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CONJUGATED POLYMERIC SYSTEMS

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by

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Abstract

CONJUGATED POLYMERIC SYSTEMS

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Kariyawasam Patuwata Withanage Pemawansa

Advisers: Professors Nan-Loh Yang and George Odian

A series of polymers containing modified polyphenylene structures have been synthesized by aromatic nuclear coupling of conjugated monomers with terminal aromatic groups and oxidative coupling of aromatic monomers with terminal acetylene groups. The monomers were cis- and trans-stilbene, diphenyl acetylene, 1,4-diphenyl-1,3-butadiyne and 4,4'-diethynylbiphenyl. The mechanism of aromatic nuclear coupling polymerization of cis- and trans-stilbene is probably radical cationic. Polymer structures were characterized by ^{1}H and ^{13}C NMR, IR, ESR, VPO and chemical methods. Results of such experiments revealed that aromatic nuclear coupling is a facile route to modified polyphenylenes. However, this reaction could be complicated if the monomer has triple bonds or double bonds attached to its phenyl groups. The electrical and thermal properties of these polymers were studied and correlated with their structures to obtain structure-property relationships. The results showed that tractability and electrical conductivity are not mutually exclusive for these polymers. Higher ionization potential, non-planar structures and cumulated double bonds presented barriers for the electrical conductivity of these doped polymers. The results of the thermal

property studies showed that the flexibility of the backbone, large pendant groups and non-planar or non-linear structures could lower the thermal stability of a conjugated polymer remarkably.

ACKNOWLEDGEMENT

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I. INTRODUCTION AND LITERATURE SURVEY

The performance, cost and processibility advantages of organic polymers have led to the increasing displacement of conventional metals and inorganic materials in a variety of areas. However, these application possibilities have been limited to those in which electrical conductivity was not an absolute requirement. Nearly a decade ago, it has been appreciated that there could be many advantages of conducting polymeric systems over the conventional metallic and semiconductors(1).

Theoretical studies have shown that the electronic conductivity of an organic polymer is not an impossible process. It has even been predicted that an organic polymer consisting of a conjugated carbon backbone with highly polarizable side groups("Little model", Fig.1) could exhibit superconducting properties at high temperatures(2,3).

The proposed macromolecular superconductor (Little model) presented a very challenging problem for the synthetic organic chemists. As a result of this, a large number of organic polymers and molecular complexes have been synthesized, characterized and their electrical properties have been studied(4). Although the total synthesis of the "Little model" has not been accomplished yet, the conjugated spine and its related structures have been synthesized. Typical examples of such polymers are I, II and III. These polymers contain large electronic band gaps. An electronic transition from the valency band to the conduction band requires a large amount of energy(Fig.2). Under normal conditions such an electronic transition would not be

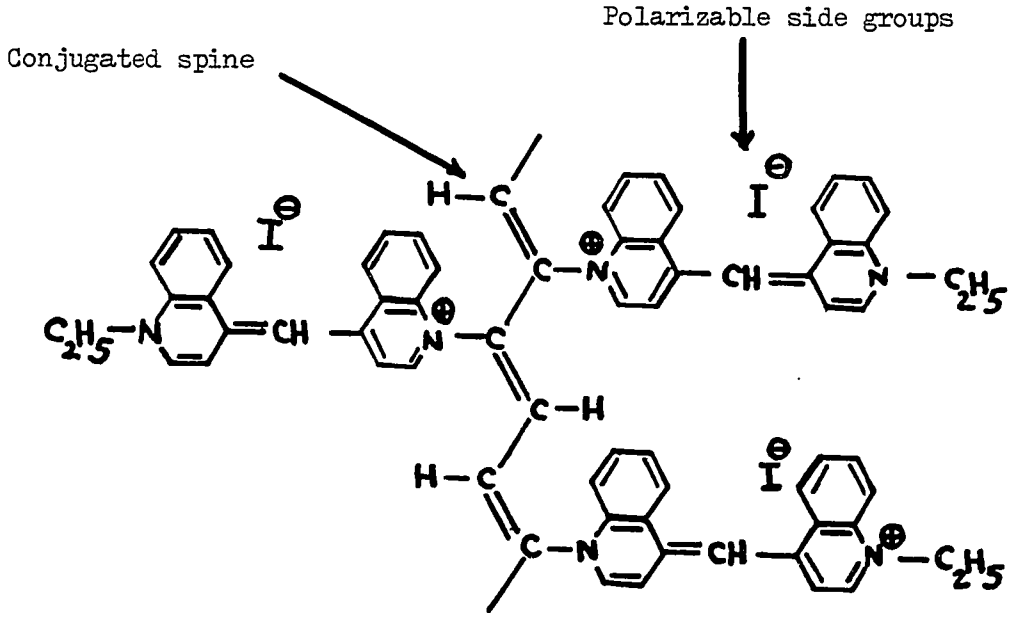


Figure 1. "Little model", a proposed macromolecular superconductor.

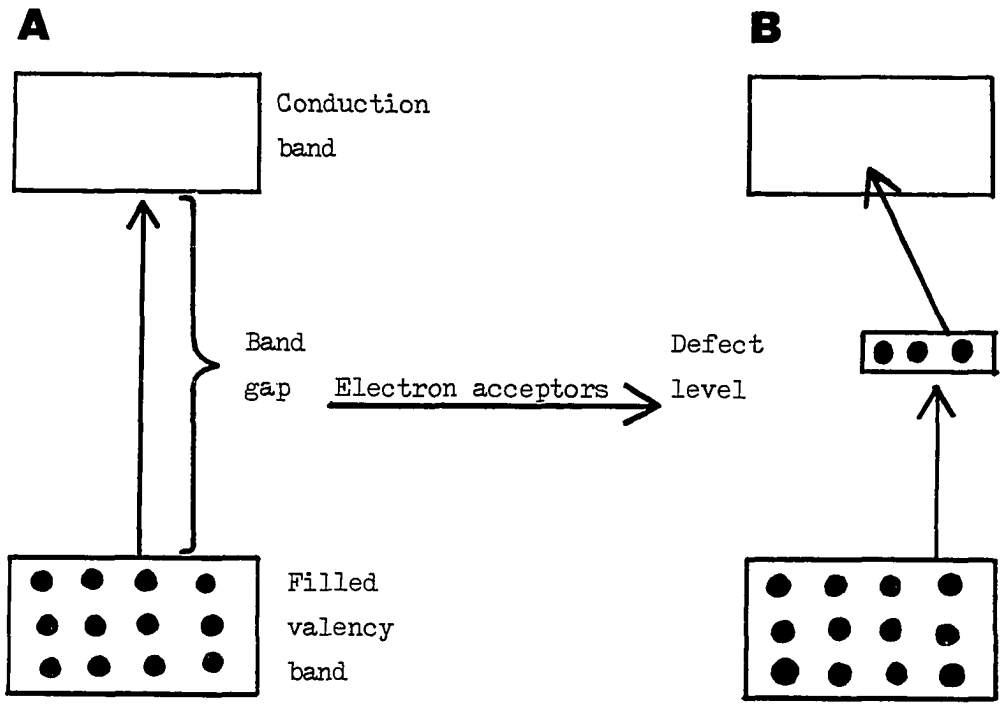
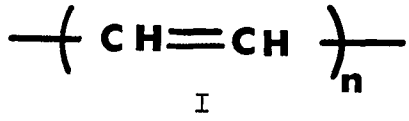


Figure 2.Band levels of A. Native polymer, B. Doped polymer.

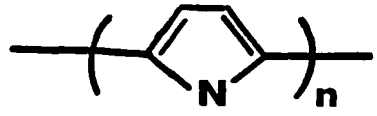


I

Polyacetylene

II

Polyphenylene



III

Polypyrrole

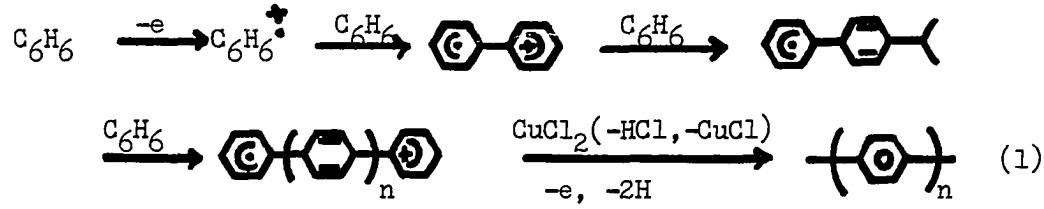
possible and they are insulators in the native state. However, the above situation could be changed by incorporating electron acceptors into the polymer matrices. Electron acceptors abstract electrons from the valency band and lower the band gap(Fig.2). Under such conditions, an electron transition from the defect level to the conduction band requires a relatively small amount of energy. At room temperature, the available thermal energy is sufficient to bring about this transition. Thus they exhibit conducting properties when they are doped with electron acceptors. Depending on the dopant level, they assume conductivities anywhere in the range of the metallic regime to the insulator state. Due to this reason, much attention has been given to the conjugated spine of the "Little model" and its related structures, over the last few years(5).

Polyphenylene and polyacetylene, two of the most thoroughly investigated systems, form conductive doped systems with the highest

conductivity values ever reported for charge transfer complexes of organic polymers(6-11). Compared to polyphenylene, polyacetylene has a lower ionization potential(4.7 eV) and requires mild electron acceptors such as iodine to form metal-like conductive charge transfer complexes(7-9). However due to its insolubility and poor stability towards oxygen, this system has not yet been developed to meet practical applications. Polyphenylene has a higher ionization potential compared to polyacetylene and requires very strong electron acceptors such as AsF_5 to promote its conductivity to the metallic regime(10,11). In fact AsF_5 is the only electron acceptor sufficiently effective for this purpose. Intractability, again, and the poisonous nature of the dopant are the major draw backs of the polyphenylene system. Although substantial progress has been made, the above problems associated with these two systems have not been solved yet. Modifications of these two systems to overcome their deficiencies without sacrificing their electrical conductivities, or the development of novel conducting polymers with tailor-made properties require the basic knowledge of the structure-property relationship of electro-active polymers. With this view in mind, we have initiated this program to investigate the properties of polymeric systems which are structurally related to the above two polymers.

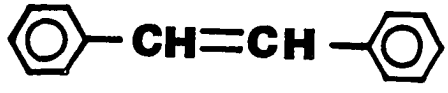
Aromatic nuclear coupling can be a facile synthetic route to modified polyphenylene(12). Benzene, one of the simplest aromatic monomers, polymerizes to polyphenylene by the following reaction

sequence(13).



(1)

More complex aromatic monomers such as naphthalene(12) and biphenyl (14) react in a similar manner under the same conditions. We have chosen this route to prepare modified polyphenylenes by extending the scope of this reaction to conjugated monomers with terminal aromatic groups. The following readily available monomers, IV, V, VI were selected for the above purpose.

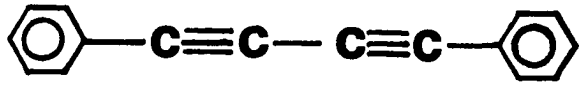


IV

Cis- and trans-stilbene

V

Diphenyl acetylene



VI

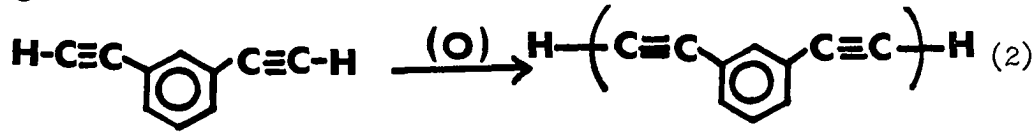
1,4-diphenyl-1,3-butadiyne

These monomers have never been polymerized by aromatic nuclear coupling before. As is the case for any novel reaction, the detailed characterization of the structures of the final products and

investigation of the reaction mechanism are essential to understand this reaction route.

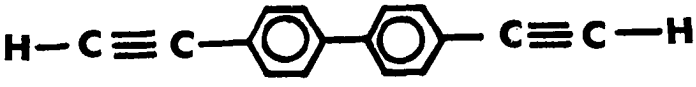
Oxidative coupling of aromatic monomers with terminal acetylene groups also can be an effective method to prepare modified polyphenylene. However, unlike aromatic nuclear coupling, this reaction produces well defined tailor-made polymeric structures(reaction 2), (15).

eg.

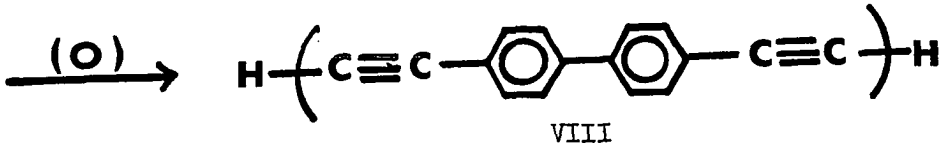


(2)

We have selected this route to polymerize 4,4'-diethynylbiphenyl(VII) to yield the polymer structure VIII.



VII



(3)

VIII

One other purpose of this synthesis was to compare the properties of this polymer with the properties of 1,4-diphenyl-1,3-butadiyne polymer synthesized by aromatic nuclear coupling. The polymers synthesized by the two different routes should have the same

structure(except for end groups).

In addition to their conducting(electrical) properties, conjugated polymers in general enjoy high thermal stability(16). The above four polymers also belong to this class and may exhibit very interesting thermal properties. Investigation of the thermal properties of these four polymers with a view to understand the origion of the thermal stability of conjugated polymers is also an objective of this project.

II. EXPERIMENTAL

A. Materials

The following compounds were used as received: Anhydrous $CuCl_2$ (Aldrich), anhydrous $AlCl_3$(technical grade, sublimed, Fisher), iodine (Fisher certified, resublimed), bromine(Baker analysed, reagent grade), cis-stilbene(97%, Aldrich), 1,4-diphenyl-1,3-butadiyne(99%, Aldrich), biphenyl(99%, Aldrich), acetyl chloride(99%, Aldrich), PCl_5(Aldrich), PCl_3(98%, Aldrich), CuCl(99%, Aldrich) and 10% Pd on carbon black (Alfa Products). Solvents were Fisher reagent ACS grade and dried over 4Å molecular sieves for a few weeks. Trans-stilbene(96%, Aldrich) was recrystallised three times from absolute ethanol before use.

B. Aromatic nuclear coupling

For the polymerization of cis and trans-stilbenes by aromatic nuclear coupling, cupric chloride was used as the oxidant. The polymerization of diphenyl acetylene and 1,4-diphenyl-1,3-butadiyne by this method was carried out using atmospheric oxygen as the oxidant.

1. Polymerization using $CuCl_2$ oxidant

Aluminum chloride, 30.0 g(0.225 mole), and $CuCl_2$, 15.0 g(0.112 mole), were mixed in 300 ml of CS_2. Trans-stilbene, 10.0 g(0.055 mole) was added slowly to the above mixture with stirring at room temperature. After a short induction period, the reaction mixture started to evolve an acidic gas and turned into a black viscous slurry. The reaction was allowed to proceed for a total of five hours. The supernatant CS_2 layer was discarded and the residue was treated with water, extracted into CH_2Cl_2, washed several times with water, dried over

$MgSO_4$ and the CH_2Cl_2 was evaporated. A brown powder, partially soluble in acetone was obtained. It was extracted with acetone to remove any unreacted monomer. The product was further purified by precipitating a CH_2Cl_2 solution with n-pentane three times. The yield of the purified product was 26%. The resulting polymer, poly(trans-stilbene), was soluble in CS_2, $CHCl_3$, CH_2Cl_2 and o-dichlorobenzene.

The polymerization of cis-stilbene under the same conditions using the same molar ratio of reagents to monomer, for a reaction period of five hours yielded an insoluble product. However, poly(cis-stilbene) obtained after a two hour reaction period was soluble in CH_2Cl_2, CS_2, $CHCl_3$ and o-dichlorobenzene.

2. Electron spin resonance investigation of initiating species

Aluminum chloride, 0.30 g(2.2 mmole), and 1.0 ml of CS_2 were placed in an ESR tube and its ESR spectrum was recorded at room temperature. Trans-stilbene, 0.1 g (0.5 mmole), was added to the above mixture and the ESR spectrum of the resulting mixture was taken immediately. The reaction was quenched by treating it with water immediately, the organic layer was extracted into CS_2, dried over $MgSO_4$, and evaporated to reduce the volume to one milliliter. The ESR spectrum of this solution was taken at room temperature with the same ESR spectrometer settings used for the unquenched reaction mixture.

3. Isolation of reaction products at one hour.

Trans-stilbene, 1.0 g(5.5 mmole), was dissolved in a minimum amount of CS_2. Aluminum chloride, 3.0 g(22.5 mmole), was added slowly to the above solution and stirred at room temperature for one hour.

The reaction mixture was treated with water, extracted into CS_2, dried over $MgSO_4$ and then the CS_2 was evaporated.

