insight as to the driving forces behind this action. If this self ordering could be introduced when the polymer is either in solution or in a molten state the effect of an electric field on this phenomena may produce some interesting effects.

The single most important development to come out of this work is the anionic-to-metathesis transformation reaction and its use for the polymerisation of acetylene. This reaction could now be used to produce other novel materials whose properties maybe of even greater interest.

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APPENDIX ONE

SUPPORTING PUBLICATIONS

Makromol. Chem., Rapid Commun. **8**, *119 – 122 (1987)*

Studies in electroactive polymers, 1

Metathesis polymerization of acetylene

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Introduction

The synthesis of polyconjugated polymers, particularly polyacetylene, has generated considerable scientific interest of late because such polymers have been shown to be electrically conductive when doped with materials such as iodine or arsenic pentafluoride. The synthetic routes to polyacetylene include polymerization of acetylene initiated by Ziegler-Natta catalysts[1] or the indirect route demonstrated by Feast et al.[2] which involves the metathetic polymerization of a strained bicyclic alkene followed by an elimination reaction to form polyacetylene. Metathesis catalysts have also been used to polymerize monomers such as phenylacetylene, but to our knowledge the one-step polymerization of acetylene by this particular metathesis catalyst has not been reported. The work that we wish to report at this stage is part of a more extensive study of the metathesis system and its applicability to the synthesis of polyconjugated polymers and copolymers.

Experimental part

Polymerization of acetylene: The preparation of suitably pure reaction components, such as solvent (cyclohexane) and catalyst (WCl_6 and $AlEtCl_2$), has been described adequately elsewhere[3]. Acetylene was stored in a cylinder as a solution in acetone and was purified by passing the gas through concentrated sulfuric acid and then an aluminium oxide or calcium chloride drying column. The acetylene required for the polymerization reaction was stored in a 2 dm^3 flask fitted with greaseless taps and Quickfit joints. This flask was attached to the apparatus as shown in Fig. 1. The required volume of dry solvent was then distilled under vacuum into the apparatus and the greaseless tap to the vacuum line was closed. In one series of experiments acetylene was then admitted to the reaction vessel and allowed to form a saturated solution before the catalyst components were then added by syringe through the rubber septum cap as solutions in cyclohexane. In another, the components of the catalyst were added to the system, allowed to react for a pre-determined time and then the monomer was admitted to the reaction vessel. In each set of experiments the polymerization was then allowed to proceed for 48 h before the reaction was terminated by the addition of ethanol to destroy the catalyst components. Separate reactions were also carried out in which the individual catalyst components were added to the solvent to ensure that the polymerization of acetylene could not be initiated by one of the components on its own.

In a typical experiment $4{,}25 \cdot 10^{-5}$ mol of WCl_6 was added to 25 ml of cyclohexane followed by $2{,}5 \cdot 10^{-5}$ mol of $AlEtCl_2$. The reaction system showed all the colour changes that are nor-

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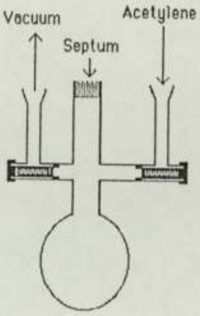

Fig. 1. Apparatus for the polymerization of acetylene

mally associated with the metathesis reaction and after approximately 30 min at ambient temperature a black precipitate began to form in the reaction vessel. Polymerization was allowed to proceed for 48 h after which time the polymer obtained was filtered, weighed and analysed for carbon and hydrogen contents.

Analysis of polymer: Carbon and hydrogen contents of the polymers obtained from the reactions were carried out using a CHN analyser. Although the use of these data alone would not normally be considered sufficient evidence for a particular structure, under the circumstances no other method of analysis proved to be suitable because the polymer was an intractable material.

Results

In the first series of experiments in which the polymerization of acetylene was carried out by the addition of the catalyst components to a saturated solution of acetylene low yields of polyacetylene were obtained. The dependence of the yield of polymer on the initial mole ratio of W:Al is shown in Tab. 1 along with the results obtained for the reactions using the individual catalyst components.

