polymer review

Synthesis of block and graft copolymers containing polyacetylene segments

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The area of conducting polymers has been the subject of a great deal of discussion in the literature over the last 15 years. Polyacetylene is the material that has received the most attention during this period with strenuous efforts being made to produce a soluble copolymer containing polyacetylene segments. This paper is an overview of the synthetic techniques that have been used in order to try and produce these materials, which are both highly conducting and soluble in common organic solvents. Special emphasis has been placed upon the work which has led to the development of new catalyst systems and the work that has combined previously well characterized catalyst systems to produce novel materials.

(Keywords: polyacetylene; block copolymer; graft copolymer; synthesis; conducting polymers)

INTRODUCTION

Organic compounds have conductivities which are typically many orders of magnitude less than those of metals. The polymeric sub-group is at the lower end of this conductivity range and polytetraflourethylene is one of the best insulating materials known. In most polymeric materials it is difficult to observe any electronic conductivity whatsoever. However, there is a special class of polymers that have a conjugated π-electron backbone and exhibit special electronic properties. Polyacetylene is the simplest member of this class. It is therefore studied most often and serves 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*). The first studies on acetylene polymerization were reported in 1866 by Berthelot[1,2]. The first extensive investigations into the polymerization of acetylene to high molecular weights, using Zeigler/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 shiney, 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} ohm^{-1} cm^{-1}) to semi-conductor to metal (10^3 ohm^{-1} cm^{-1}), depending on the nature and amount of dopant incorporated as shown in *Figure 2*. This disclosure sparked off an immense effort to discover more about doped polyacetylene, both with regard to the mechanism of its conductivity and its 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 metals in industries such as electronics. Unfortunately the infusibility, instability and insolubility of polyacetylene has impeded both the scientific characterization 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, based on the assumption that the soluble part of these materials would solubilize the previously insoluble polyacetylene.

Of these two approaches the block and graft copolymers have provided materials that are both soluble and highly conducting. It is the purpose of this review to outline the preparation and properties of these materials.

BLOCK COPOLYMERS CONTAINING POLYACETYLENE

The initial driving force for the production of copolymers containing polyacetylene was to use them to provide the

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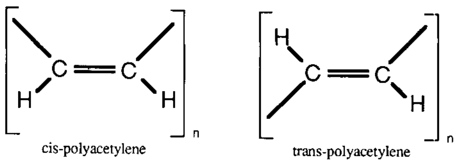

Figure 1 *Cis* and *trans* configurations of polyacetylene

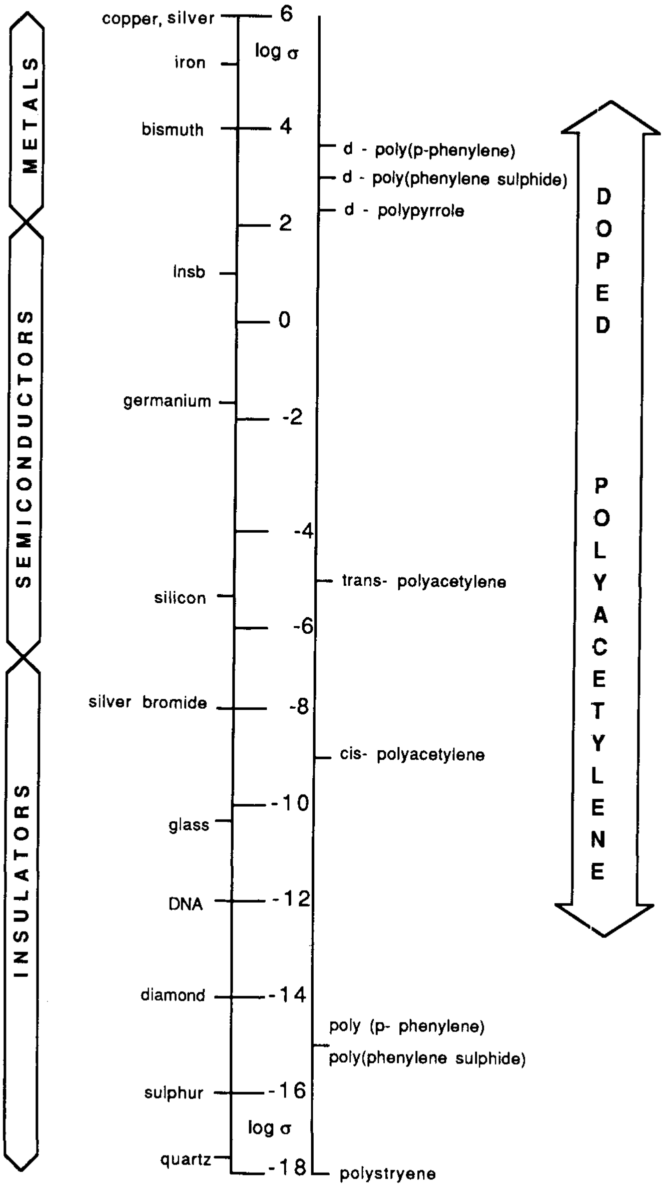

Figure 2 Comparison of the electrical conductivity of metals, semiconductors and insulators; d, doped materials