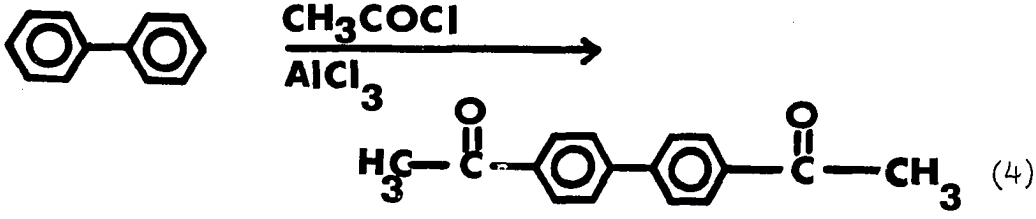
4. Polymerization using atmospheric oxygen as the oxidant

Diphenyl acetylene, 3.6 g(20 mmole), was dissolved in 250 ml of pentane. Aluminum chloride, 10.6 g(80 mmole), was added to the above solution and stirred at room temperature for 24 hours. The solvent was evaporated and the product was treated with water in an ice bath. The dark brown product obtained was pulverized with water, filtered and dried. The unreacted monomer was removed from the product by extracting with n-pentane for a period of two weeks in a soxhlet extractor. The yield of the product, poly(diphenyl acetylene), was 61%. This polymer was soluble in CS_2, $CHCl_3$, CCl_4, CH_2Cl_2, toluene, benzene and tetrahydrofuran.

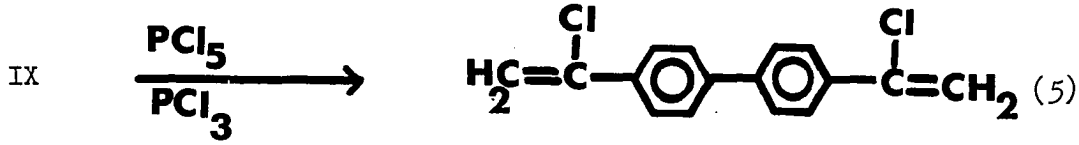
Under the above conditions, using the same monomer to catalyst ratio, 1,4-diphenyl-1,3-butadiyne polymerized to yield a dark black polymer, poly(1,4-diphenyl-1,3-butadiyne). The insoluble fraction of the polymer was 60%(w/w). The rest was soluble in CS_2, $CHCl_3$, benzene toluene, CH_2Cl_2, CCl_4 and tetrahydrofuran.

C. Oxidative coupling

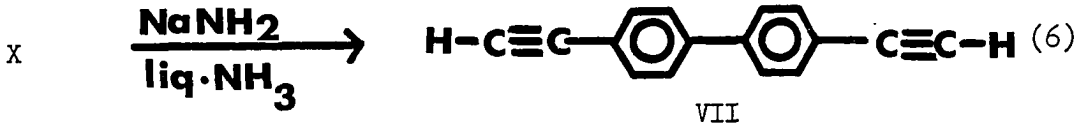
The polymerization of 4,4'-diethynylbiphenyl was carried out by oxidative coupling(reaction 3, section I). The monomer, 4,4'-diethynylbiphenyl, was synthesized by the following reaction sequence.



IX (4)



X (5)



VII (6)

1. Synthesis of 4,4'-diacetylbiphenyl

Aluminum chloride, 60.0 g(0.450 mole), was suspended in 300 ml of CS_2 and then biphenyl, 10.0 g(0.065 mole), was added slowly into the above suspension with stirring. Once addition was completed, CH_3COCl, 26.0 ml(0.366 mole), was added dropwise from a dropping funnel at room temperature. The reaction mixture was refluxed on a water bath until no HCl evolution took place. At this stage, the reaction mixture was slowly added into ice cold water, extracted into CH_2Cl_2, washed several times with water, dried over $MgSO_4$ and

the CH_2Cl_2 was evaporated. A brown colored product was obtained. The product was decolorized several times with activated charcoal and recrystallized from absolute ethanol to yield colorless gleaming leaflets. The yield of the recrystallized product, IX, was 53.7%. The observed melting point, 191°C, of the recrystallized product was identical to the literature melting point of 4,4'-diacetylbiphenyl (17).

2. Synthesis of 4,4'-di(1-chlorovinyl)biphenyl

Recrystallized IX, 5.0 g(0.021 moles), was dissolved in a minimum amount of PCl_3 in a dry nitrogen atmosphere. Phosphorous pentachloride, 9.0 g(0.043 moles), was added slowly to the above solution and the mixture refluxed on a water bath at 45°C overnight. The solvent was distilled off under reduced pressure and the reaction mixture treated with 250 ml of 20% sodium acetate saturated with N_2. The precipitated off-white solid product, X, was filtered under nitrogen and dried under vacuum in the dark. This product underwent a rapid color change followed by a significant decrease in solubility, upon storage in air exposed to light. The dark brown product obtained after a few weeks was completely insoluble. Due to this unstable nature of the product, no attempt was made to purify and identify the product. The dried crude product was used immediately as the starting material for the next reaction(reaction 6).

3. Synthesis of 4,4'-diethynylbiphenyl

A small amount of fresh cut Na was added into 400 ml of liquid NH_3 to form a dark blue solution. A few crystals of $Fe(NO_3)_3$ catalyst(0.2 g), was added to the above solution and stirred until it turned to a brown solution. To this solution, freshly cut Na,

2.0 g, was added and stirred until it formed a grey suspension of $NaNH_2$. The dried crude product, X, of the previous reaction was added slowly to the above $NaNH_2$ suspension and stirred for one hour. The dark green slurry formed was treated with 5 g of NH_4Cl, evaporated at room temperature, treated with water, filtered and dried to obtain a light yellow product. This product was sublimed at 140°C under vacuum(0.2 mm) to obtain an off-white powder. The sublimate was decolorized several times with activated charcoal and recrystallised three times from absolute ethanol to yield colorless thin needles, VII. The yield of the recrystallised product was 0.90 g. The melting point of the recrystallized product, 166-166.5°C, was identical to the literature melting point of 4,4'-diethynylbiphenyl(18).

4. Polymerization of 4,4'-diethynylbiphenyl

Recrystallised VII, 0.30 g(1.5 mmole), was dissolved in a mixture containing 25 mls of pyridine and 50 mls of o-dichlorobenzene. Cuprous chloride, 0.50 g(5.0 mmole), was added to the above solution and refluxed at 110°C for 3.5 hours with O_2 gas passing through the reaction mixture. The reaction mixture was added to a solution containing 500 ml of methanol and 10 ml of concentrated HCl, and finally to a large amount of methanol. A brown insoluble product VIII, was obtained.

D. Thermal polymerization of 1,4-diphenyl-1,3-butadiyne

The thermal polymerization of 1,4-diphenyl-1,3-butadiyne was performed according to a literature procedure(19). The solid 1,4-diphenyl-1,3-butadiyne was heated gradually in a pre evacuated ampoule until it turned to a light red liquid. This liquid reacted vigorously to form a black solid. The polymer was precipitated by methanol from benzene solution to yield a dark black solid soluble in CS_2, $CHCl_3$, CCl_4, toluene and benzene.

E. Chemical reactions of poly(trans-stilbene)

1. Bromination

Poly(trans-stilbene), 0.20 g, was dissolved in a minimum amount of CS_2 and cooled to 0°C in ice bath. A bromine solution containing 0.1 ml of bromine in 10 ml of CS_2 was added slowly to the above solution and stirred for 24 hours in the dark. During this reaction an acidic gas was evolved. The solvent and the unreacted bromine were distilled off on a water bath at reduced pressure. The product obtained was a black powder.

2. Hydrogenation

Poly(trans-stilbene), 0.20 g, was dissolved in a minimum amount of $CHCl_3$ and 0.025 g of 10% Pd on carbon black was added. This mixture was hydrogenated for ten hours using 52 psi hydrogen pressure at room temperature. The catalyst was filtered off and the solvent evaporated. The solid product obtained was washed several times with methanol and dried. The product was a dark brown powder similar in appearance to the starting parent polymer.

Hydrogenation of poly(trans-stilbene) using a large amount of catalyst(polymer to catalyst ratio of 1:1) for a long period of time (two weeks) produced a dark brown material.

F. Doping of polymers

Iodine doping was done by exposing the solid polymer to iodine vapor at 95°C for a period of 24 hours. Iodine uptake was measured by the weight increase of the sample. AsF_5 doping was done by exposing the solid polymer to AsF_5 gas at room temperature for a period of 24 hours.

G. Measurements

1. Electrical

For the electrical conductivity measurements, iodine doped samples were compressed in between two 440-C stainless steel pellets using a polypropylene guide ring. The D.C. electrical resistance of the samples were measured at room temperature using a Keithley Model 160 digital multimeter. The entire contact time of the doped polymer with the electrode was less than 15 minutes for each measurement. After the measurement, there was no observable chemical reaction between the electrode and the doped polymer. The electrical measurements of the AsF_5 doped samples were done by using a four point probe. The AsF_5 doping of polymers and their electrical measurements were performed by Dr. R.H.Baughman at the Allied Chemical Corporation.

2. Molecular weight.

The number-average molecular weight, $\bar{M}_n$, was measured with reference to a benzil standard using a Hewlett Packard(model 302B) vapor

pressure osmometer. The $\bar{M}_n$ for the polymer was calculated by using the following equation.

$$K = \bar{M}_n \times \left(\frac{v}{c}\right)_{c=0}$$

where,

v = bridge output(μv)

c = % concentration(w/w).

The constant K was obtained from the data obtained for a series of standard benzil(molecular weight = 210) solutions with concentrations varing from 1.024%(w/w) to 0.128%(w/w). The reliability of the K value was tested by using another standard(polystyrene) having molecular weight closer to the molecular weight of the unknown polymer. The error in the observed K value for polystyrene was 10%. The molecular weight measurement of poly(trans-stilbene) was done at 110°C using o-dichlorobenzene as the solvent system. The concentrations of the polymer solutions were varied from 9.212%(w/w) to 1.152%(w/w). The molecular weight measurements of poly(diphenyl acetylene) and poly(1,4-diphenyl-1,3-butadiyne) solutions were varied from 11.534%(w/w) to 1.441%(w/w) and 0.835%(w/w) to 0.104%(w/w) respectively. The v versus c plots for the solutions were linear throughout their concentration ranges.

3. Spin density

For the ESR spin density measurements, a JEOL model JES-Me-3X, X band ESR spectrometer with a TE_{105} cylindrical dual cavity was used. The spin density was measured against a known quantity of

crystalline diphenyl picrylhydrazyl, DPPH, as the primary standard. The quantity of DPPH was determined experimentally by measurement of its optical density in benzene, $\lambda_{max} = 519$ nm, $\log \epsilon = 4.89$. A sample containing manganous ions dispersed in magnesium oxide, was used as an internal standard to correct for any changes in the cavity Q. The quality factor of the cavity Q is proportional to "energy stored/energy dispersed per cycle". The spin density calculations were based on the assumption that the number of spins is proportional to the area under the ESR absorption curve. The number of spins in the DPPH sample was assumed as the number of molecules in the DPPH sample. The area under the ESR absorption curve was obtained by the following numerical double integration method (20).

$$\text{Area} = 1/2 \; d^2 \sum_{r=1}^{n} (2n - 2r + 1)h_r$$

The values, d,n and h for a first derivative curve are shown in Fig.3.

For the relative spin density measurements of polymer solutions, the ESR spectra of the polymer solutions with known volumes (0.5 ml) were recorded against the Mn marker. The size of the above liquid samples was always less than the size of the effective volume of the ESR cavity.

4. Spectroscopic

The infrared and UV-VIS spectra were recorded with a Beckman IR 4260 Research Infrared spectrophotometer and a Cary 118 C spectrophotometer respectively. Proton CW NMR spectra were recorded with a JEOL JNM-MH-100, 100 MHz nuclear magnetic resonance spectrometer. The proton and carbon FT NMR spectra were recorded with an IBM NR-80

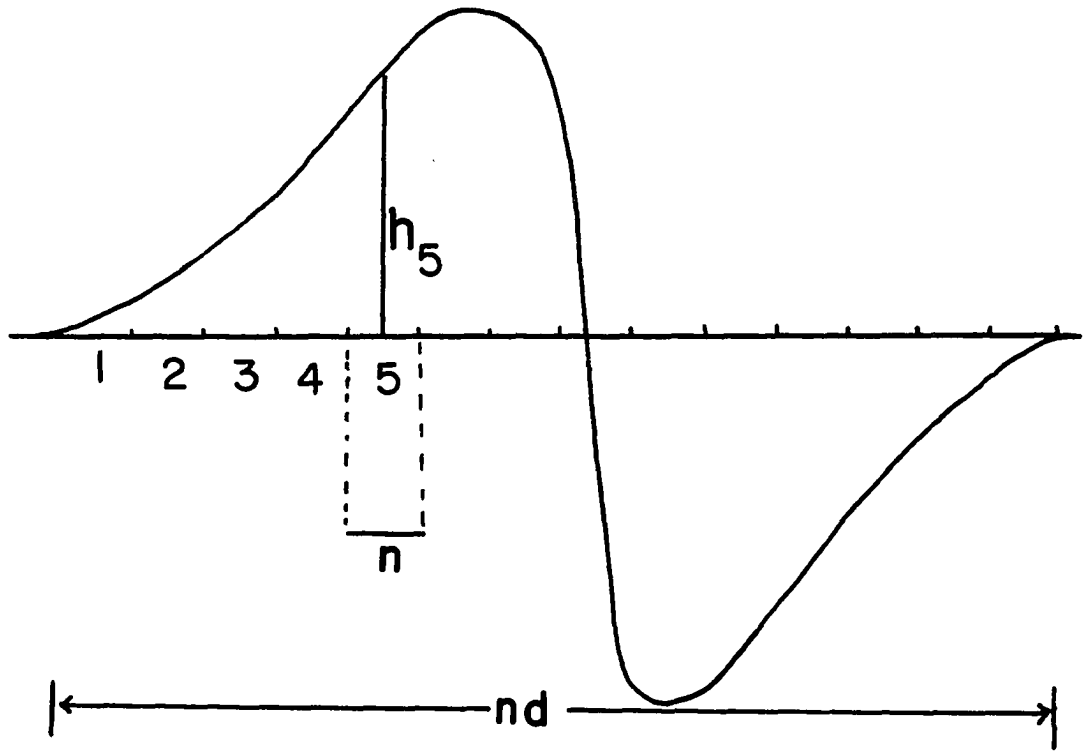


Figure 3. A typical first derivative ESR spectrum. The values d, n and h were used for the numerical double integration (20).

(80 MHz proton, 20 MHz carbon), nuclear magnetic resonance spectrometer. The solid state carbon spectra, CPMAS, were obtained by using an IBM WP-100 (25 MHz carbon), nuclear magnetic resonance spectrometer through Dr. P.Murphy at IBM corporation.

H. Elemental analysis

The elemental analysis of poly(trans-stilbene) was performed by Schwarzkopf Laboratories, Inc. The elemental analysis of poly(diphenyl acetylene) and poly(1,4-diphenyl-1,3-butadiyne) were performed by Galbraith Laboratories, Inc.

III. RESULTS AND DISCUSSION

A. Poly(trans-stilbene)

1. Paramagnetism

Solid poly(trans-stilbene) exhibited ESR singlets having linewidths, ΔH_{msl}, of 8.0 G and 6.0 G under vacuum and in air respectively (Fig.4). The height of the ESR first derivative curve of the solid polymer in air was 5.4 times higher than that of the solid polymer under vacuum. The spin density of the solid polymer under vacuum was 7.5×10^{15} spins/gram and these unpaired electrons were stable towards water and solvents. The effect of air on spin density was reversible (Fig.4). The signal intensity grew in intensity when the sample was exposed to air and reduced in intensity when it was subjected to vacuum. However, by applying vacuum for a long period of time, the intensity of the signal was reduced to a minimum value of 7.5×10^{15} spins/gram and remained constant. These results indicate that oxygen interacts with the polymer perhaps by an electron transfer process.

The effect of poly(trans-stilbene) concentration on spin density is given in table 1. The relative spin density of poly(trans-stilbene) decreases as concentration increases. The most concentrated sample, solid polymer, has the lowest relative spin density. Apparently, at higher concentrations recombination of unpaired electrons can takes place, probably by an intermolecular electron transfer process.