Tab. 1. Polymerization of acetylene with $WCl_6/AlEtCl_2$ catalyst[a)]

$\frac{[WCl_6]\cdot 10^4}{mol\cdot dm^{-3}}$	$\frac{[AlEtCl_2]\cdot 10^4}{mol\cdot dm^{-3}}$	Yield in g	Ratio C:H
20	80	0,09	1,05:1
10	20	0,09	1,03:1
8,5	5	0,03	0,9:1
20	200	0,0	—
0	200	0,0	—
40	0	0,0	—

a) Temp.: 20 °C; polymerization time: 48 h.

The polymerization of acetylene was then carried out using pre-mixed catalyst solutions at ambient temperature although in normal metathesis systems the activity of W/Al systems appears to be much lower when pre-mixing of the catalyst components is carried out. The dependence of the yield of polyacetylene in this reaction series is shown in Tab. 2 for a range of reaction variables.

It can be seen from Tab. 2 that the catalyst system appears to be more active if pre-reaction of the catalyst components is allowed to take place.

Tab. 2. Polymerization of acetylene with pre-mixed catalysts[a)]

$\frac{[WCl_6] \cdot 10^3}{mol \cdot dm^{-3}}$	$\frac{[AlEtCl_2] \cdot 10^3}{mol \cdot dm^{-3}}$	Pre-mix time	Yield in g	Ratio C:H
2,9	5,9	16 h	0,26	0,9:1
5,1	10,3	5 min	0,2	0,8:1
2,6	8,0	45 min	0,2	1,1:1

a) Temp.: 20 °C; polymerization time: 48 h.

The results do not, however, show any significant dependence of the yield on the pre-reaction time or the mole ratio of the catalyst components. This is most likely due to the fact that the polymer produced is an intractable solid and the catalyst site becomes buried in the polymer particle during the course of reaction and the real activity is not shown. To study such changes in catalyst activity will require the generation and study of soluble catalyst and polymer systems, an area of investigation currently being undertaken within this department.

Tab. 3. Polymerization of acetylene using $WCl_6/AlEt_3$

$\frac{[WCl_6] \cdot 10^4}{mol \cdot dm^{-3}}$	$\frac{[AlEt_3] \cdot 10^4}{mol \cdot dm^{-3}}$	Yield in g	Ratio C:H
3,5	6,8	0,18	0,91:1
3,5	13,8	0,20	0,83:1
3,5	20,3	0,16	0,61:1
6,8	6,8	0,26	0,82:1

a) Temp.: 20 °C; polymerization time: 48 h.

Experiments have also been carried out using $AlEt_3$ as cocatalyst in the reaction. The catalyst components were added to a saturated solution of acetylene, without pre-mixing the catalyst reagents. A black precipitate of polyacetylene began to form immediately on the addition of $AlEt_3$ to the solution. Tab. 3 shows the dependence of the yield of polyacetylene on the mole ratio of W/Al in these reactions.

Discussion

The yields of polymer quoted in the tables above are not by any means high, but this may be a reflection on the nature of the catalyst system that in other metathesis reactions is known to be notoriously inefficient and also to the fact that the active site for the polymerization is occluded in the polymer particle. The catalyst used for this polymerization is a system that shows high activity towards linear and cyclic alkene metathesis and it is assumed that a metathesis propagation step is to be invoked in this case also because the individual components of the catalyst do not show any activity towards polymerization. However, it has to be borne in mind that the combination of a transition metal halide and an alkylaluminium compound is a typical Ziegler-Natta catalyst system, and it may well be that in this particular case the components are acting as a simple co-ordinated anionic catalyst system.

It would appear that the use of $AlEt_3$ and pre-mixed catalyst systems, when $AlEtCl_2$ is cocatalyst, lead to higher activity catalyst. This may well be a result of the generation of a lower oxidation state for the transition metal in the catalysis than is required for olefin metathesis as under those conditions pre-mixing catalysts and the use of trialkylaluminium compounds leads to low activity catalysts. However, recent work to be published shortly tends to favour the reaction taking place by a metathesis-type route.