means to begin to characterize polyacetylene and to provide information such as molecular weight, molecular weight distribution and steric homogeneity. For these reasons Wegner and coworkers[19] copolymerized acetylene with a number of l-alkylnes 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. 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 pentafluoride caused the copolymer films to become conductive, reaching a maximum value of $45\,ohm^{-1}\,cm^{-1}$ for a copolymer containing 55% polyacetylene doped with arsenic pentafluoride. 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 to those of homo-polyacetylene. They showed no fibrillar morphology and swelled in toluene and pentane, were highly elastic when wet, though they are insoluble and did not exhibit melting behaviour.

'Soluble' copolymers of a high molecular weight were synthesized 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 solubilizing block. The polyacetylene retains the electrical and spectroscopic properties of the homo-polymer, but it is claimed that now it is isolated from other polyacetylene chains in solution, effectively removing the chain–chain and interfibril perturbations of the single chain properties of polyacetylene. However, in recent years some workers have published evidence for aggregation in solution[49].

The starting point for production of the copolymer was a carrier polymer (either polyisoprene or polystyrene) which is nearly monodisperse, with a number average molecular weight of 2×10^5, that had been modified by oxidation to contain electrophilic sites. The electrophilic sites were epoxides introduced without chain scission by *m*-chloroperbenzoic acid. Acetylene was polymerized using a $Ti(OBu)_4/AlEt_3$ catalyst in 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 'solubilized polyacetylene' refers to polyacetylene copolymers which are able to pass through filters with pores sizes as small as 0.2 μm and which are not readily separated from the carrier homopolymer by centrifugation. The oligomers were prepared by a room temperature polymerization of acetylene in the presence of acetone. The polymerization 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 polymerization took 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 characterization question is the microscopic state of the solubilized polyacetylene. Small amorphous aggregates, micro crystals or single chains are all possible states for the system. A recent light scattering study[25] found the persistance 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].

N.m.r. 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 n.m.r. signal from solutions of the solubilized polyacetylene. This result is of no real surprise because previous n.m.r. 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 solubilized polyacetylene may have restricted motion within the aggregate resulting in an extremely broad signal. A dried sample of the solubilized polyacetylene was examined by solid state n.m.r. and a signal attributable to *trans*-polyacetylene[27–29] was observed at 138 ppm 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 per cent 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. The first was the use of doped polyacetylene as a macromolecular initiator for the synthesis of graft copolymers and the second was the use of a transformation reaction as a route to block copolymer synthesis.

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

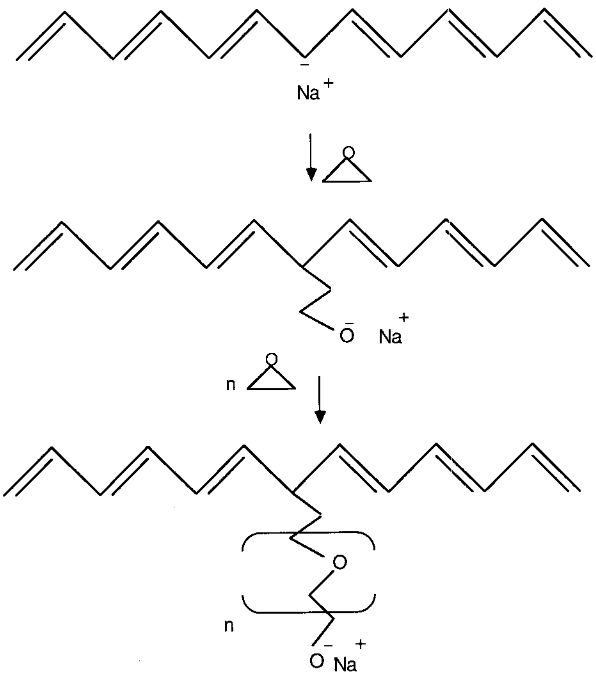

Figure 3 Ring opening polymerization of ethylene oxide

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

The synthesis of the block copolymer was achieved by using a 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 polymerization. In this case a catalytically active titanium based species was generated by the alkylation of $Ti(OBu)_4$ with polystyryl-lithium (*Figure 4*).