The absence of any hyperfine structure in the ESR spectrum of the polymer in the solid state and solution indicates that these unpaired electrons are delocalized. Formation of such stable

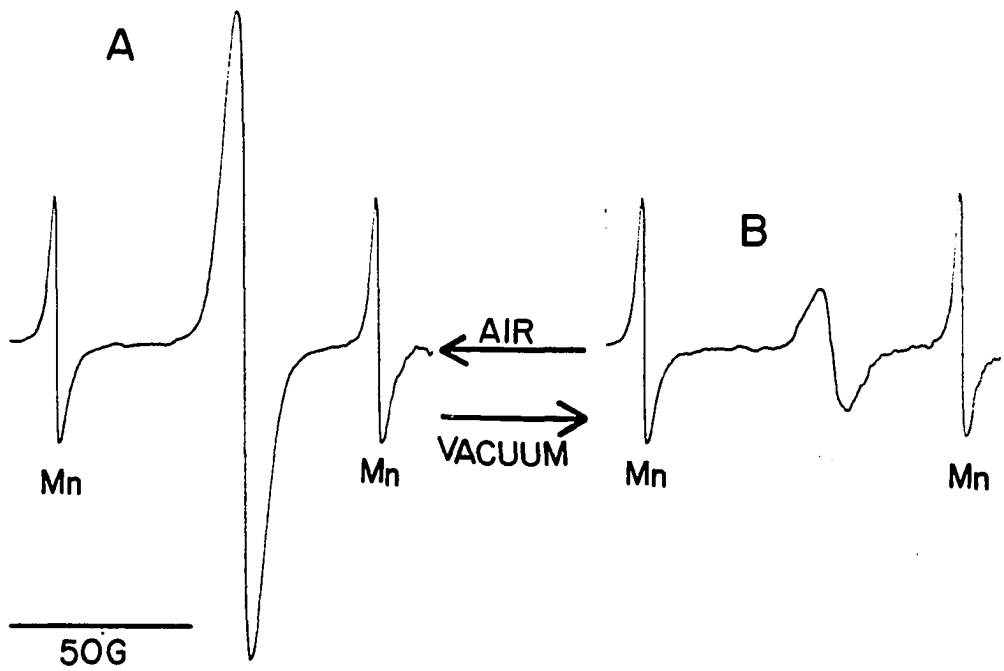


Figure 4. ESR spectra of solid poly(trans-stilbene) in air(A) and in vacuum(B), taken under the same spectrometer settings.

Table 1. Relative spin densities of poly(trans-stilbene)

% concentration(w/v)	relative spin density
0.5	100
1.0	100
2.0	72
3.0	70
4.0	73
5.0	76
solid polymer in air	43
solid polymer in vacuum	8

and delocalized unpaired electrons in the polymer suggests a conjugated system in its structure.

2. Characterization

The number-average molecular weight of poly(trans-stilbene) was 4.8×10^3, corresponding to a degree of polymerization of 26. The elemental analysis results showed that carbon, hydrogen and ash contents add up to 98.78% :

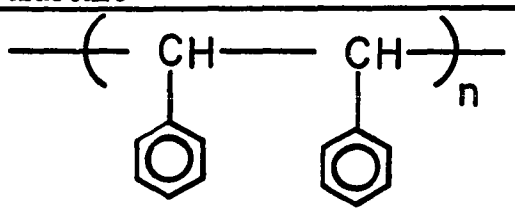
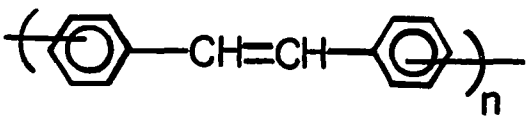
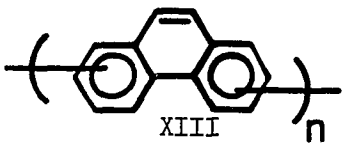
C	H	Ash
92.92%	5.26%	0.6%

The remaining, 1.22% may be chlorine. Chlorine was a common impurity present in polymers synthesized by this method. Polyphenylene(21) and poly(diphenyl acetylene), (Section IIID2), synthesized by this method contained chlorine, 2.5% and 1.45% respectively. The observed % H value, 5.26, of poly(trans-stilbene) was lower than the theoretical % H values of structures XII and XI(Table 2) and was in between the theoretical % H values of structures XII and XIII.

The infrared spectrum of poly(trans-stilbene) is shown in Fig.5 in comparison with trans-stilbene monomer. The absorption observed at 950 cm^{-1} for the monomer is indicative of trans CH=CH units(22). There was no absorption for the polymer at this wavenumber suggesting that the trans C=C units of the monomer are converted into some other structural units upon polymerization.

The ^{13}C NMR spectrum of poly(trans-stilbene) showed absorption signals only in the region 115 - 150 ppm(Fig.6), revealing the presence of sp^2 carbons. The sp^3 carbons of hydrocarbons usually appear in the 0 - 60 ppm region. Failure to observe any signal in the

Table 2. Weight % of carbon and hydrogen

Structure	% C	% H
 XI	93.33	6.67
 XII	94.38	5.62
 XIII	95.45	4.55
Experimental value for poly(trans-stilbene)	92.92	5.26

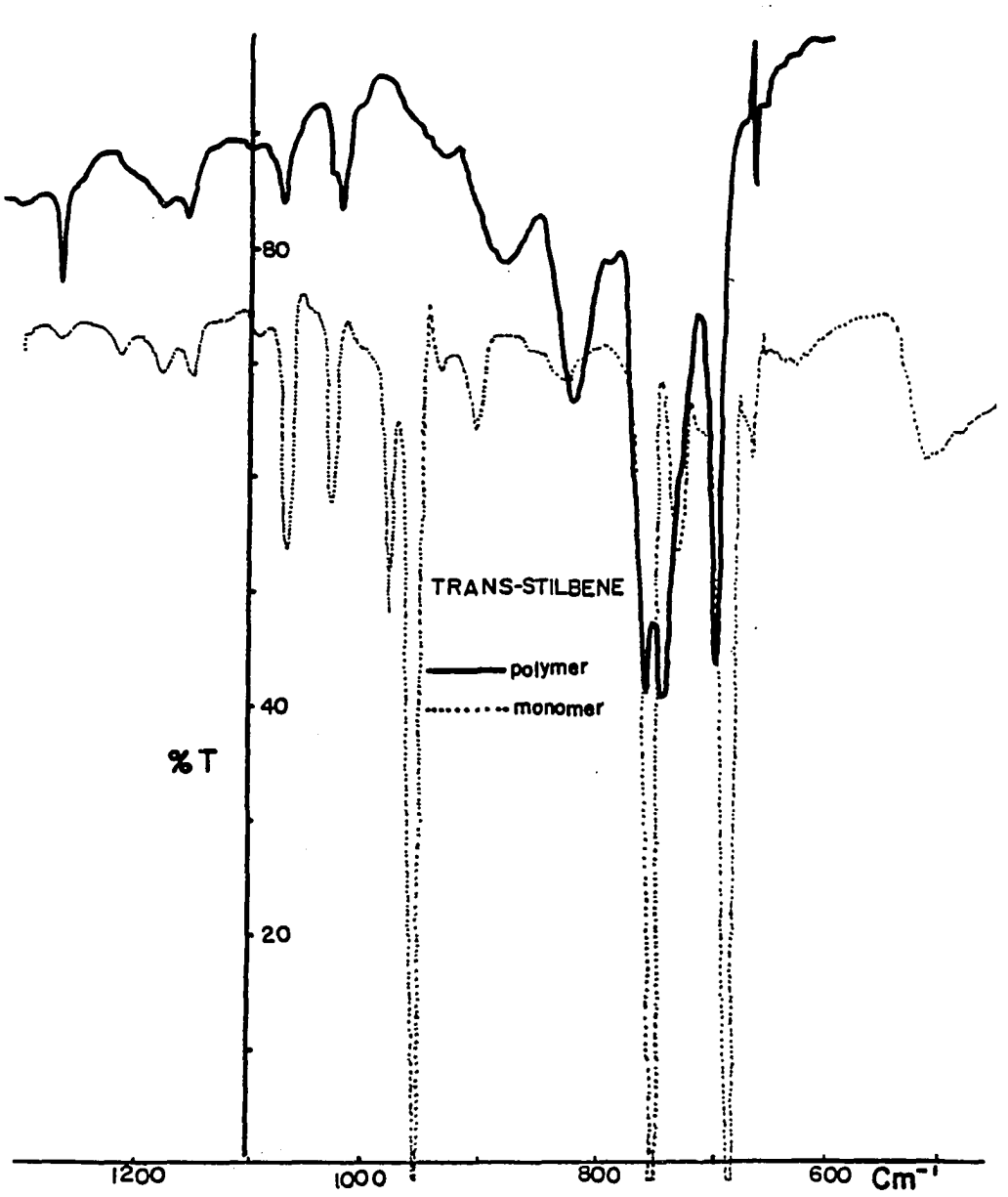


Figure 5. Infrared spectra of poly(trans-stilbene) and trans-stilbene in CS_2

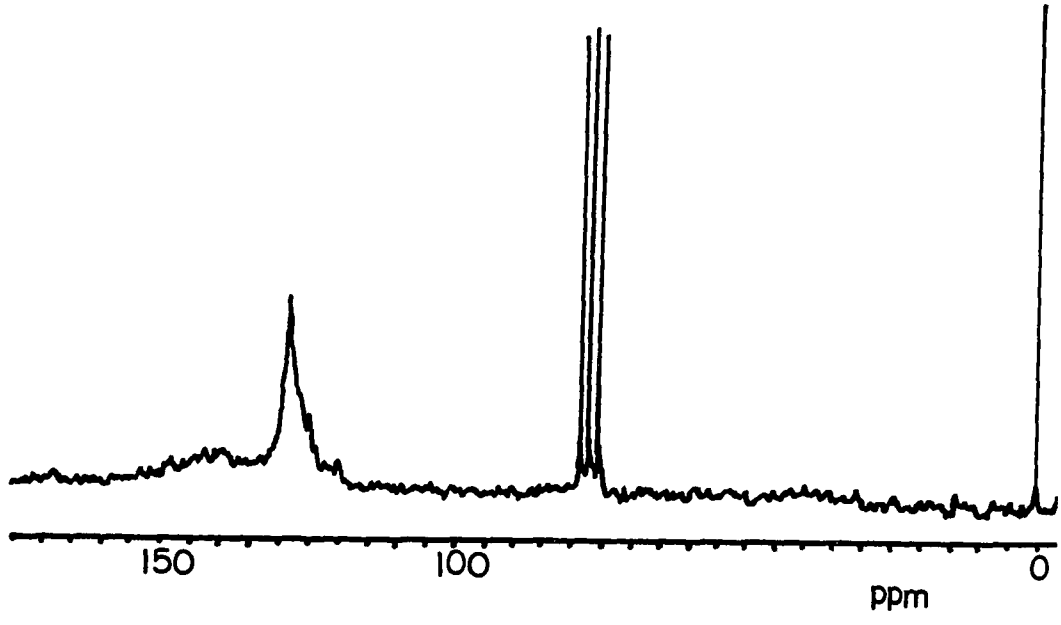


Figure 6. ^{13}C NMR spectrum of poly(trans-stilbene).
Conditions: 15%(w/v) in $CDCl_3$, chemical shifts (C.S.) relative to TMS at room temperature, 7362 transients, 45° pulse angle, 4 seconds between pulses.

sp^3 region may be due to long ^{13}C relaxation times. The correct observation of NMR peaks for such carbons requires long delay times between radiowave pulses. We have carried out the NMR experiment for accumulation times as long as 36 hours, with low pulse angles, 25°, and delay times as long as 2 minutes. These experiments did not reveal any hint of additional peaks, indicating that the polymer is free from sp^3 carbons.

The presence of sp^2 carbons were further established through chemical reactions. Under mild hydrogenation conditions at room temperature with 10% Pd on carbon black catalyst and 52 psi hydrogen pressure, a reaction time of eight hours yielded products with sp^3 carbon atoms having chemical shift values of 29.6 and 37.7 ppm (Fig.7). This shows the addition of hydrogen to C=C bonds. Under mild hydrogenation conditions, aromatic C=C bonds do not undergo hydrogen addition and the above results indicate the presence of non-aromatic C=C bonds. If these non-aromatic C=C bonds are located in a polymer backbone as in structure XII(table 2), then the complete hydrogenation of these double bonds should produce a non-conjugated, colorless product free from unpaired electrons.

The hydrogenation of poly(trans-stilbene) for a long period of time(two weeks) using a large amount of catalyst(polymer:catalyst ratio of 1:1) failed to yield a colorless product free from unpaired electrons. This indicates that the polymer contains non-aromatic C=C bonds, but its main backbone is aromatic. Bromination

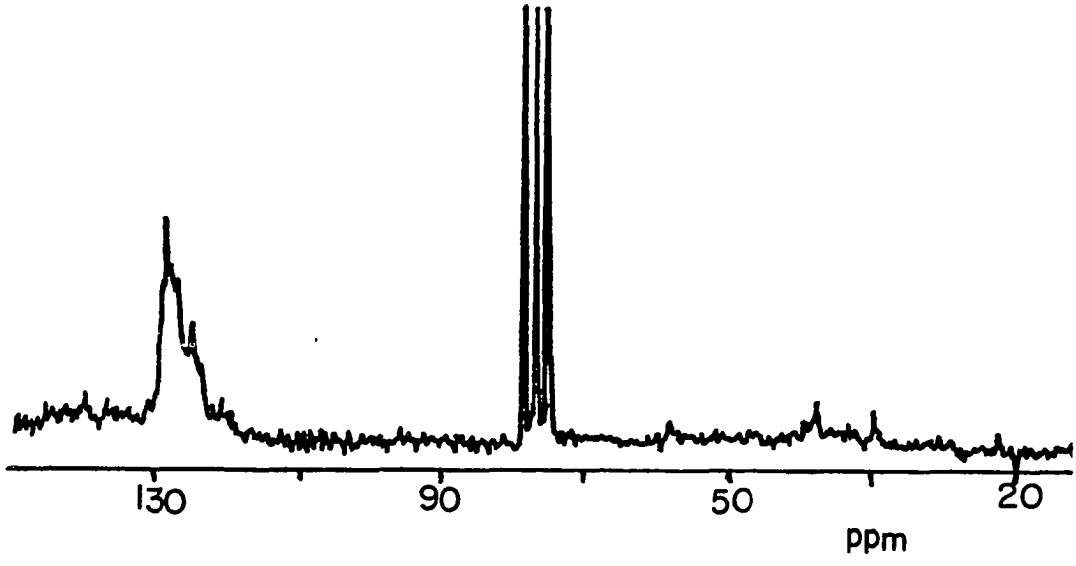


Figure 7. ^{13}C NMR spectrum of hydrogenated poly(trans-stilbene). Conditions: Saturated solution in $CDCl_3$, C.S. relative to TMS at room temperature, 12889 transients, 45° pulse angle, 4 seconds between pulses.

of poly(trans-stilbene) confirmed the presence of non-aromatic C=C double bonds. The ^{13}C NMR spectrum of the brominated poly(trans-stilbene) exhibited peaks at 36.5 ppm and 46.7 ppm indicating the formation of sp^3 carbon atoms by addition of bromine to C=C double bonds in line with the chemical shift values for the hydrogenated product(Fig.8).

Although there were no signals observed for sp^3 carbons in the ^{13}C NMR spectrum of poly(trans-stilbene), the proton NMR spectrum (Fig.9) showed very broad peaks in the normally non-aromatic region (2.5 - 5 ppm). The ratio of signal areas for aromatic:non-aromatic protons was 3.3:1.0. Absorptions in the non-aromatic region could arise from sp^2 protons if they occupy highly shielded environments. Such environments could originate from intermolecular association or due to specific polymer conformations(intramolecular effects).

The nature of shielded environments was further investigated through temperature and dilution studies. The proton NMR spectra of poly(trans-stilbene) in the concentration range of 0.02% - 15%(w/v) showed that there are only slight variations in the shape of the non-aromatic peaks(compare Fig.10A with Fig.9). The spectrum of 0.02% polymer solution was obtained by accumulating a very large number of transients(Fig.10B). Under such conditions a very minute amount of impurities could exhibit NMR peaks. The NMR peaks in Fig.10A at 7.15 and 4.4 ppm are due to the impurities in CS_2 and external capillary lock of D_2O respectively. These peaks were subtracted from Fig.10B before integration. The intensity ratio of aromatic:non-aromatic peaks for the 0.02%(w/v) polymer solution was

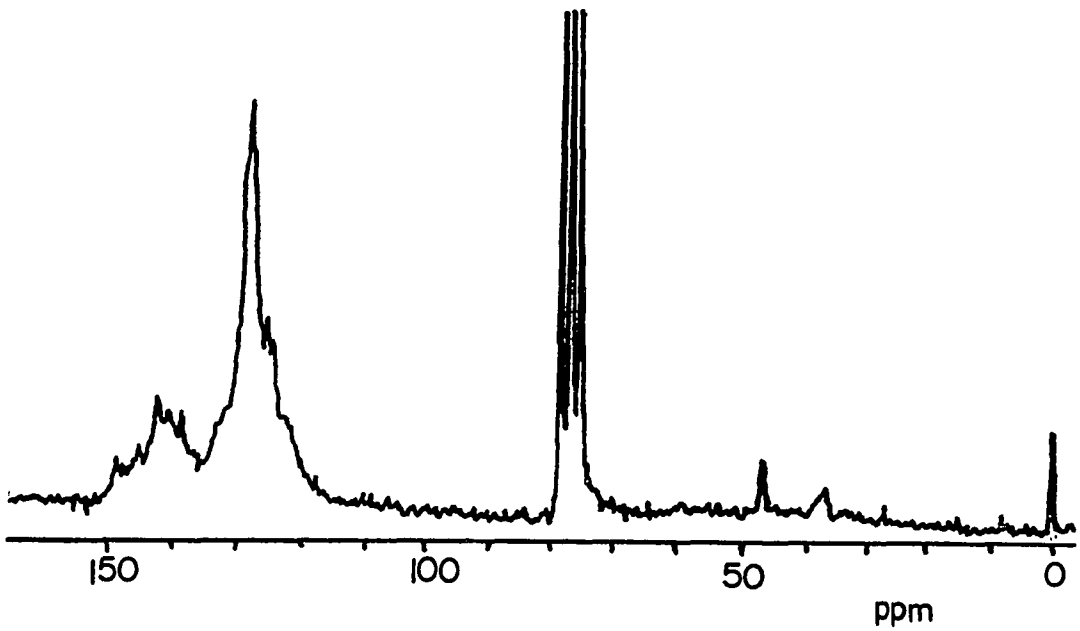


Figure 8. ^{13}C NMR spectrum of brominated poly(trans-stilbene). Conditions: Saturated solution in $CDCl_3$, C.S. relative to TMS at room temperature, 45° pulse angle, 4 seconds between pulses, 9280 transients.