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Studies in electroactive polymers, 2[a)]

Soluble polyacetylene: A new synthetic route

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SUMMARY:

Polyacetylene-*block*-polystyrene was synthesized via an anionic-to-metathesis catalysis. The polymers obtained were characterized by UV/visible spectroscopy, IR spectroscopy and gel permeation chromatography.

Introduction

Polyacetylene is one of the simplest organic polymers. It has been the focus of considerable attention in recent years due to its electrical and electronic properties[1-7)]. Polyacetylene is one of the most widely studied polymer[8)] and serves as a prototype for other conducting polymers. Its infusibility and insolubility has impeded both the scientific characterization and the development of practical applications for this material. For these reasons there has been considerable research aimed at circumventing these difficulties, mainly through the production of block and graft copolymers containing polyacetylene segments and some other solubilizing block.

Polystyrene has been one of the most widely used solubilizing blocks. Previously, these block copolymers have been prepared by alkylation of $Ti(OBu)_4$ with a living polystyryllithium cocatalyst[9-12)]. The work reported in this paper emphasizes the recently reported metathetical synthesis of polyacetylene[13)] to produce a soluble block copolymer of polystyrene and polyacetylene via an ionic to metathesis catalysis.

Experimental part

Materials: Anionic polystyryllithium was prepared, under vacuum, by using butyllithium in cyclohexane as initiator, at 60 C. By altering the concentration ratio of monomer and initiator it was possible to control the number-average molecular weight of the polystyryllithium. The polymerization of styrene was carried out for 48 h to ensure total consumption of monomer and initiator.

A solution of tungsten hexachloride (from Aldrich, Gold Label) in cyclohexane was prepared. The cyclohexane was previously dried, degassed and distilled for storage over sodium/benzophenone.

[a)] Part 1: cf.[13)].

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Acetylene (from BOC) was stored in a cylinder as a solution in acetone and was purified by passing the gas through conc. sulfuric acid and then an aluminium oxide or calcium chloride drying column. The acetylene, required for the polymerization reaction, was stored in a 2 l flask fitted with greaseless taps and "Quickfit" joints.

Polyacetylene-block-polystyrene: In a typical experiment the reaction vessel, was evacuated. To the vessel 10 ml of $1{,}7 \cdot 10^{-2}$ mol $\cdot$ l^{-1} polystyryllithium was added by means of a syringe through the rubber septum cap, this was followed by 1,6 ml of $2{,}67 \cdot 10^{-2}$ mol $\cdot$ l^{-1} WCl_6. This addition and subsequent mixing caused both solutions to become colourless. The catalysts were mixed together for approximately 60 s and then acetylene was admitted to the reaction vessel. The length of time the reaction was allowed to proceed, determines the amount of acetylene in the copolymer. Shortly after the monomer was admitted to the reaction vessel, the colourless mixture of catalysts began to turn pale-blue. The colour became deeper with time, and eventually a blue precipitate was formed after 24 h. The reaction was terminated by evacuating the excess of acetylene and by addition of ethanol. The polymer was then precipitated in methanol and the blue solid dried under vacuum for 24 h.

Analyses and measurements: Carbon and hydrogen contents of the resulting polymers were determined with a CHN analyser. IR spectra were obtained using a Perkin Elmer 599B infrared spectrophotometer. Gel permeation chromatographic data were obtained with a Perkin Elmer gel permeation chromatograph, and UV absorption spectra with a Unicam SP800 and a Beckman DU7 instrument.

Results and discussion

Composition of the copolymers

Results of typical polymerizations are shown in Tab. 1.

In each of the above preparations the ratio of W/Li was 1:4. In Exp. No. 1 and 2, because of the low molecular weight of the polystyrene block, after only 1 h of acetylene polymerization a blue/black precipitate was formed in the reaction mixture. After drying, a blue powder was obtained which was insoluble in cyclohexane at room temperature. Only a small part of the polymer is dissolved after refluxing overnight in toluene, as indicated by gel permeation chromatography of the resulting solution. In Exp. No. 3 and 4, since the solubilizing block was much larger, precipitation did not occur within 24 h of acetylene polymerization. In these cases, when the polymer had been dried, it is found to be moderately soluble in a variety of solvents such as THF, toluene and carbon tetrachloride.