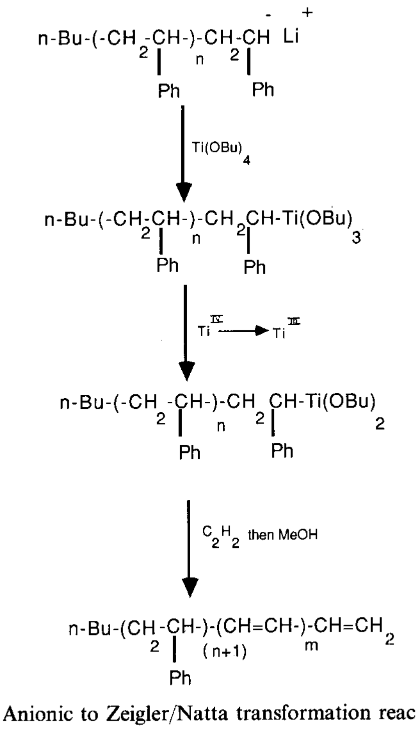

Figure 4 Anionic to Zeigler/Natta transformation reaction

G.p.c. was used to show that the polystyryl-lithium initially had a number average molecular weight of around 28 000 and after reaction with acetylene this had 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 increases, even when additional solvent was added to counteract viscosity effects. For example, when the polystyryl-lithium had a number average molecular weight of 32000 it took 15 minutes before precipitation took place; when the number average molecular weight was increased to 42000 it took 36 minutes for precipitation to occur.

Later studies centred 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 polymerized 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 $^{14}C/^{3}H$ ratio similar to that of the control. The results given do not provide definite proof of block formation, though the products do contain significant quantities of ^{14}C.

The yield of block copolymer is only about 2–5%. This may be 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 synthesized by Aldiss[38–42] using similar synthetic techniques 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 can easily be controlled. An equimolar quantity of $Ti(OBu)_4$ based on the lithium concentration is then added to the living polymer. When acetylene gas is admitted copolymers are formed as gels on the surface of the catalyst solution or as soluble materials in the reaction medium.

The length of the solubilizing block plays an important part in determining the properties of the copolymers. 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 $ohm^{-1}\,cm^{-1}$. 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 (ps) 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 of filled polymers (conducting composites). The morphology of the copolymers is also very dependent upon the content of the solubilizing 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 $[Na_{0.057}(CH)_x]$ was prepared by reacting the polyacetylene with sodium dihydronaphthalide. This charge transfer complex was then used as an initiator for the anionic polymerization of methyl methacrylate. By these means a soluble form of polyacetylene was produced but only when the molar ratio $MMA:(CH)_x > 1.5$. G.p.c. data shows that the copolymer possesses a broad molecular weight distribution. This is probably due to the considerable chain transfer and auto termination that occurs when methyl methacrylate is polymerized with organo-sodium compounds.

This soluble form of polyacetylene exhibits photoelectric behaviour and, from the absorbtion spectra threshold, the energy gap (E_g) was estimated at 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 synthesized by Bolognesi and coworkers[45–50] by grafting polyenic chains onto 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 polymerization 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 5*). The carrier polymers are either polybutadiene or polyisoprene. It should be noted that it is the quantity

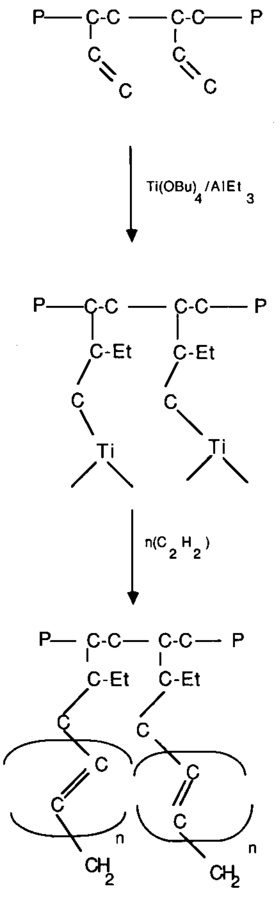

Figure 5 Reaction between $Ti(OBu)_4/AlEt_3$ and a vinyl side group followed by acetylene polymerization