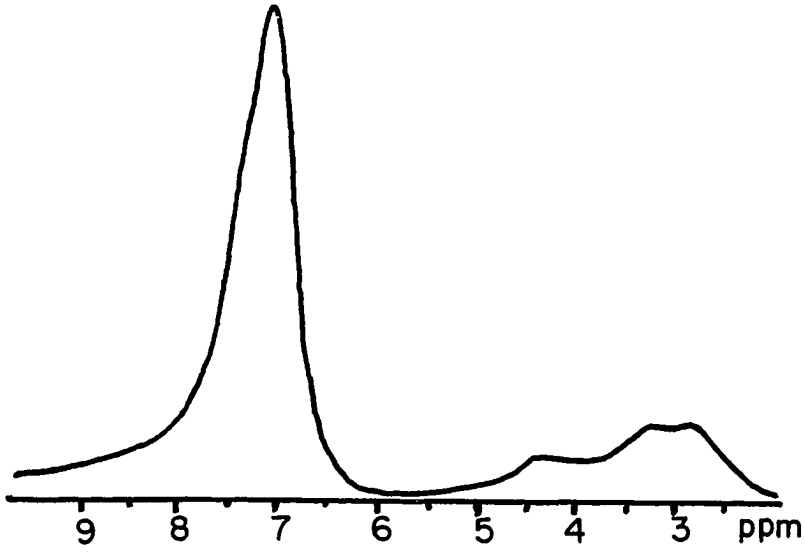


Figure 9. ^{1}H NMR spectrum of poly(trans-stilbene).
Conditions: 15%(w/v) in $CDCl_3$, C.S. relative to TMS at room temperature, 8 transients, 25° pulse angle, 3.4 seconds between pulses.

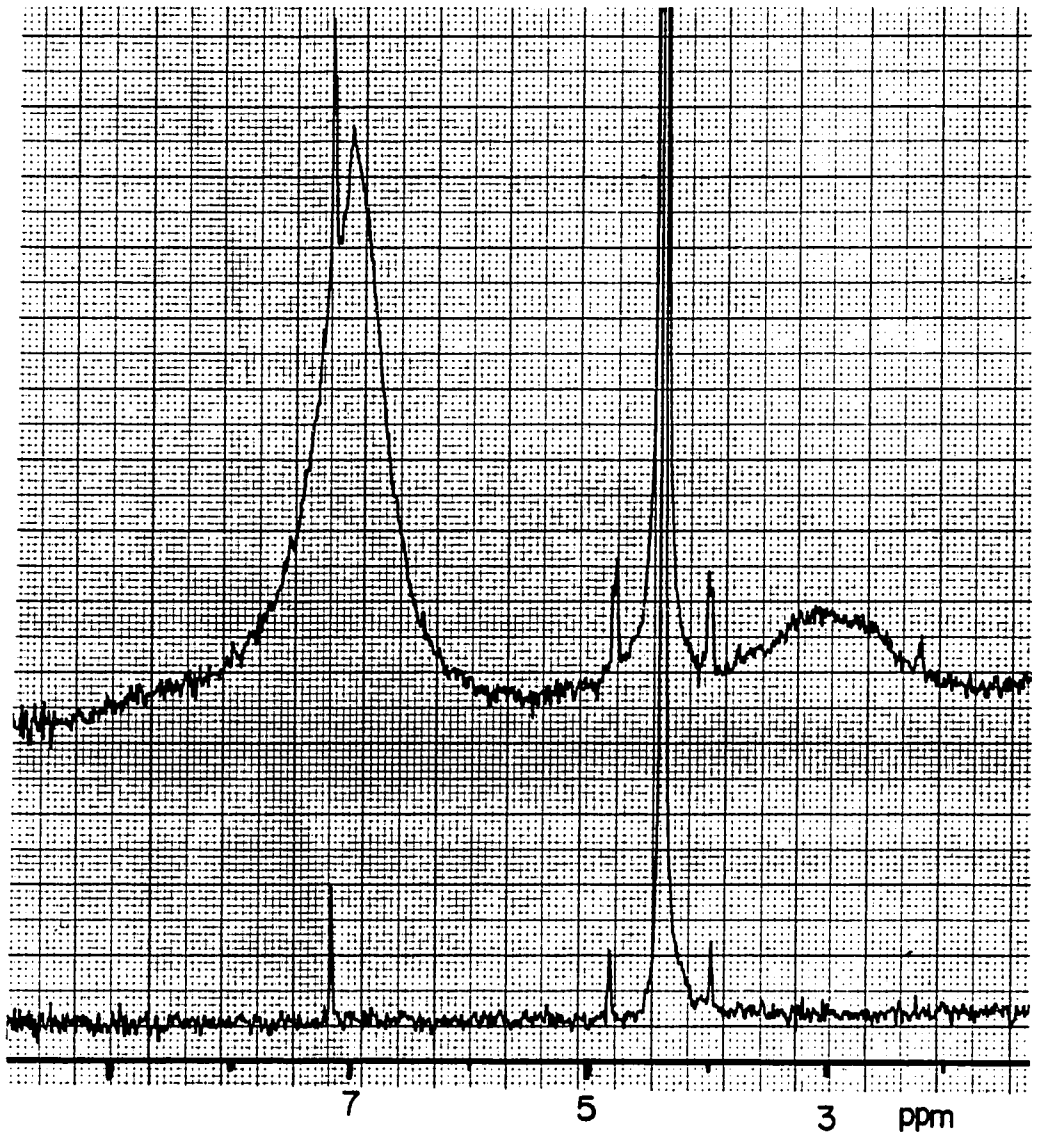
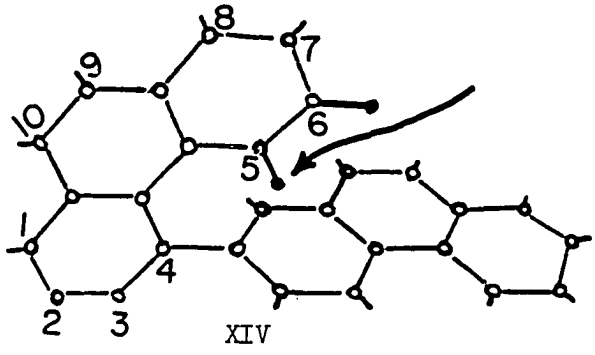


Figure 10. ^{1}H NMR spectra of A. CS_2, B. poly(trans-stilbene), 0.02% (w/v) in CS_2. Conditions: Room temperature, C.S. relative to TMS, 19215 transients, 25° pulse angle, 3.4 second delay between pulses, external capillary lock of D_2O.

3.2:1.0. Similar effects have been observed through temperature studies. The proton NMR spectra of poly(trans-stilbene) in the temperature range of 40-140°C showed that there is only a slight change in the shape of the non-aromatic peak at higher temperatures (Fig.11). The intensity ratio of aromatic:non-aromatic peaks for the polymer solution at 120°C was 3.1:1.0. If shielded environments are intermolecular in nature, then the intensity ratio of aromatic :non-aromatic peaks should be significantly affected by dilution and temperature. Since the above ratio was nearly the same for the temperature range of 29-140°C and concentration range of 0.02-15% (w/v), we conclude that the shielded environments for the sp^2 carbon atoms are intramolecular in nature.

Such intramolecular shielded environments are available for sp^2 protons if polymer structure consists of phenanthrene units with C-4 linkages (XIV) instead of stilbene (XII,table 2) or 1,2-diphenyl-ethane-type (XI,table 2) repeating units. Molecular models showed that no polymer consisting of structures XI or XII or their combinations would have shielded protons. The above structure



XIV

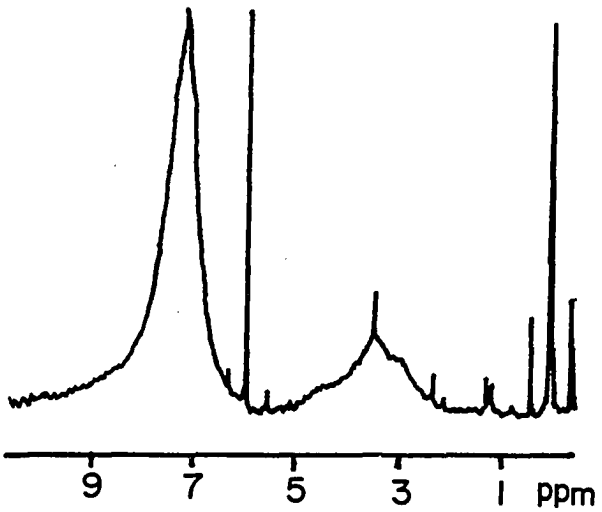


Figure 11. ^{1}H NMR spectrum of poly(trans-stilbene) at 120°C. Conditions: 15%(w/v) in deuterated 1,1,2,2 tetrachloro ethane, C.S. relative to TMS, 8 transients, 25° pulse angle, 3.4 seconds between pulses.

is a schematic model of two perpendicular phenanthrene units which are linked through C-4 carbon atom. This structure produces at least one shielded proton per each repeating unit. However, depending on the substitution pattern of the phenanthrene units and the angle between the planes of adjacent phenanthrene units, each repeating unit may produce more than one shielded proton. In such spatial arrangements, the magnitude of the ring current effects(in parts per million) should be approximately the same for carbon nuclei as for protons if they occupy the same position in space relative to the aromatic π electron cloud(23). Even if the sp^2 carbon atoms of poly(trans-stilbene) do occupy shielded environments, their ^{13}C chemical shift values will not be in the sp^3 region. This is consistent with our NMR results.

The exact structure of poly(trans-stilbene) could be obtained by analysing all the minor details of the shielded environment. The information regarding microstructures having shielded environments may not be readily obtained from ^{13}C NMR spectra(24). Carbon-13 NMR is found to be an inadequate technique to observe ring current effects(25). Hence, we will examine the proton NMR spectra of poly(trans-stilbene) and its derivatives in detail.

Addition reactions such as bromination and hydrogenation of phenanthrene usually takes place at C_9 and C_{10} positions(26). We assume that these reactions with poly(trans-stilbene) also occur at C_9 and C_{10} positions(XIV) of its phenanthrene units. The proton NMR spectrum of the hydrogenated poly(trans-stilbene) showed

the formation of new peaks at 0.95 ppm and 1.3 ppm(Fig. 12). The chemical shift values of the new peaks are somewhat lower compared to that of the C_9-H proton of dihydrophenanthrene(2.7 ppm),(27), and is accounted for by the shielded environments. Bromination of poly(trans-stilbene) also produced new peaks in the proton NMR spectrum with unusual chemical shift values(Fig. 13). The observed chemical shift values 1.8, 1.85 and 2.1 ppm of those new peaks do not correspond to the chemical shift values of C_9 and C_{10} protons of the dibromo adduct of phenanthrene. Since bromine substitution increases the δ ppm values of the protons on the same carbon atom, the δ ppm values of the C_9 and C_{10} protons of dibromophenanthrene should be much higher than the δ ppm value of the corresponding protons of dihydrophenanthrene(2.7 ppm).

The observed chemical shift values of those new peaks again correspond to a conformation in which C_9 and C_{10} protons of the phenanthrene units assume shielded environments. Molecular models showed that 1-4 or 1-8 linked phenanthrene units could have such shielded environments available for C_9 or C_{10} protons. However, the 1-8 linked structure was rejected on mechanistic grounds. We were unable to devise a reaction mechanism involving ring closure of stilbene to phenanthrene together with ring connections at C-4 and C-8 between repeating units. On the other hand, a polymer structure consisting of phenanthrene repeating units linked through C-1 and C-4 (XV) would satisfy the requirements imposed by the ^{1}H NMR results and be readily generated (Section III C).

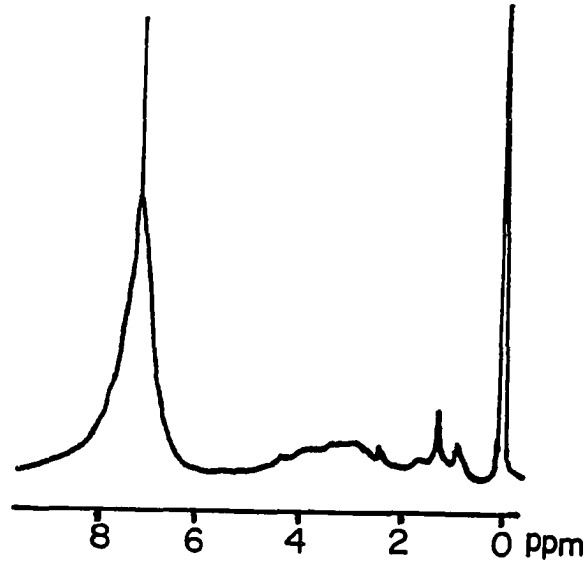


Figure 12. ^{1}H NMR spectrum of hydrogenated poly(trans-stilbene). Conditions: 10%(w/v) in $CDCl_3$, C.S. relative to TMS at room temperature, 16 transients, 25° pulse angle, 3.4 seconds between pulses.

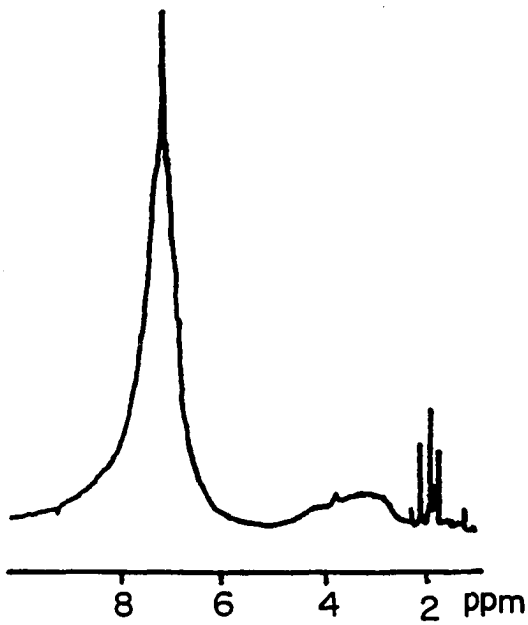
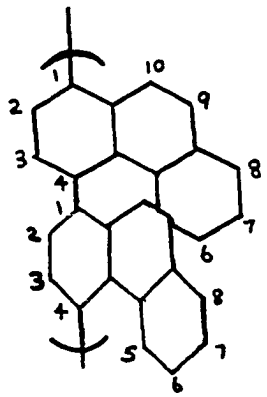


Figure 13. ^{1}H NMR spectrum of brominated poly(trans-stilbene). Conditions: 10%(w/v) in $CDCl_3$, C.S. relative to TMS at room temperature, 16 transients, 25° pulse angle, 3.4 seconds between pulses.



XV

The above structure, XV, has shielded protons at C-9 and C-5 for each repeating unit. The ratio of aromatic non-shielded to shielded protons for the structure is 3:1. The observed ^{1}H NMR peak area ratio of aromatic protons to shielded protons, 3.3:1, for poly(trans-stilbene) agrees very well with that of XV. The C-9 and C-5 protons in each repeating unit of the proposed structure, XV, of poly(trans-stilbene) are each separately located in a region under an aromatic ring from an adjacent repeating unit. This structure is also compatible with the ability of poly(trans-stilbene) to undergo hydrogenation without becoming colorless.