Tab. 1. Polymerization of acetylene with a WCl_6/polystyryllithium catalyst

Exp. and sample No.	Mol. weight of the polystyrene block	Time of acetylene polymerization in h	C:H ratio
1	3 100	20	0,975:1
2	3 100	5	1,1:1
3	61 000	24	0,83:1
4	61 000	160	0,85:1

The C:H ratios of the polymers are shown in Tab. 1, the theoretical values being 1:1 (for the copolymer and for both monomers). Samples No. 1 and 2 are very close to the theoretical value. The deviations of samples 3 and 4 are probably due to the increased acetylene content, which has proved difficult to be analyzed by this technique.

Structure of the copolymers

The IR spectra (Fig. 1) are typical traces of (a) polystyrene and (b) polystyrene/polyacetylene copolymer, synthesized by this technique at room temperature. The copolymer spectrum includes the bands at 1015 and 450 cm^{-1}, which are characteristic of *trans*- and *cis*-polyacetylene. In fact, the copolymer spectrum contains bands from both polystyrene and polyacetylene. The intensity of the band at 740 cm^{-1} is commonly used[14] to evaluate the *cis*-polyacetylene content in the copolymer. Though, in this case it is overlapped by a band from polystyrene caused by C—H out of plane deformation, making an estimate of the cis/trans ratio very difficult.

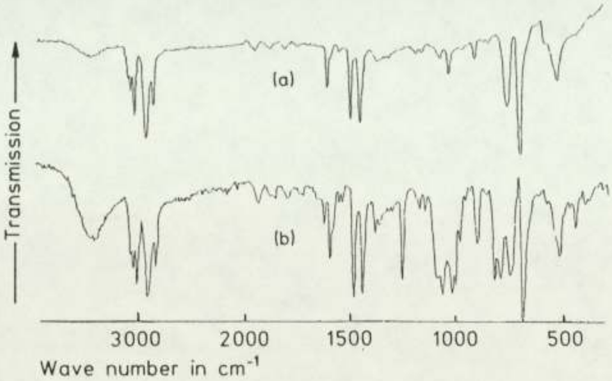

Fig. 1. IR spectrum of (a): polystyrene (b): polystyrene-*block*-polyacetylene

Although the IR spectrum of the copolymer is consistent with the presence of both polystyrene and polyacetylene, this is not sufficient proof of block formation. Evidence for block formation comes from GPC studies. A sample of homopolystyrene, taken from the living polystyryllithium prior to it's reaction with WCl was found to have a number-average molecular weight of 3100. For sample No. 1 as already mentioned, the polymer was initially thought to be insoluble, but after being refluxed in toluene for 12 h, the toluene was found to contain polymer of molecular weight 10000.

The homopolystyrene used for the preparation of sample No. 4 has a number-average molecular weight of 61000. The GPC of a sample, directly taken from the reaction vessel after acetylene polymerization and diluted with THF, revealed two peaks (since there was no fractionation) one corresponding to the original homopolystyrene and another peak corresponding to a molecular weight >200000. It is difficult to explain this result as being due to anything but block copolymer formation. It is also noticed that, with time, solutions of the copolymer gradually produce a very fine precipitate. This behaviour was previously observed[15)] in a similar solution and is explained by the gradual crystallization of the polyacetylene domains.

The UV/visible spectrum of a typical copolymer preparation in toluene is shown in Fig. 2. It shows the expected maximum absorbance in the 500 – 700 nm range due to the polyacetylene chains in solution.