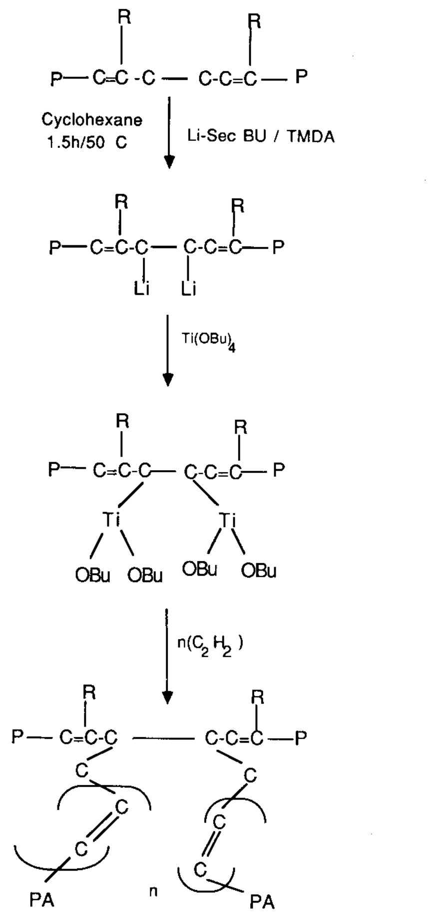

Figure 6 Lithiation followed by reaction with $Ti(OBu)_4$ and acetylene polymerization

of titanium in the reaction mixture that dictates the number of sites activated.

The second preparation is based on the formation of carbanions on the carrier polymer and is a three step reaction (*Figure 6*). Initially there is a reaction of s-butyllithium with *cis*-1,4-polybutadiene in dry cyclohexane. The presence of tetramethylene diamine (TMDA) favours the formation of carbanions in the allylic positions of the polymer matrix. Secondly, there is 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 are reduced to Ti(III) species. Acetylene is then polymerized to produce a copolymer which is dark blue. Upon doping with iodine the copolymer has a conductivity of $1.4 \times 10^{-3}\,\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$. Once again the conductivity depends 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 areas). Light scattering experiments from the solubilized polyacetylene provide further evidence for aggregation in solution, with a radius of gyration of 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) $\{CH_2{-}CH_2{-}CH{=}CH\}_n$ as an alternating copolymer of acetylene and ethylene and as the enthalpically least stable isomer of poly(acetylene-co-ethylene) $[(CH_2CH_2)_x{-}(CH{=}CH)_y]$. Their aim was to achieve a positional isomerization 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 isomerization is thought to be as shown in *Figure 7*. The progress of the isomerization was followed by i.r. and u.v. spectroscopy. The final product has a conductivity of $5 \times 10^{-7}\,\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1}$. 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 is found not be be a function of the temperature but is a function of the strength of the base used.

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 naphthenate/diethyl aluminium chloride in toluene. The purified polymer is either a yellow viscous liquid or waxy polymer. This random copolymer can be readily deprotonated with alkyl-lithium to produce an anionic polymer with the expected spectroscopic