B. Poly(cis-stilbene)

The ^{13}C NMR and ^{1}H NMR spectra of poly(cis-stilbene) are given in figures 14 and 15 respectively. These spectra were identical to the corresponding spectra of poly(trans-stilbene), indicating that both stilbenes undergo polymerization by this method to yield the same final product. This could wery well be possible if both isomers go through a common intermediate during the reaction course. Under similar conditions, the cis isomer polymerizes to become an insoluble polymer before the trans isomer does. The trans-stilbene polymer obtained after a reaction time of five hours was a soluble polymer. By using reaction times longer than five hours, an insoluble polymer was obtained. On the other hand, poly(cis-stilbene) obtained by using reaction times longer than two hours was completely insoluble. This indicates that compared to the trans isomer, the cis isomer polymerizes at a considerably faster rate and suggests that the cis isomer has the more appropriate geometry required for the polymerization.

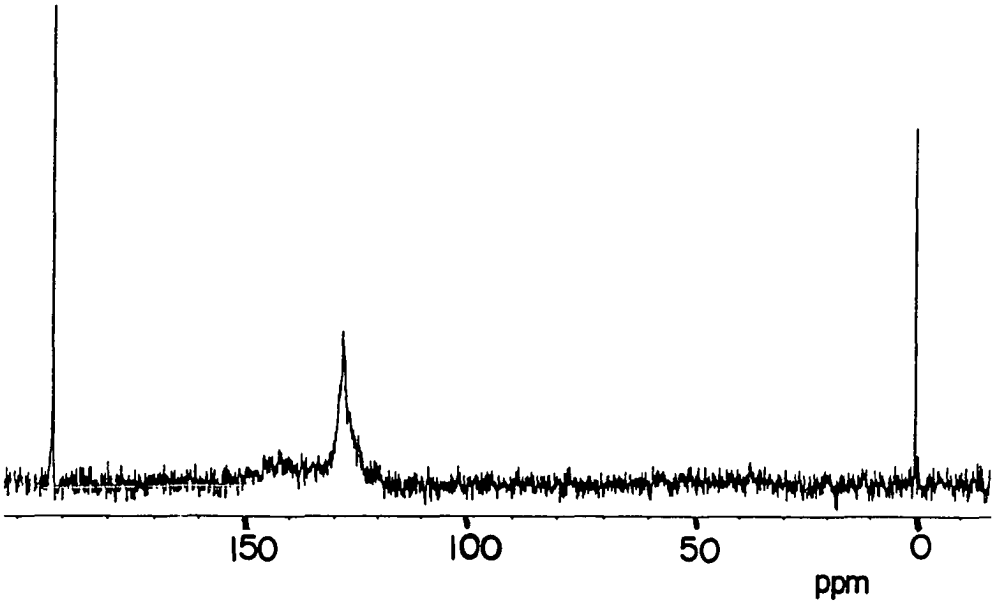


Figure 14. ^{13}C NMR spectrum of poly(cis-stilbene). Conditions: 10%(w/v) in $CDCl_3$, C.S. relative to TMS at room temperature, 7000 transients, 45° pulse angle, 4 seconds between pulses.

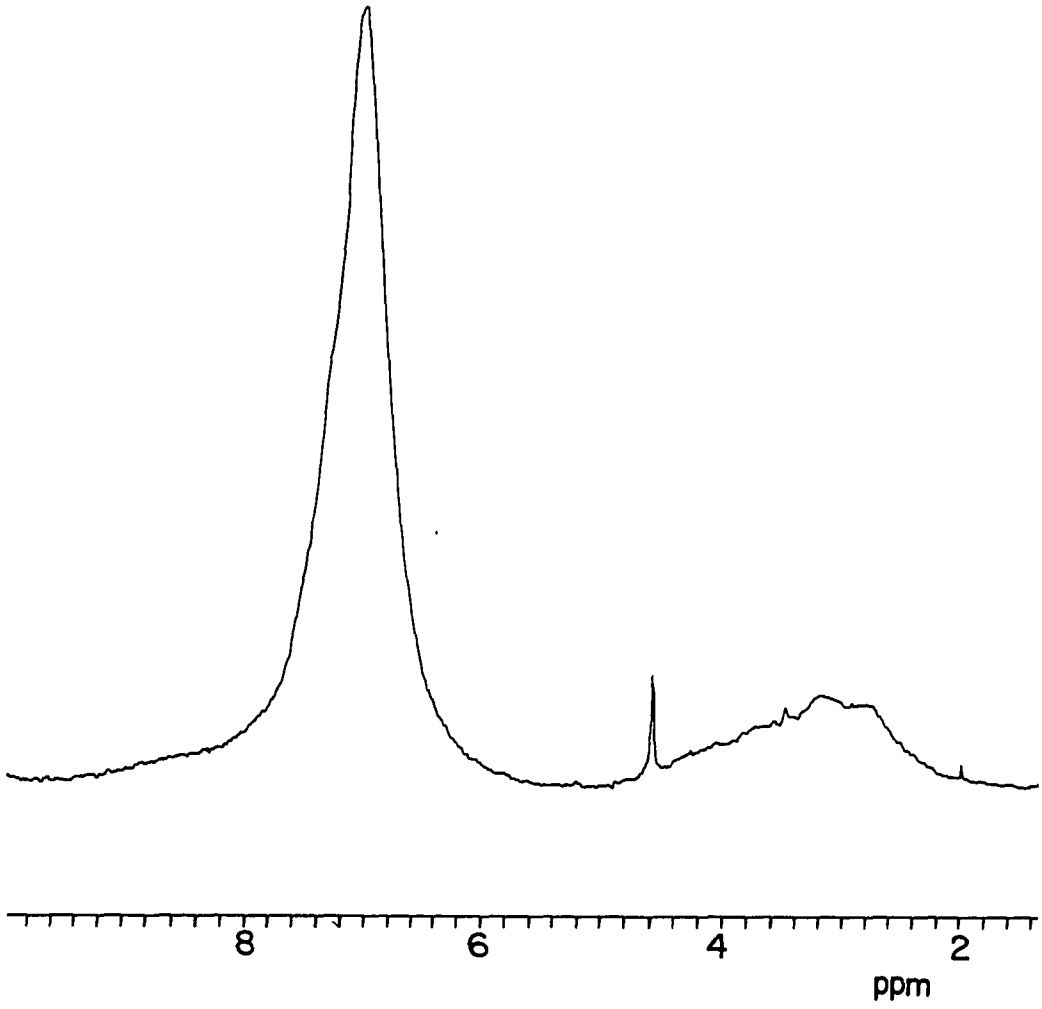
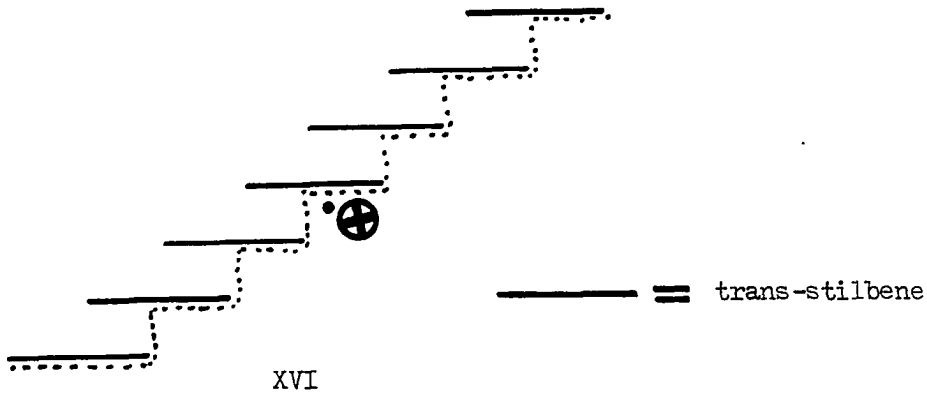


Figure 15. ^{1}H NMR spectrum of poly(cis-stilbene).
Conditions: 10%(w/v) in $CDCl_3$, C.S. relative to TMS at room temperature, 8 transients, 25° pulse angle, 3.4 seconds between pulses, external capillary lock of D_2O.

C.Polymerization mechanism of cis and trans-stilbenes

The ESR spectrum of a suspension of aluminum chloride in CS_2 showed that it does not contain any unpaired electrons(Fig.16A). When this suspension was treated with trans-stilbene, it immediately developed a light brown color and exhibited an ESR singlet(Fig.16B), revealing that trans-stilbene with aluminum chloride forms some species which contain delocalized unpaired electrons. Unlike the unpaired electrons of poly(trans-stilbene), these unpaired electrons were not stable towards water. The system irreversibly and completely lost its unpaired electrons by treatement with water(Fig.16C). Hence, the paramagnetic species in this system can not be attributed to a polymeric system with a long conjugated backbone. On the other hand, the monomer radicals do not contain a sufficiently long system of conjugation to exhibit an ESR singlet unless they are physically associated. The delocalized nature of the unpaired electrons could be explained by the formation of a complex(XVI) which consists of tightly associated stacked monomer units.



XVI

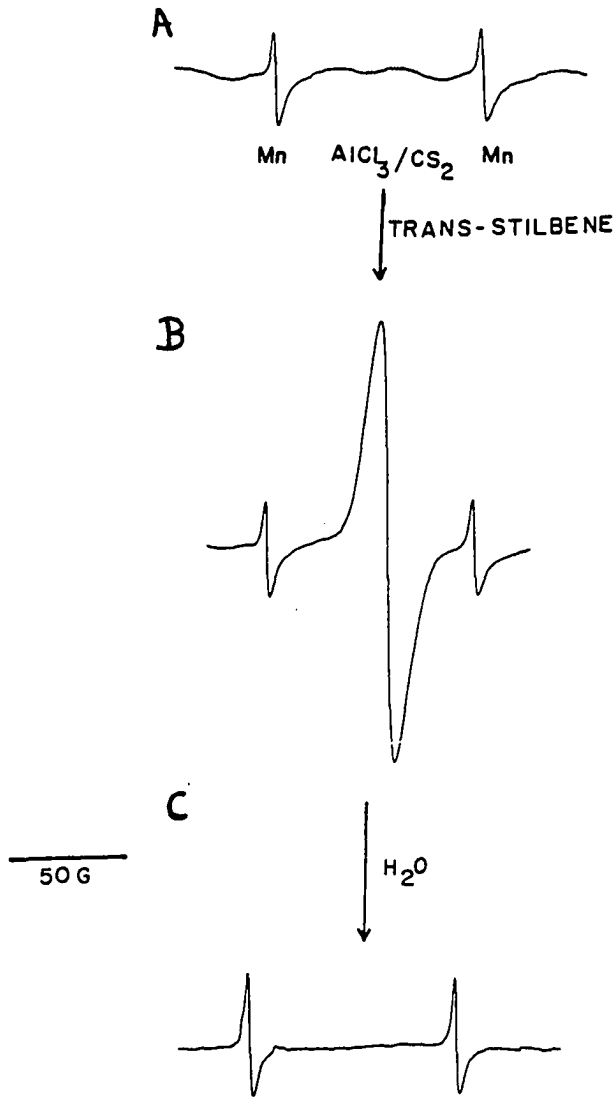
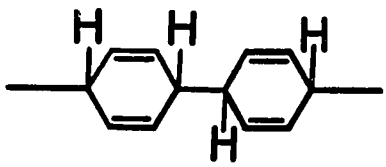


Figure 16. Room temperature ESR spectra of A. $AlCl_3/CS_2$, B. $AlCl_3/CS_2$ system soon after the addition of trans-stilbene, C. system in B after extraction with water.

The unpaired electrons in the above complex are delocalized over a large number of monomer units. Such complexes have been used to explain the delocalized nature of the free radicals which were formed in the initial stage of polymerization of benzene(28). In such reactions, the π system loses an electron and becomes a radical cation. Although we do not have any direct evidence to prove that these radicals are cations, the radical species present in our system are attributed to radical cations based on the reactivity of aluminum chloride towards other π systems(Reaction 1, section I), (29, 30, 31).

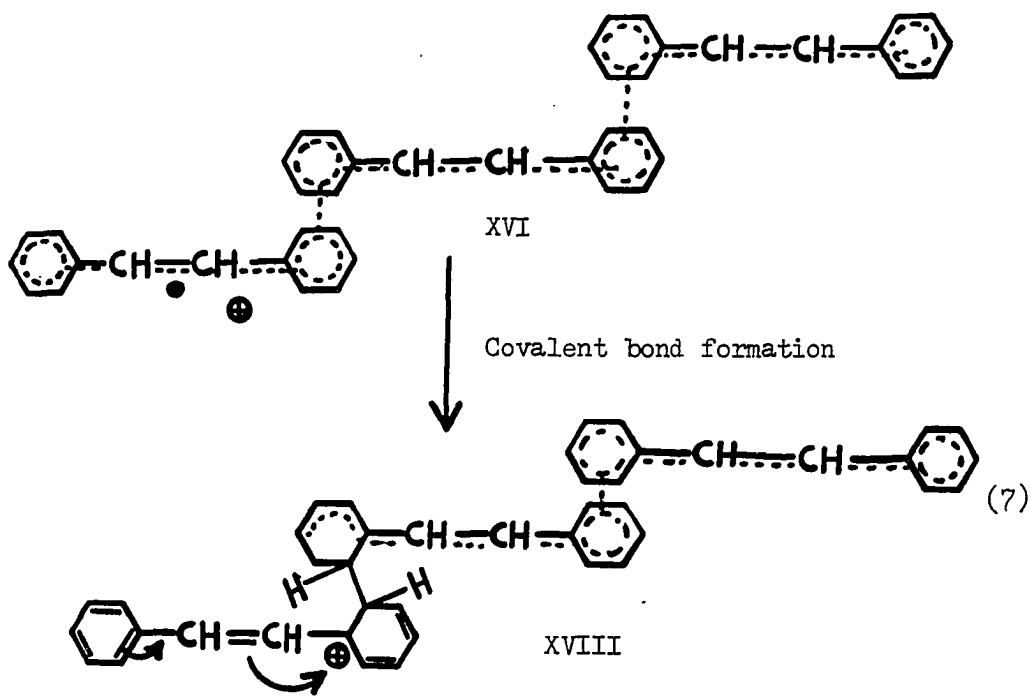
The delocalized radical cations of π systems such as benzene undergo covalent bond formation by linking appropriate carbon atoms of the monomer units(Reaction 1, section I). This leads to the formation of new sp^3 and sp^2 carbon atoms. In the presence of an oxidant, the system rearomatizes by losing its sp^3 protons. Cupric chloride is a very effective oxidant for the above purpose(32). Less effective oxidants such as ferric chloride and atmospheric oxygen have also been used in the polymerization of benzene(33, 34). However, under such weak oxidative conditions, unoxidized p-quinoid moieties(XVII) have been observed in the final product of polyphenylene even after a reaction time of two weeks(34)



XVII

If this mechanism is indeed applicable to our system, it may be possible to isolate analogous unoxidized products by using a less effective oxidant and a short period of reaction time.

The reaction of trans-stilbene with aluminum chloride using atmospheric oxygen as the oxidant yielded an orange colored product after a reaction time of an hour. This product contained 20 different sp^3 carbon atoms having chemical shift values in the region 35 - 65 ppm and 39 different sp^2 carbon atoms with chemical shift values in the 120 - 155 ppm region(Fig.17). These carbon atoms could be formed by covalent bond formation of the delocalized radical cation of trans-stilbene according to reactions 7 and 8.