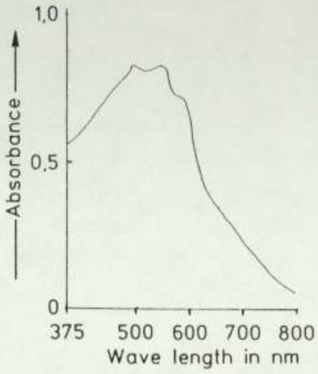

Fig. 2. UV/visible spectrum of polystyrene-*block*-polyacetylene in toluene

Conclusions

From this initial study it can be seen that it is possible to employ the metathesis reaction to produce polyacetylene-*block*-polystyrene using an anionic-to-metathesis transformation reaction. The important factor in this synthesis is the ability to control the block length of both the acetylene and the styrene. The anionic polymerization of styrene and the control of the molecular weight have been well documented, but in this synthesis the normal Ziegler/Natta type catalysts for the polymerization of acetylene was replaced by the newer metathesis catalyst. The advantage of the metathesis catalyst is that the rate of polymerization of the acetylene is much slower than with the Ziegler/Natta type catalysts. This enables the molecular weight of the acetylene segment to be as accuratly controlled as the styrene segment.

Further work is being conducted on the physical properties of these copolymers including their morphology and various electrical properties. Investigations are also being conducted into the nature of the active species present during the acetylene polymerization.

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Studies in electroactive polymers, 3[a)]
Synthesis of cyclopentene/acetylene copolymers using metathesis catalysts

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SUMMARY:

Copolymers containing acetylene and pentenamer units were synthesized by sequential addition of cyclopentene and then acetylene to an active metathesis catalyst system. The formation of block copolymers was indicated by UV-vis spectroscopy, gel permeation chromatography and infra-red spectroscopy.

Introduction

The potential usefulness of an electrically conductive polymeric material has been recognised for several years[1)]. Although several polymers such as polyacetylene (which is known to exhibit appreciable conductivity when doped with certain reagents such as iodine) may be fairly easily synthesized[2)], intractibility and insolubility severely limit both the characterisation and potential applications of these materials. It is for this reason that the production of 'soluble polyacetylene' has been the focus of much recent research.

The most common mechanism by which polyacetylene chains may be solubilised is by chemically bonding them to a carrier polymer which is itself soluble in common organic solvents. Thus, provided that the carrier chains are sufficiently long, the resulting block or graft copolymer will usually be rendered soluble.

Theoretically, block copolymers of this type could be synthesized by sequential addition of acetylene and another monomer to a Ziegler/Natta catalyst, but in practice the active site lifetimes in such systems are too short. This is mainly due to the presence of chain transfer reactions which produce 'dead' homopolymers and deactivate the catalyst. This problem does not arise if the carrier polymer is synthesized first by anionic polymerisation, which allows careful control of chain length, followed by transformation of the active centres to Ziegler/Natta sites which will polymerise acetylene. This method has been used successfully to produce soluble copolymers of acetylene with styrene, isoprene and butadiene[3–5)].

[a)] Part 1: A. J. Amass, M. S. Beevers, T. R. Farren, J. A. Stowell, *Makromol. Chem., Rapid Commun.* **8**, 119 (1987); Part 2: J. A. Stowell, A. J. Amass, M. S. Beevers, T. R. Farren, *Makromol. Chem.* **188**, 1635 (1987).

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Following our recent report of the formation of block copolymers of styrene and acetylene using anionic-to-metathesis transformation reactions[6], we would now like to report the formation of polypentenamer/acetylene block copolymers by sequential addition of the monomers to a metathesis catalyst system. During the cyclopentene ring-opening polymerisation the polypentenamer chains produced are terminated by tungsten complexes which assumedly form the loci of acetylene monomer addition. The formation of block copolymers indicates that acetylene shows far greater activity towards this active site than does cyclopentene. It would appear that such a route is not available using Ziegler/Natta catalysts as, although termination occurs in both Ziegler/Natta and metathesis systems, the double bonds present in the dead polypentenamer may compete for metathesis active sites thus creating a pseudo living system.

Experimetnal part

Materials

Dried, degassed cyclohexane was prepared as described previously[7] and was distilled from sodium/benzophenone under high vacuum into a reservoir flask or used directly to prepare solutions containing tungsten hexachloride (Aldrich) or dichloroethylaluminium (Schering). Cyclopentene (Aldrich) was purified by standing over freshly cut sodium slices followed by distillation onto sodium/benzophenone. Acetylene was stored in a cylinder as a solution in acetone and was purified by passing the gas through concentrated sulfuric acid and then a calcium chloride drying column. The gas was collected in a 2 dm^3 storage bulb which was fitted with greaseless taps and Quickfit joints and could be connected to the polymerisation vessel at (A) (see Fig. 1).