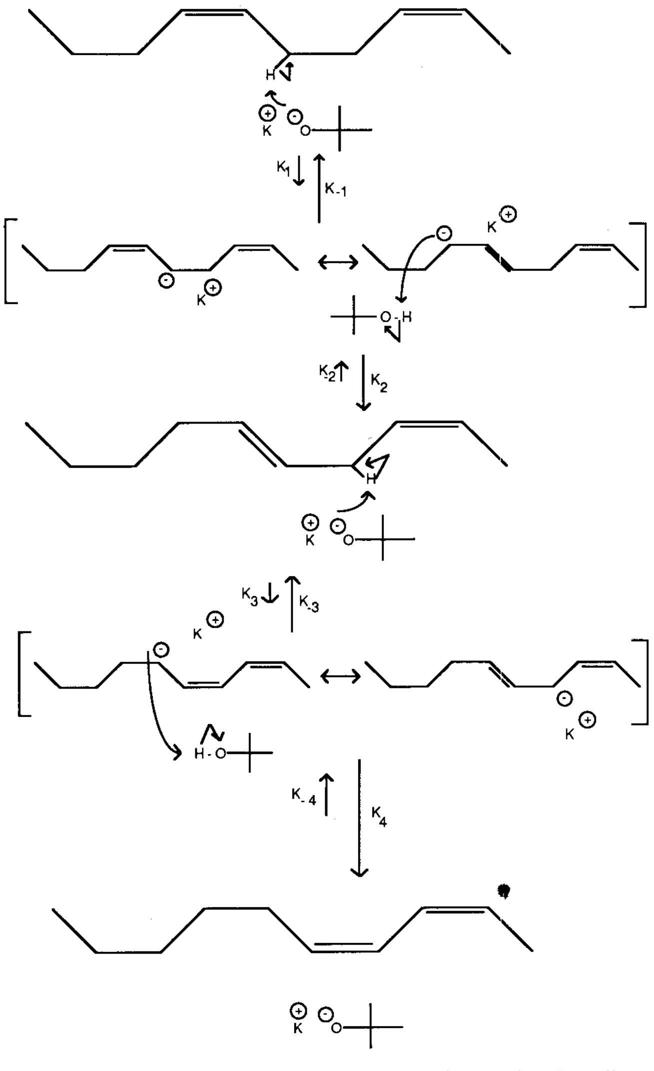

Figure 7 Base catalysed isomerization of acetylene/butadiene copolymer

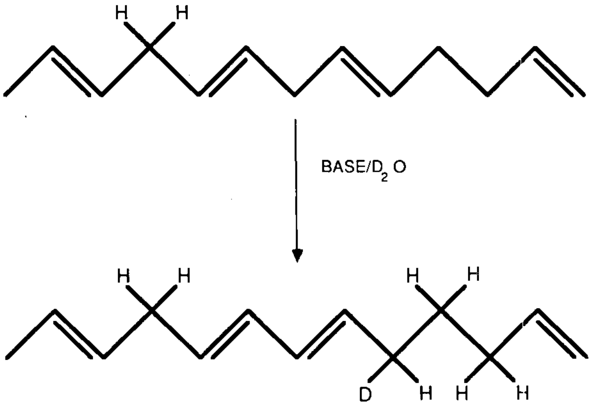

Figure 8 Base catalysed isomerization of poly 1,3-butadiene

characteristics. Reprotonation with D_2O generates a modified neutral polymer in which double bonds have been brought into conjugation (*Figure 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 show 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 polymerization of F-propene and acetylene gas mixtures[58]. The films formed were examined by elemental analysis and i.r. 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 $1.4\times10^{-4}\,ohm^{-1}\,cm^{-1}$. This rose to $5\times10^{-1}\,ohm^{-1}\,cm^{-1}$ for the insoluble copolymer containing 78% acetylene. None 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 9*). It is thought that the polyacetylene segment has a molecular weight of 1200. The low temperature nature of the reaction resulted in an all *cis*-polyacetylene portion of the copolymer, though appreciable isomerization to the *trans*- isomer was observed over a period of 23 h at room temperature. As yet the electrical properties of this material have not been determined.

CONCLUSIONS

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. There is little doubt that it is the problems associated with the control of the molecular weight of the polyacetylene segments that has yet to be overcome. This means that there is a real need to develop a new catalyst system that is active towards acetylene polymerization. The Ziegler catalyst which has been predominantly used up to this time appears to provide little control over the molecular weight of the acetylene block, and invariably leads to insoluble polymers.

It is noticeable that unlike vinyl polymers which have been investigated and manufactured in large quantities, the polymerization of acetylenes has not been the subject of much study because of the difficulty of obtaining high molecular weight materials by conventional radical, cationic or anionic polymerization. Only a few transition metal catalysts are known to polymerize acetylene by Ziegler/Natta or metathesis catalysis to yield high molecular weight polymers. It is our belief that utilization of one of the recently reported[61,62] metathetical type catalyst systems could be used to control the acetylene polymerization.

The electrical properties of all the copolymers have been shown to depend on the polyene content, which is not surprising since it is an inherent property of the polyene chain. In order to restrict the polymerization of acetylene we have utilized an anionic-to-metathesis transformation reaction to produce a catalytic site which is much less active to acetylene polymerization[63].

The electrical conductivity of the copolymers generally is not high enough to make them interesting to the electronic industry. This is not surprising because the

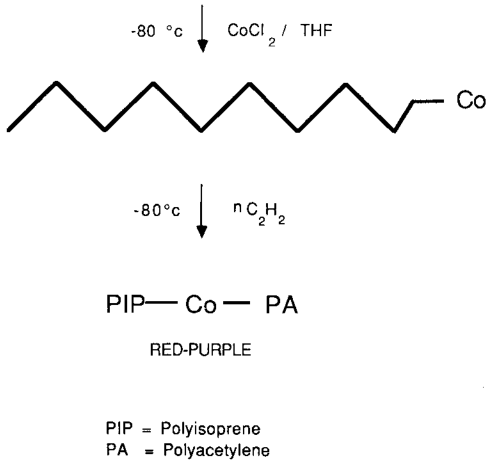

Figure 9 Anionic to Ziegler/Natta transformation reaction using cobalt

solubilizing monomer is usually an insulator. With the development of new catalyst systems (e.g. anionic to Ziegler/Natta transformation reaction) this problem could be overcome by using new comonomers such as poly-n-vinyl carbazole which is soluble in many organic solvents, initiated by anionic polymerization and photoconductive. This means a new range of materials could be synthesized which may play a leading role in the industries of the future.

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