(7)

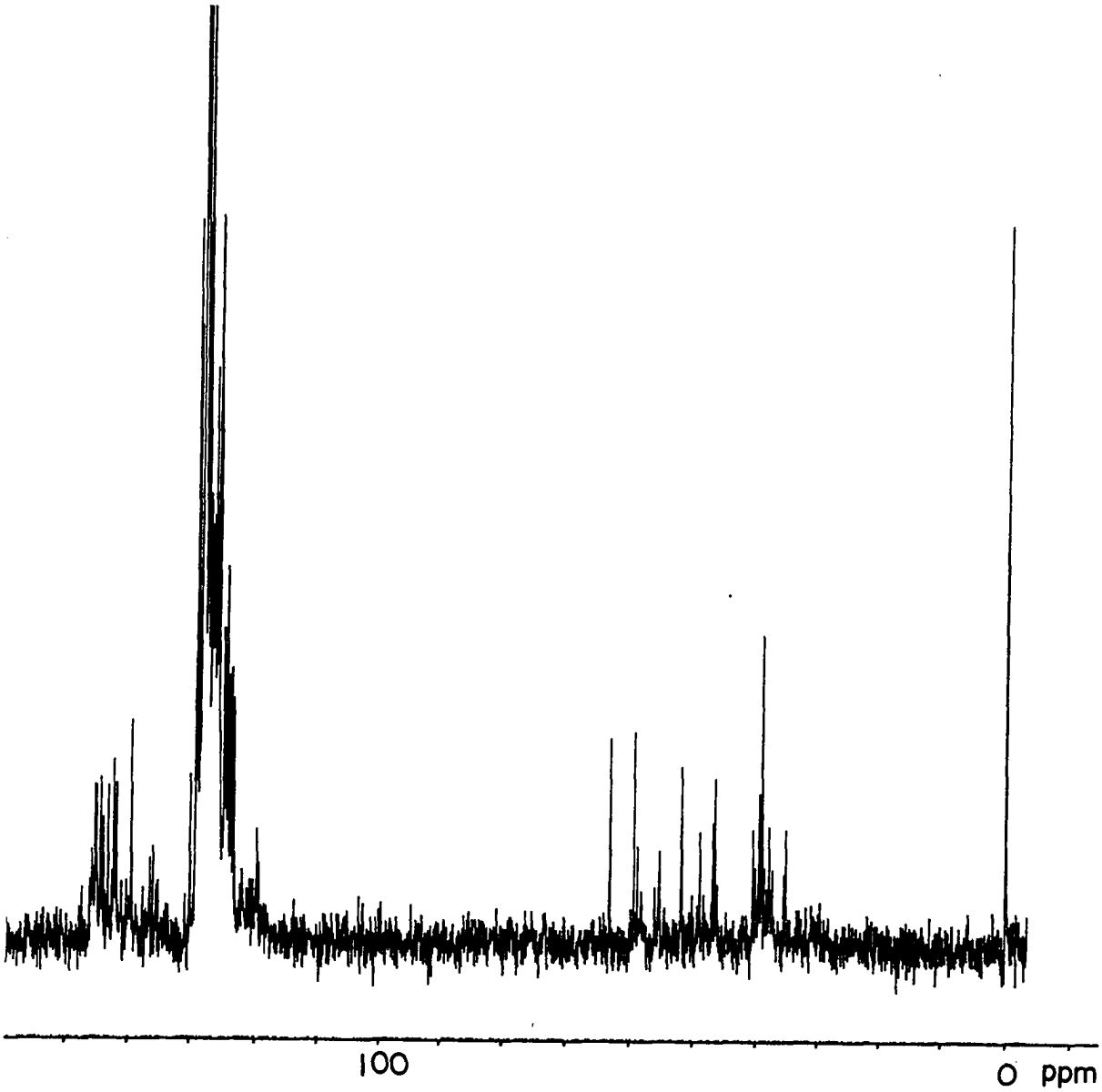
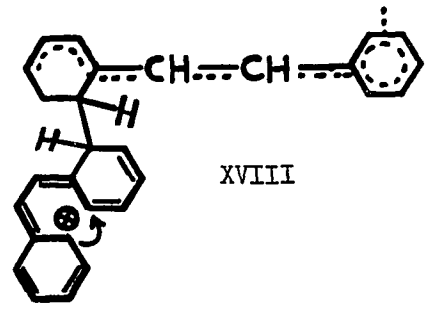
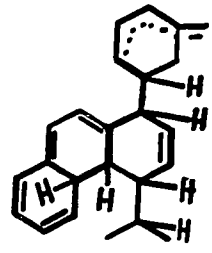


Figure 17. ^{13}C NMR spectrum of the products of $AlCl_3$/trans-stilbene reaction by using atmospheric oxygen as the oxidant and a reaction time of an hour. Conditions: 20%(w/v) in CS_2, C.S. relative to TMS at room temperature, 3414 transients, 45° pulse angle, 4 seconds delay between pulses.

XVIII ⇌ 

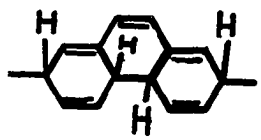
XVIII

XVIII ⟶ 

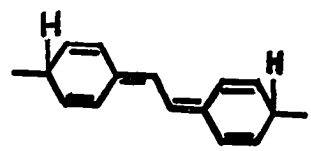
XIX (8)

The broken lines in structure XVI represents delocalized π electrons or partial covalent bond character. Covalent bond formation of XVI would produce XVIII. The formation of XIX from XVIII involves a six-membered ring closure of a carbocation similar to the formation of phenanthrene from dibenzil in the intramolecular Scholl reaction (35).

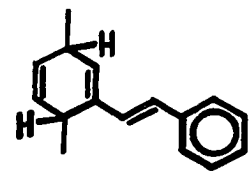
In a similar manner, one can postulate the formation of structures such as XX, XXI, XI(Table 2, section IIIA2), XXII, XXIII, XXIV, XXV and various combinations.



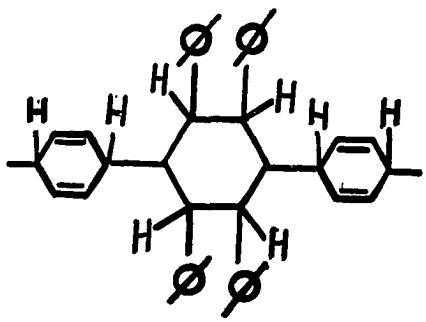
XX



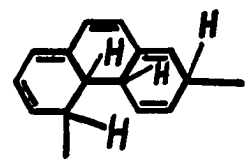
XXI



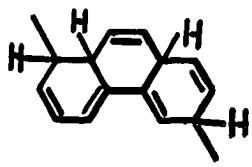
XXII



XXIII



XXIV



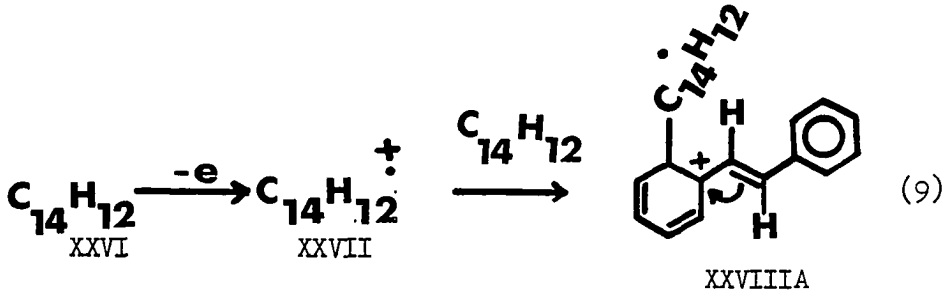
XXV

Many of the above possible structures may form at the initial stage of the polymerization. However, due to steric and electronic reasons, most of them would stop propagation at the oligomer level. The observed average degree of polymerization of 26 for poly(trans-stilbene) does not correspond to an oligomer. The most sterically and electronically favoured propagation of the propagating species

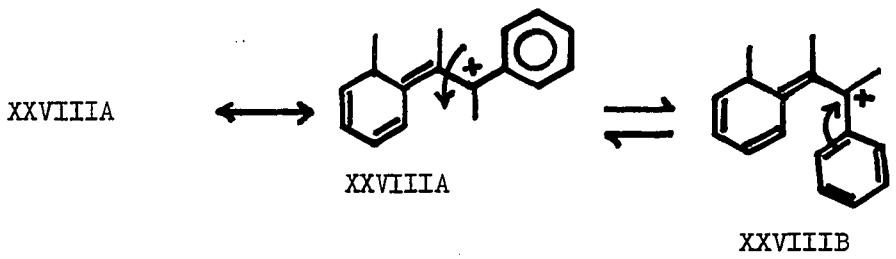
of the structures XIX, XX, XXI, XXII, XXIII, XXIV and XV could only achieve degree of polymerization as high as 26. The sterically and electronically less favoured propagation may form oligomers which could be readily eliminated during the purification process. The observed 26% yield of the recrystallized poly(trans-stilbene) suggests the possible elimination of such low molecular weight and irregular products during the purification process. The reaction products obtained at one hour could be highly contaminated with all these possible side products.

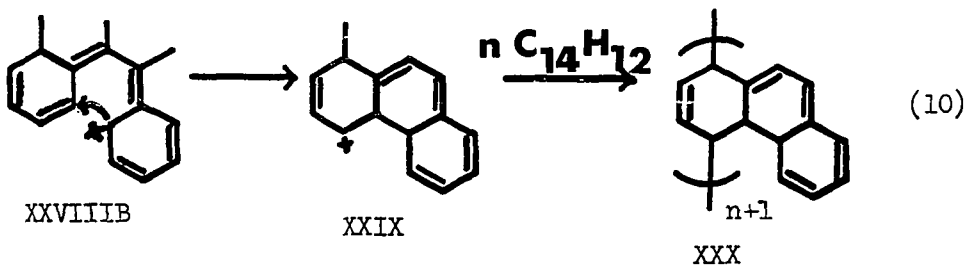
The ^{13}C NMR peaks of the above products in the range of 35-65 ppm(for sp^3 carbons) also suggests that atmospheric oxygen is not an effective oxidant for short reaction periods such as one hour. However, by using strong oxidants such as $CuCl_2$, the system lost all its sp^3 hydrogens within a period of five hours as observed through ^{13}C NMR spectra(see Fig. 6).

The formation of the proposed polymer structure, XV(Section IIIA2) for poly(trans-stilbene) could be explained in terms of the following reaction mechanism:

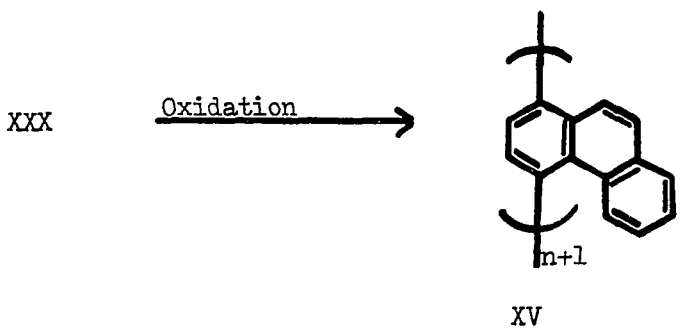


XXVIIIA (9)





(10)



(11)

Species XXVII is the radical cation of trans-stilbene which was discussed earlier. It undergoes covalent bond formation leading to the formation of XXVIIIA. Although attack of the stilbene radical cation on stilbene would be expected to occur equally well at the para and ortho positions, only ortho attack can yield the phenanthrene units linked together through C-1 and C-4 positions. A bond

rotation of XXVIIIA leads to formation of XXVIIIB which could be the common intermediate in the polymerization process of cis- and trans-stilbenes. Our observation that cis-stilbene polymerized much faster than trans-stilbene to give the same final polymer indicates the importance of XXVIIIB relative to XXVIIIA. The formation of XXIX from XXVIIIB involves the six-membered ring closure of a carbocation similar to the formation of phenanthrene from dibenzil in the intramolecular Scholl reaction(35). By repeating this reaction sequence many times, the polymer structure XXX could be obtained. The oxidation and rearomatization of XXX yields the proposed polymer structure XV of poly(trans-stilbene) which consists of phenanthrene units linked through the C-1 and C-4 positions.

D. Poly(diphenyl acetylene)

1. Paramagnetism

Similar to poly(trans-stilbene), poly(diphenyl acetylene) exhibited a singlet ESR spectrum in the solid state(compare Fig.18 with Fig.4B). It also exhibited a singlet ESR spectrum in solution. The line width ΔH_{msl}, of the ESR singlet of the solid was 8.02 G. The spin density of the solid polymer under vacuum was 7.4×10^{16} spins/gram. These unpaired electrons were stable towards water and solvents, suggesting a conjugated backbone in the polymer structure. The effect of air on spin density is shown in Fig.19. The spin density reduced when it was subjected to vacuum(a to b to c in Fig.19), and increased(e to f in Fig.19) when it was exposed to air. However, by applying vacuum for a long period of time(d to e in Fig.19), the spin density approached a constant value of 7.4×10^{16} spins/gram. These results indicate that oxygen interacts with the polymer, perhaps by an electron transfer process.

The dilution studies showed that the relative spin density versus concentration is approximately linear below 3.5%(w/v)(Fig.20). At higher concentrations, the spin density deviates upwards from linearity, possibly due to intermolecular electron transfers or conformational effects.

2. Characterization

The observed number-average molecular weight of poly(diphenyl acetylene) was 3.9×10^3 corresponding to a degree of polymerization of 22. The elemental analysis results showed the presence of chlorine,

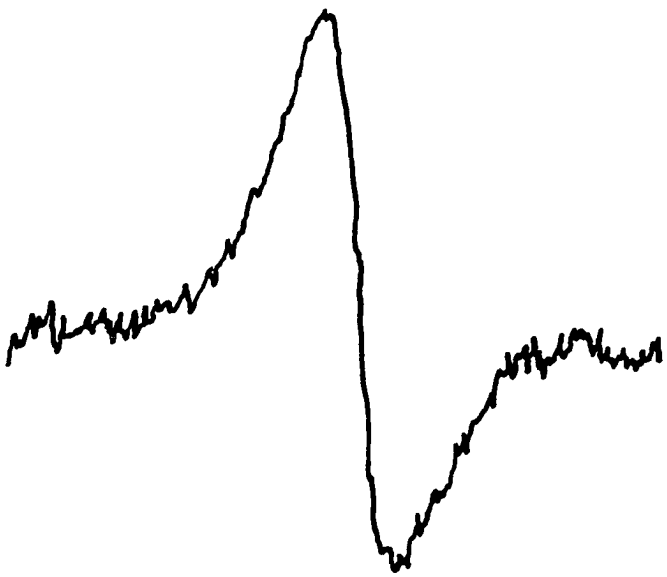


Figure 18. Room temperature ESR spectrum of solid poly(diphenyl acetylene) under vacuum.

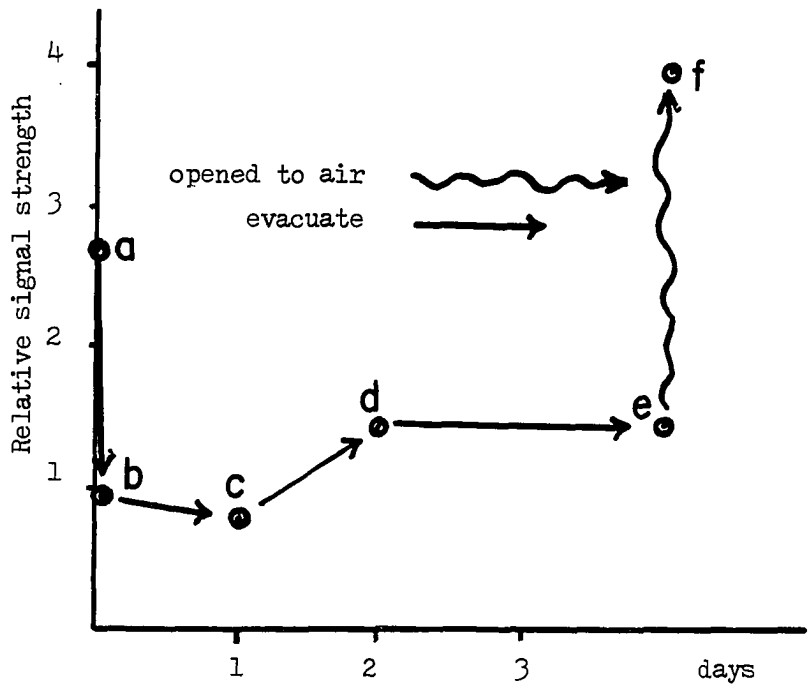


Figure 19. Effect of air on spin density of poly(diphenyl acetylene).