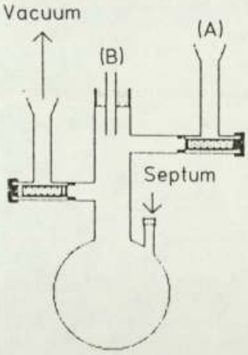

Fig. 1. Apparatus for the copolymerisation of cyclopentene and acetylene (see text)

Polymerisation procedure

The vessel used for the copolymerisations is shown in Fig. 1. A cyclohexane reservoir was attached to the flask at (B). In a typical experiment, the polymerisation vessel was evacuated and 26 cm^3 of cyclohexane was added from the reservoir. 0,12 mol of cyclopentene were then distilled into the reaction chamber under high vacuum. The catalyst components were added to this solution by syringe through the rubber septum cap. Thus, $1,6 \cdot 10^{-4}$ mol WCl_6 was added followed by $6,4 \cdot 10^{-4}$ mol $AlEtCl_2$, a time delay of 2 min being allowed between additions. The cyclopentene ring-opening polymerisation was allowed to proceed for 13 min producing the usual brown coloured solution commonly associated with such reactions. Acetylene was then admitted to the reaction chamber and the brown solution gradually changed to black. After 24 h, the reaction mixture was poured into excess methanol and a black elastomer was isolated, which was dried under vacuum at 30 °C for 24 h. The polymer was found to be soluble in several common organic solvents (e.g. cyclohexane, toluene, THF, ...) producing red/brown solutions which slowly decolourised to form black insoluble precipitates.

Analysis of materials

The ultraviolet/visible spectra of 1% solutions of the copolymer were recorded on a Beckman DU7 spectrophotometer using cyclohexane as solvent and reference. Gel permeation chromatographic data was obtained using a Perkin-Elmer chromatograh with THF as solvent. The column eluent was analysed by a differential refractometer and a variable wavelength UV-vis detector connected in series. Infra-red spectra were recorded using a Perkin-Elmer F. T. I. R.

Results and discussion

Polymerisation

Tab. 1 shows the effects of cyclopentene pre-polymerisation time on the yield and solubility of the products obtained in this series of experiments. In experiment 1, the catalyst components were added to a mixture of the two monomers in cyclohexane. The initially formed brown solution turned purple and a black precipitate formed after 2 min. After 20 h, the black precipitate was filtered from a yellow solution. In contrast, the copolymerisations in which cyclopentene was first polymerised by metathesis before acetylene was admitted to the reaction vessel produce highly viscous, intensely coloured copolymer solutions. The products of these reactions could be obtained by precipitation in methanol and appeared as black elastomeric materials which would redissolve in common organic solvents.

From the results shown in Tab. 1 it would appear that the yield of soluble material increases as the time delay between the addition of catalyst and acetylene admission increases. Whether the relative amounts of copolymer and homopolymer in the samples are also affected still remains unclear.

Tab. 1. Copolymerisation of cyclopentene and acetylene[a)]

Sample	$\frac{[\text{Cyclopentene}]}{\text{mol}\cdot\text{dm}^{-3}}$	$\frac{[WCl_6]\cdot 10^3}{\text{mol}\cdot\text{dm}^{-3}}$	Cyclopentene polymerisation time in min	State (yield in g)
1	2,67	3,6	0	Insoluble (0,2)
2	2,75	3,1	5	Soluble (0,9)
3	2,77	3,5	13	Soluble (1,4)
4	2,75	3,6	90	Soluble (3,5)

[a)] Mole ratio $[WCl_6]/[AlEtCl_2] = 1:4$, volume of solution: 45 cm^3, acetylene polymerisation time: 20 h, temp.: 20 °C.

UV-vis spectroscopy

Fig. 2 shows the UV-vis absorption spectrum of a sample of polypentenamer, prepared by the method outlined previously, but without the addition of acetylene. There is essentially no absorption at wavelengths greater than 340 nm. Fig. 3 shows the UV-vis spectrum of one of the copolymer samples pepared by this technique. Apart from the peak at 214 nm a new, broad absorption is present, centred around 400 nm, which extends well into the visible region. This absorption resembles that obtained for suspensions of crystalline polyacetylene, however, the maximum for these systems reportedly occurs at 685 nm[8]. It would therefore appear that the copolymer samples consist of a mixture of variable length polyene segments which are attached to polypentenamer chains. The observed shift of the polyene chain absorption to shorter wavelengths suggests that these chains are, however, relatively short. Indeed, when the spectrum is examined more closely, remnants of the multiple peak absorptions characteristic of short polyene chains can be seen clearly. By comparision with the polyene spectra[9] an average polyene chain length in the copolymer sample may be tentatively estimated as being between eight and ten units.

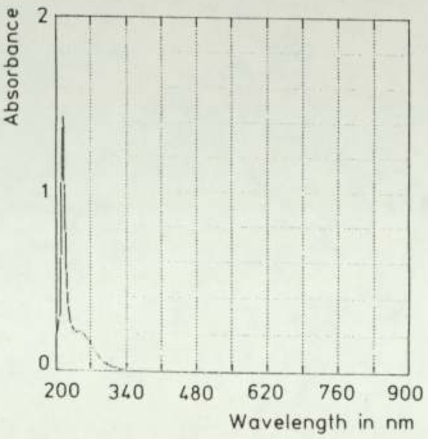

Fig. 2.

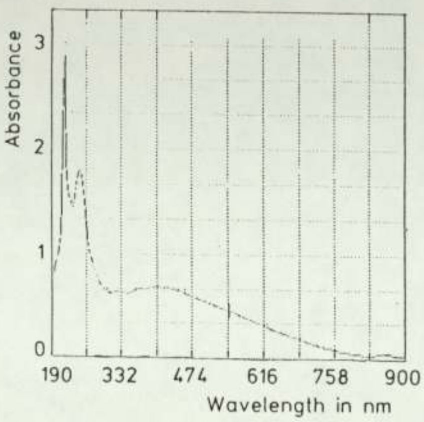

Fig. 3.

Fig. 2. UV-vis spectrum of polypentenamer in cyclohexane

Fig. 3. UV-vis spectrum of polypentenamer-*block*-polyacetylene in cyclohexane

The UV-vis spectrum of the yellow filtrate obtained from experiment 1 is shown in Fig. 4 and is consistent with this solution also containing a mixture of low molecular weight polyenes; however, the absence of any broad absorption in the visible region indicates that these units are not attached to polypentenamer chains.

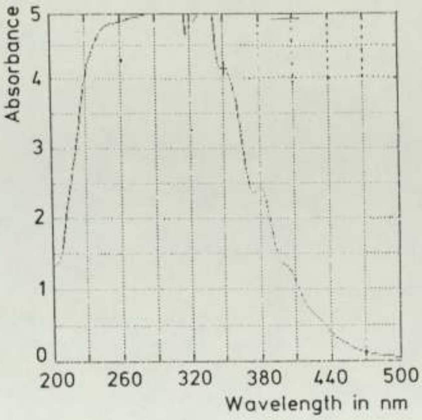

Fig. 4.

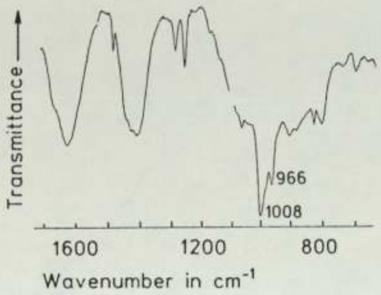

Fig. 5.