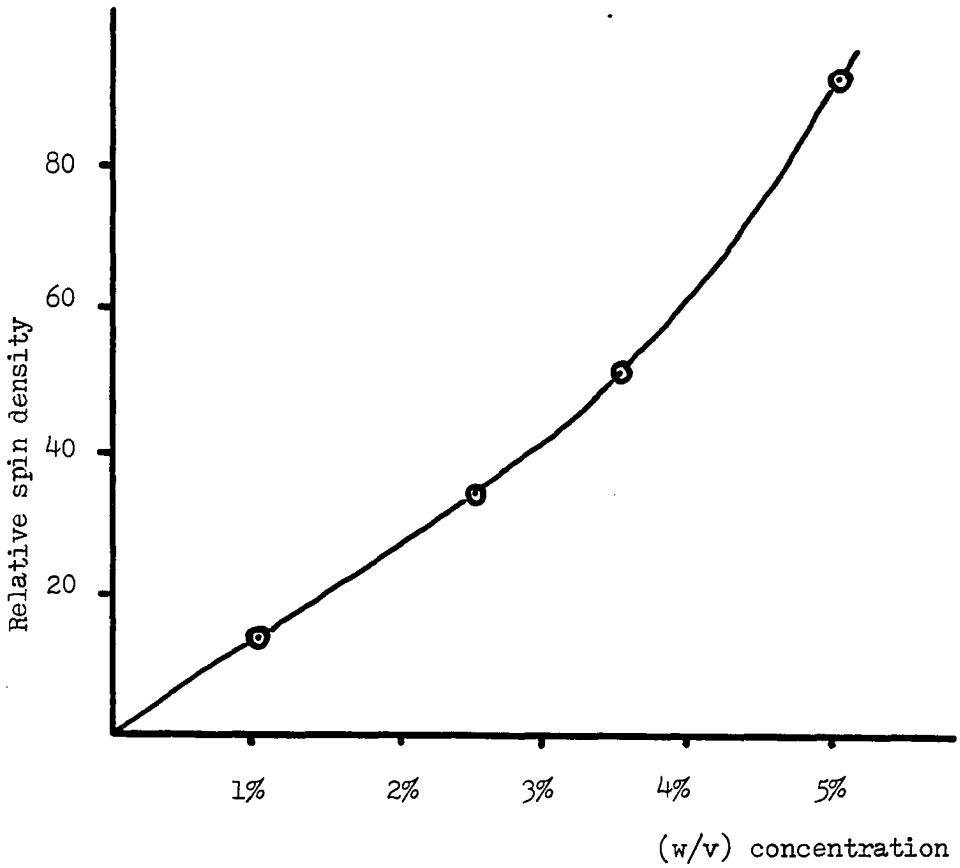


Figure 20. Relative spin densities of poly(diphenyl acetylene) solutions

aluminum and oxygen in addition to carbon and hydrogen:

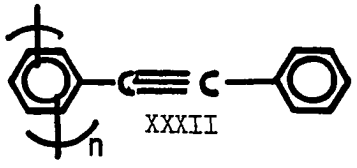
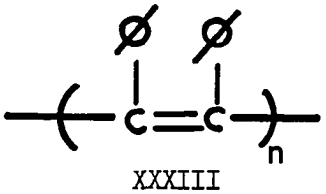
C	H	Cl	Al	O
84.45%	5.35%	1.45%	0.61%	2.94%

The above percentage compositions add up to 94.8%. The rest may be residue due to incomplete combustion. The observed % C value was much lower than the theoretical % C values of XXXI, XXXII and XXXIII(table 3) suggesting an incomplete combustion. The observed % H value, 5.35 was in between the theoretical % H values of structures XXXI and XXXIII. Since C-Al bonds are usually not stable towards water, the Al impurities are probably not incorporated in the polymer structure. It is not clear if oxygen and chlorine impurities are incorporated in the polymer structure. These impurities in polymers are common for this method of synthesis. Other polymers such as polyphenylene prepared under the same conditions also contained similar impurities(21):

C	H	Cl	Residue
89.7%	4.6%	2.5%	2.3%

The proton NMR spectrum of the polymer(Fig.21) consists of only one broad peak at 7.2 ppm, revealing the presence of sp^2 protons. The IR spectrum of the polymer(Fig.22) showed a new absorption band at 3000-2800 cm^{-1} which normally indicates sp^3 C-H vibrations (36). However, aromatic C-H vibrations could also appear at this wave number if aromatic units are located in a conjugated system. We have also observed this unusual IR band at 3000-2800 cm^{-1} for the aromatic C-H vibrations of poly(1,4-diethynylbiphenyl),(Section IIIE3). Since there was no peak for sp^3 protons in the proton NMR

Table 3. Weight % of carbon and hydrogen.

Structure	% C	% H
 XXXI	95.46	4.54
 XXXII	95.46	4.54
 XXXIII	94.38	5.62
Experimental values for poly(diphenyl acetylene)	84.45	5.35

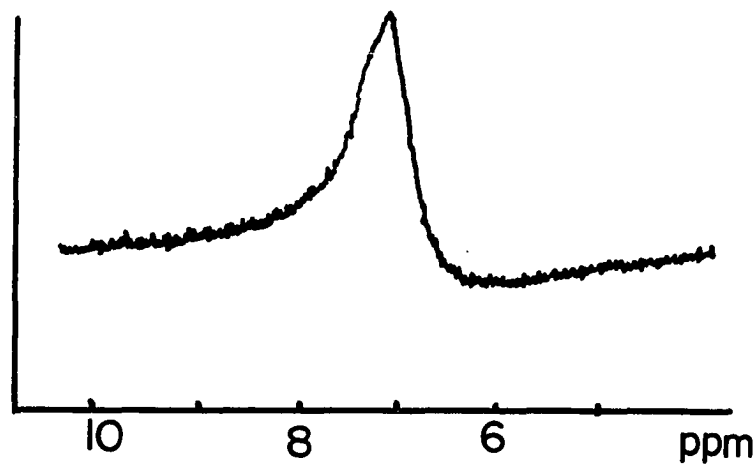


Figure 21. ^{1}H(CW) NMR spectrum of poly(diphenyl acetylene)
Conditions: 10%(w/v) in $CDCl_3$ at room temperature, C.S. relative to TMS.

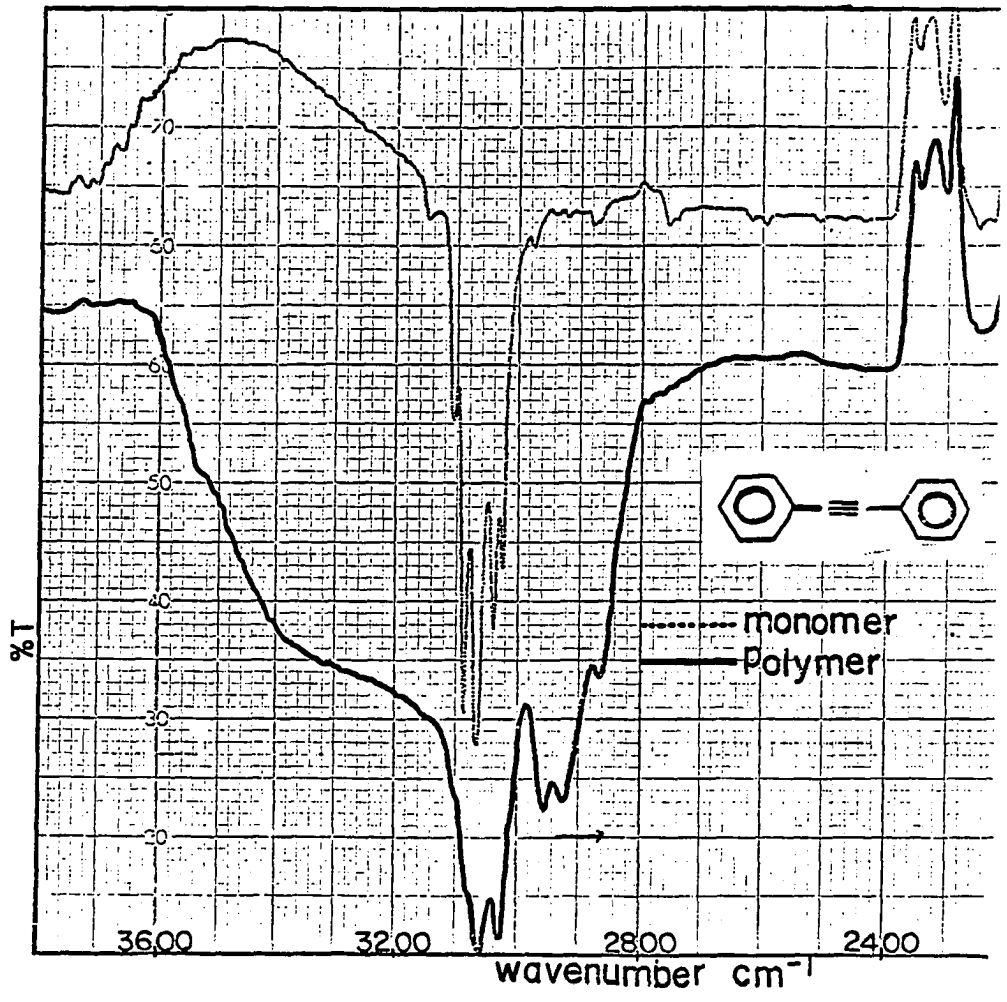


Figure 22. IR spectra of diphenyl acetylene monomer and polymer in CS_2, 2300-3700 cm^{-1}.

spectrum of poly(diphenyl acetylene), this new band was assigned to C-H vibrations of the aromatic groups which are located in a conjugated system. This suggests the presence of disubstituted phenyl rings in the polymer structure. The substitution pattern of the phenyl rings could be identified by the C-H out of plane vibrations in the region of 740-900 cm^{-1}(37). There was a weak absorption for the polymer(Fig.23) at 830 cm^{-1}, indicating that the major substitution pattern of the phenyl rings are non-para.

The ^{13}C NMR spectrum of the polymer(Fig.24) consists of peaks only for sp^2 carbons in the region 115-155 ppm. The acetylenic carbons usually appear in the region 65-90 ppm. The sp carbons normally have long relaxation times(38) and the correct observation of NMR peaks for such carbons require long delay times between radiowave pulses. We have carried out the NMR experiment for accumulation times as long as 36 hours, with low pulse angles, 25° and delay periods as long as 2 minutes. These experiments did not reveal any hint of additional peaks, indicating that C ≡ C bonds of the monomer units are converted by polymerization into structural units which contain sp^2 carbons.

3. The proposed polymer structure

There are two different functional groups in the diphenyl acetylene monomer which could be involved in the polymerization process. Polymerization via phenyl rings only leads to formation of structures XXXI and XXXII(table 3). Polymerization involving triple bonds only could form structure XXXIII. Polymerization involving both the phenyl and acetylene groups could lead to

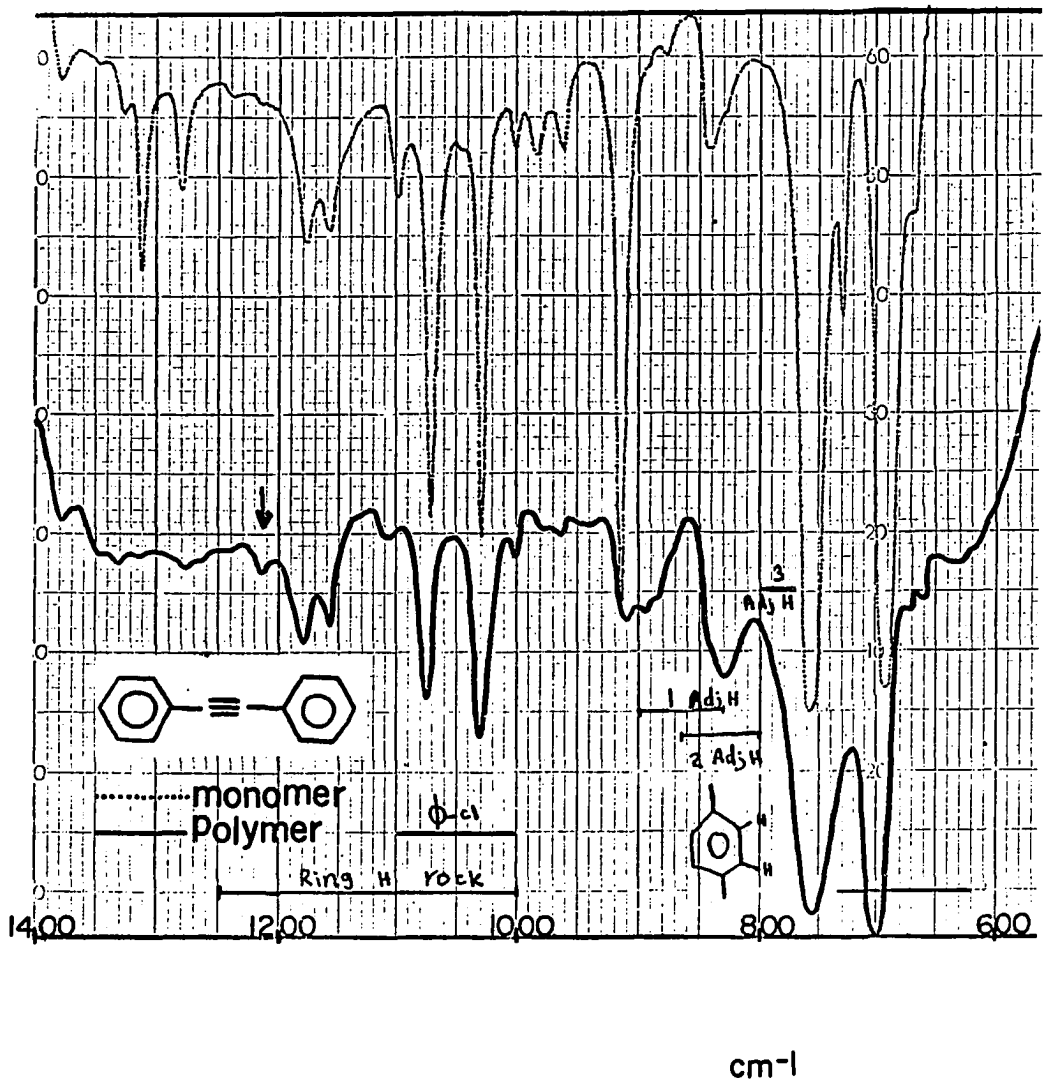


Figure 23. IR spectra of diphenyl acetylene polymer and monomer in CS_2, 600-1400 cm^{-1}.

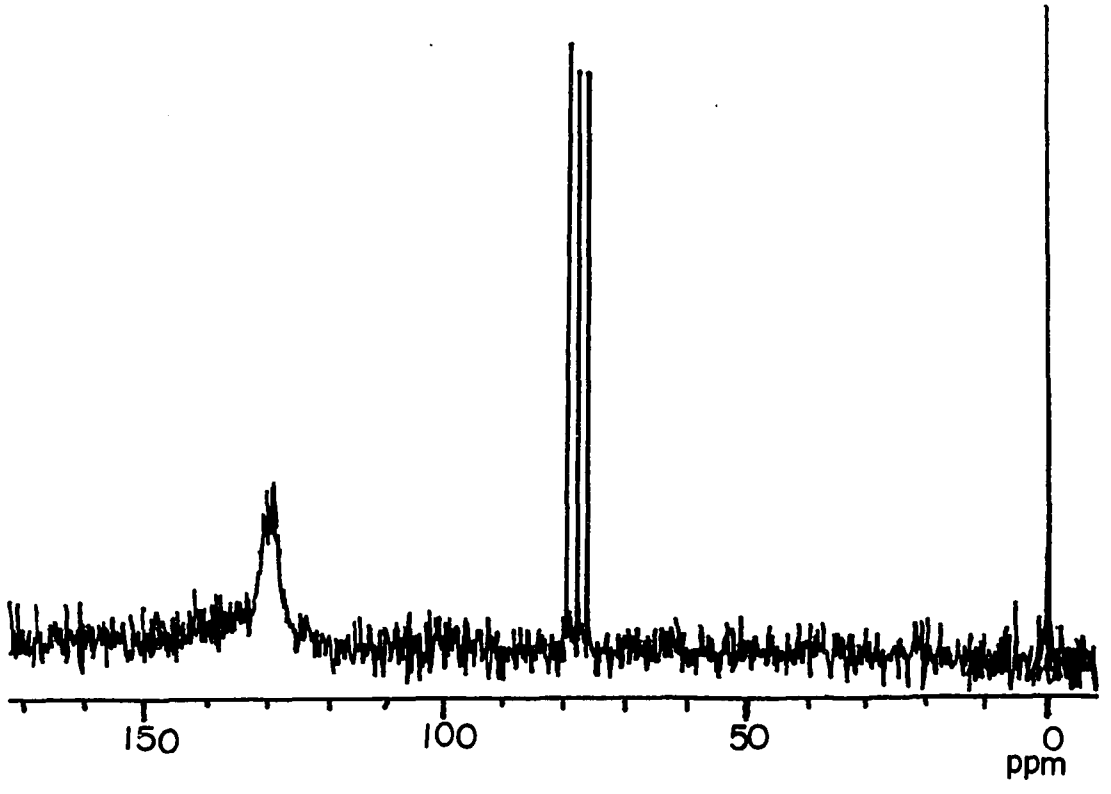
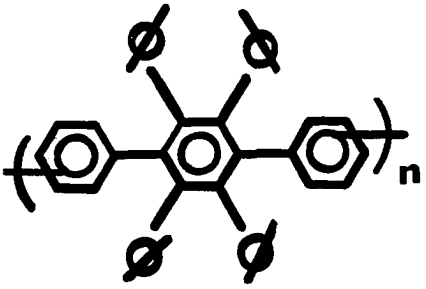
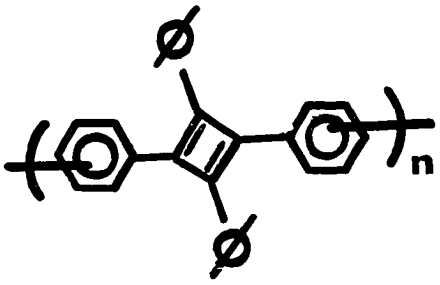


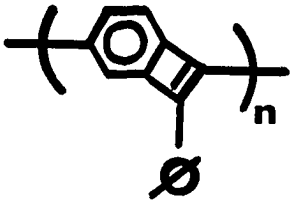
Figure 24. ^{13}C NMR spectrum of poly(diphenyl acetylene).
Conditions: 15%(w/v) in $CDCl_3$ at room temperature, C.S. relative to TMS, 1200 transients, 45° pulse angle, 4 seconds delay between pulses.