Fig. 4. UV-vis spectrum of soluble material from experiment 1

Fig. 5. Infra-red spectrum of the insoluble polypentenamer-*block*-polyacetylene obtained in experiment 1

Infra-red spectroscopy

The infra-red spectrum of the black solid obtained in experiment 1 is shown in Fig. 5. The peak at 966 cm^{-1} is consistent with the presence of *trans*-polypentenamer units$^{10)}$ and the absorption at 1 008 cm^{-1} has been tentatively assigned to the C—H in plane bending mode of the *trans*-polyacetylene segments which usually occurs at about 1 012 cm^{-1}.

The infra-red spectra of the copolymers obtained in experiments 2 – 4 showed absorptions typical of polypentenamer but not those of polyacetylene. It can only be concluded that the amount of acetylene incorporated is zero or very low.

Gel permeation chromatography

A typical GPC trace for one of the copolymer samples is shown in Fig. 6. The bimodal distribution which is common for polypentenamer prepared by ring-opening polymerisation is clearly visible from the differential refractometer response, but a small shoulder at high molecular weight is also apparent.

The UV-vis detector response at 400 nm shows that the sample contains some high molecular weight material which is absorbing in the visible region. As polypentenamer itself shows no absorption at this wavelength, such a result can only be explained by concluding that the sample contains some polyene units which have become attached to polypentenamer chains. This evidence also seems to suggest that the materials produced in these experiments consist mainly of polypentenamer homopolymer chains, the presence of which masks the copolymer distribution in the refractometer trace, except for the small high molecular weight shoulder.

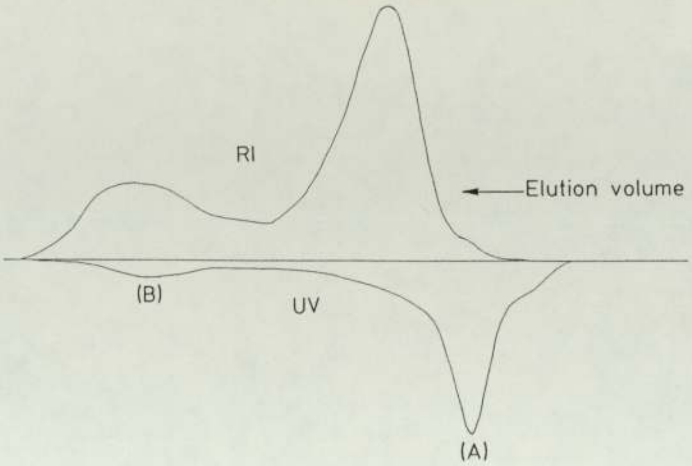

Fig. 6. Gel permeation chromatograph trace of soluble polypentenamer-*block*-polyacetylene using refractive index (RI) and UV (at 400 nm) detection

The fact that the copolymer distribution, as seen in the UV-vis trace, seems to extend towards very high molecular weights and yet the polyene segments may only be short can be explained by the aggregation of the polyene chains which has recently been reported to occur in 'soluble polyacetylene' systems[11]. The aggregation into micellar type structures would be expected to occur since the solubility parameters of the polyene chain in the solvent are so unfavourable. Direct correlation between the high molecular weight material and the broad UV-vis absorption centered around 400 nm can be made by considering the change in the GPC UV-vis detector response for the same copolymer sample as the wavelength is varied. Tab. 2 details the relative heights of the two main peaks obained from the UV-vis detector at various wavelengths. As the wavelength increases, the absorption due to the higher molecular weight material increases relative to that of lower molecular weight. It is also interesting to note that as the wavelength decreases, not only does the high molecular weight

Tab. 2. Variation of UV-vis detector response with wavelength

Wavelength in nm	Height of peak (A)/height of peak (B)
450	4,1
400	2,9
350	1,9
300	1,2

peak diminish, but the secondary peak at lower molecular weight becomes more significant. This peak may be due to oligomers containing polyene segments.

Conclusions and further work

Although the results presented here would seem to indicate copolymer formation, at present this synthetic technique does not allow its separation from homopolymer. Attempts are at present being made to improve the yields of copolymer and to control the respective block lengths. The samples already produced are currently being characterised by various means including electrical conductivity measurements.

T. R. Farren and J. A. Stowell would like to thank the *University of Aston* for the provision of financial support during the course of this work.

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