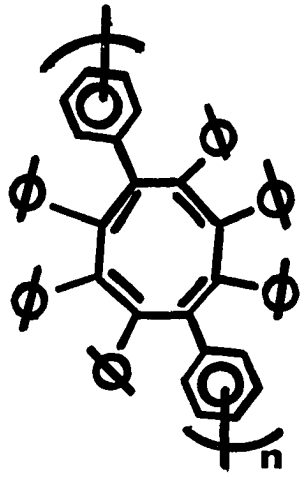
XXXIV



XXXV



XXXVI



XXXVII

more complicated structures such as XXXIV, XXXV, XXXVI and XXXVII. Since there was no peak observed for the acetylenic carbons in the ^{13}C NMR spectrum of poly(diphenyl acetylene), structures XXXI and XXXII containing C≡C triple bonds can be ruled out. Structure XXXIII does not contain any disubstituted phenyl rings and is not in agreement with the observed IR data for poly(diphenyl acetylene). Structures XXXIV, XXXV, XXXVI and XXXVII satisfy the conditions imposed by the ^{13}C NMR and infrared spectral data.

The structure of poly(diphenyl acetylene) may consists of any of the structures, XXXIV, XXXV, XXXVI and XXXVII or combination of these structures. The exact structure can not be defined based on the structural evidence available at present.

The repeat units in structures, XXXIV and XXXV, consist of the cyclic trimer and dimer of diphenyl acetylene, respectively. The formation of the above cyclic-trimer has been observed in the reaction of diphenyl acetylene with Ziegler-Natta catalysts(39). Cyclic-dimer has been proposed as the intermediate in a photo-chemical reaction of diphenyl acetylene to octaphenyl cubane (40). Tetraphenylcyclobutadiene is an unstable compound. However, there is a possibility that the cyclic-dimer gains stability when it is located in a polymeric structure as in XXXV or XXXVI. Since there are no data available on the stability of such polymeric systems, the structures XXXV and XXXVI can not be ruled out.

The above possible structures of poly(diphenyl acetylene) suggests that the aromatic nuclear coupling is complicated by the presence of the triple bond. Both the functional groups, phenyl rings and triple bonds, can be involved in the polymerization process.

E. Poly(4,4'-diethynylbiphenyl)

Poly(4,4'-diethynylbiphenyl) was prepared by the oxidative coupling of 4,4'-diethynylbiphenyl(Reaction 3, section I). The monomer, 4,4'-diethynylbiphenyl, was synthesized through reactions 4, 5 and 6(Section IIC).

1. Characterization of 4,4'-diacetylbiphenyl

The observed melting point 191°C, for the recrystallized product, IX(Section IIC1), was identical to the reported melting point of 4,4'-diacetylbiphenyl(17). The ^1H NMR spectrum of IX (Fig.25) showed an AB quartet at 8.1 ppm for the aromatic hydrogens and a singlet at 2.72 ppm for the methyl protons. The intensity ratio of quartet:singlet was 4:3. The structure 4,4'-diacetylbiphenyl, IX(Section IIC), satisfies all the requirements imposed by the NMR data and is consistent with structure IX(Section IIC1).

2. Characterization of 4,4'-diethynylbiphenyl

The product, 4,4'-di(1-chlorovinyl)biphenyl, of reaction 5 (Section IIC) was not stable at room temperature in air. It became insoluble and turned dark brown upon storage. By using this insoluble material as the starting material for reaction 6(Section IIC), we were not able to isolate any 4,4'-diethynylbiphenyl. Due to the unstable nature of 4,4'-di(1-chlorovinyl)biphenyl, no attempt was taken to purify and characterize it. Hence the dried crude product of reaction 5 (Section IIC), was immediately reduced with $NaNH_2$ to obtain 4,4'-diethynylbiphenyl.

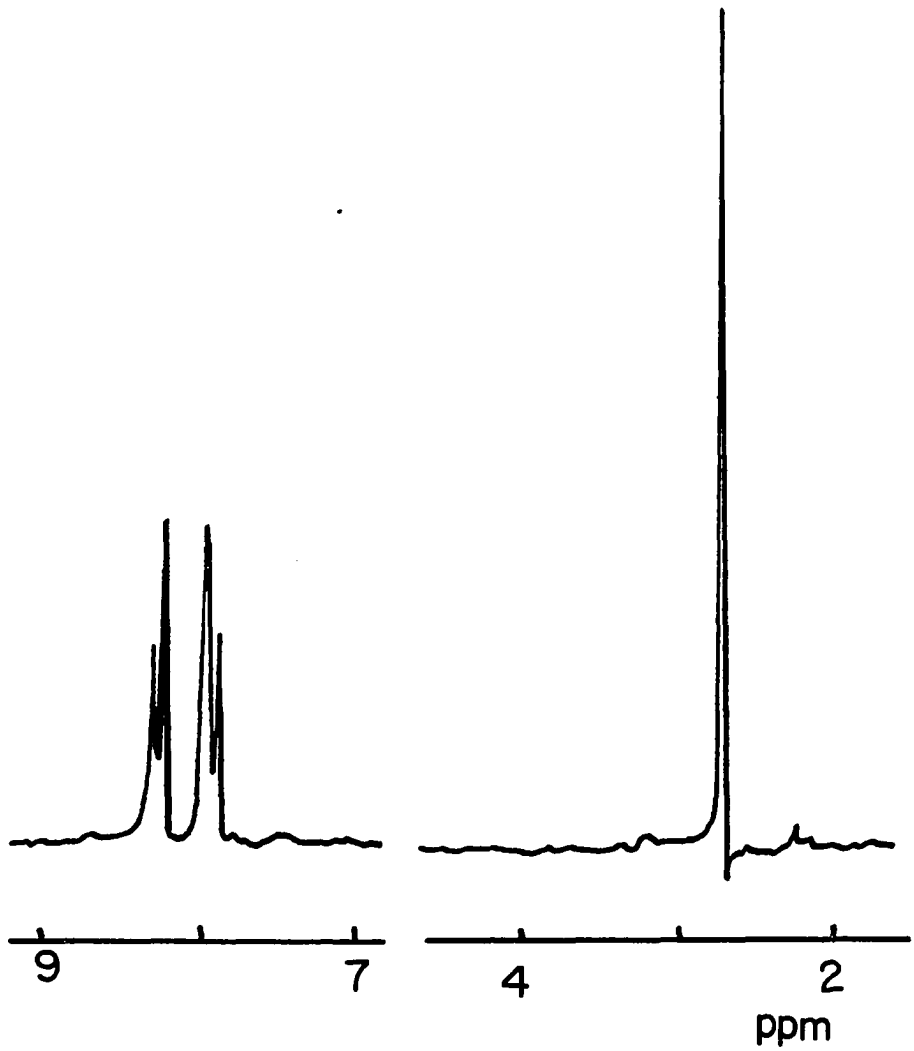


Figure 25. ^{1}H(CW) NMR spectrum of 4,4'-diacetylbiphenyl.
Conditions: 10%(w/v) in $CDCl_3$ at room temperature, C.S. relative to TMS.

The ^{1}H NMR spectrum(Fig.26) of VII(Section IIC3) showed that it contains two types of protons, acetylenic and aromatic at 3.0 ppm(singlet) and 7.4 ppm(singlet) respectively. The integrated intensity ratio of these peaks, aromatic:acetylenic of 4:1, suggests that two acetylenic groups are linked to each biphenyl unit(structure VII, section I).

The IR spectral data also supported the assignment of structure VII for the above product. Infrared absorptions observed at 3260 cm^{-1}(very strong) and 3015 cm^{-1} are indicative of $\equiv$C-H groups(41) and aromatic C-H groups(37), respectively(Fig.27). A weak absorption at 2150 cm^{-1} was observed for C$\equiv$C vibrations (Fig.28). The substitution pattern of the phenyl groups could be identified by its C-H out of-plane rocking vibrations in the region of 740-900 cm^{-1}(37) and the observed absorption at 830 cm^{-1} is indicative of 1,4 para dissimilar substitution(Fig.29).

The ^{13}C NMR spectral data confirmed the assignment of structure VII for the above product. The ^{13}C NMR spectrum of VII (Fig.30) showed six peaks; two of them in the acetylenic(sp) region(65-90 ppm) and the other four peaks in the aromatic(sp^2) region of 115-155 ppm. The assignment of the acetylenic peaks was based on the chemical shift values of its model compounds. Model compounds given in table 4, having phenyl or substituted phenyl structures, were tabulated. Regardless of their β substitution(not equal to a phenyl unit), the α carbon atom always has a higher chemical shift value than that of the β carbon atom(42).

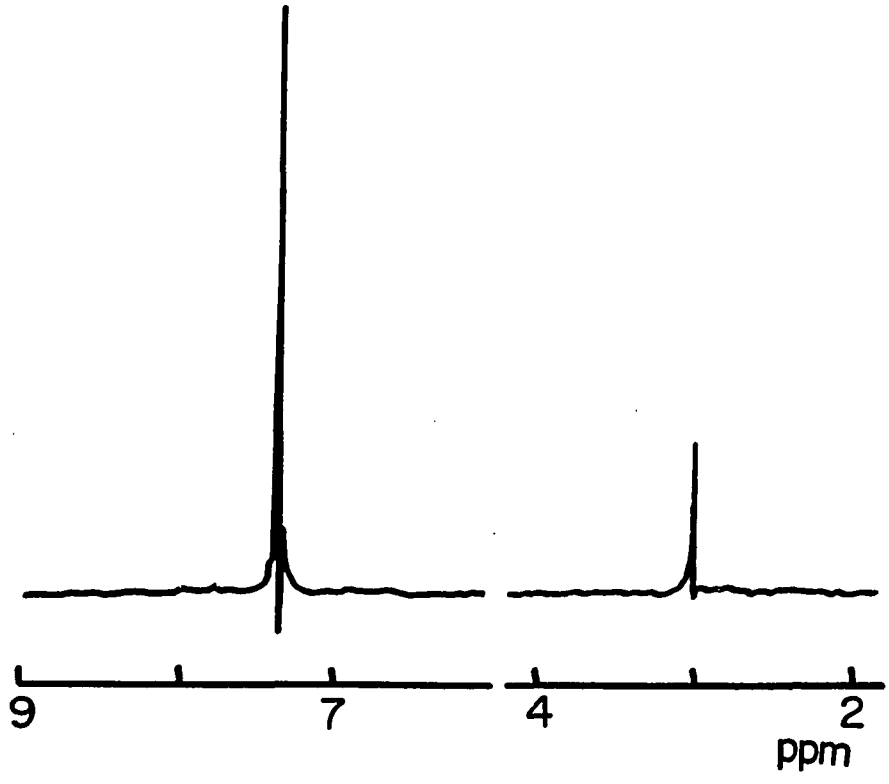


Figure 26. ^{1}H(CW) NMR spectrum of 4,4'-diethynylbiphenyl. Conditions: 10%(w/v) in $CDCl_3$ at room temperature, chemical shifts relative ro TMS.

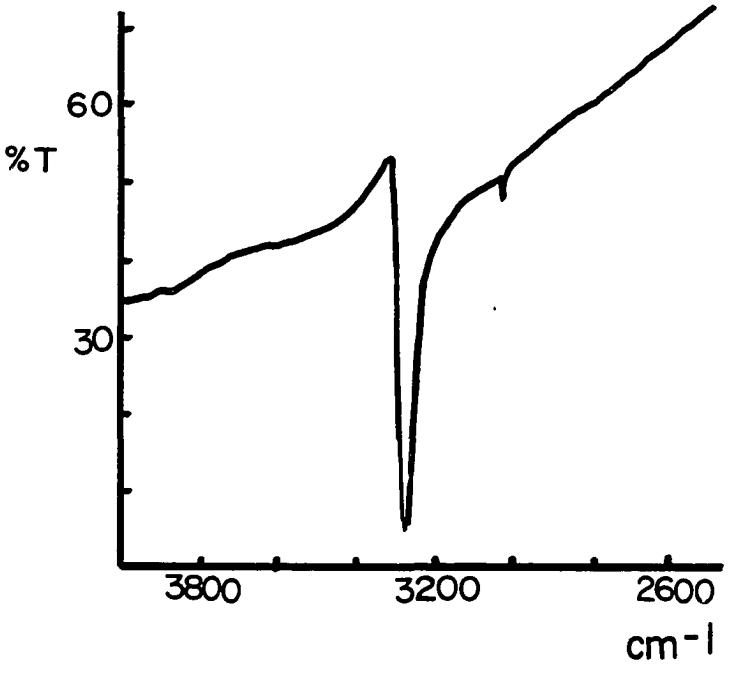


Figure 27. Infrared spectrum of 4,4'-diethynylbiphenyl in KBr mull, 2600-4000 cm^{-1}.

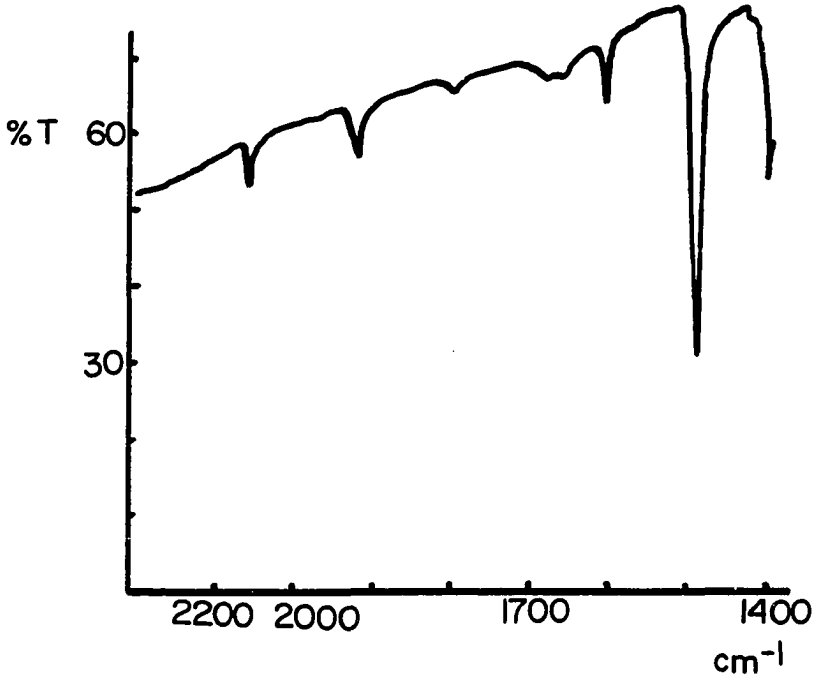


Figure 28. Infrared spectrum of 4,4'-diethynylbiphenyl in KBr mull, 1400-2400 cm^{-1}.

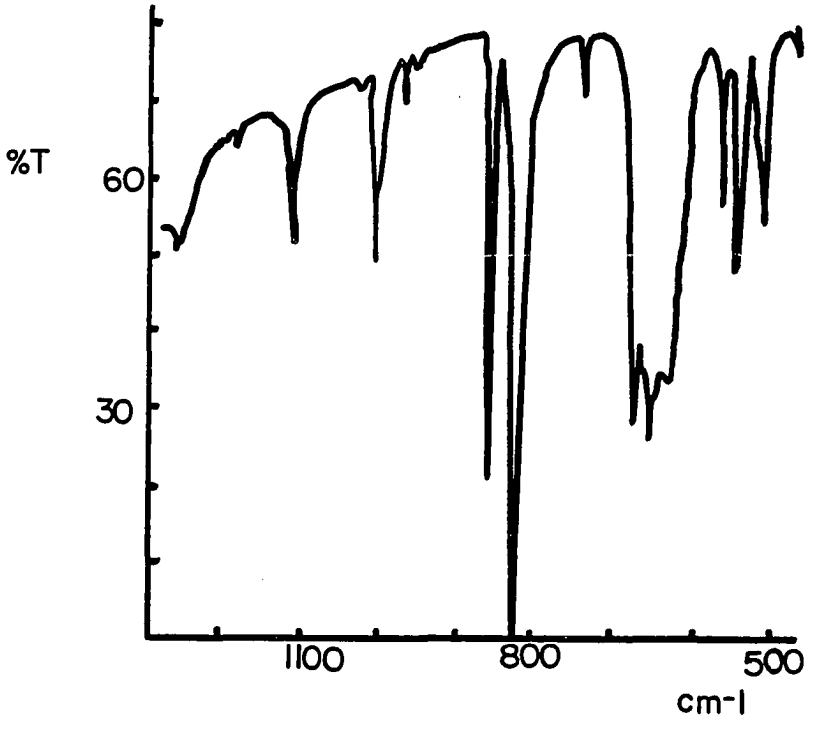


Figure 29. Infrared spectrum of 4,4'-diethynylbiphenyl in KBr mull, 1200-500 cm^{-1}.

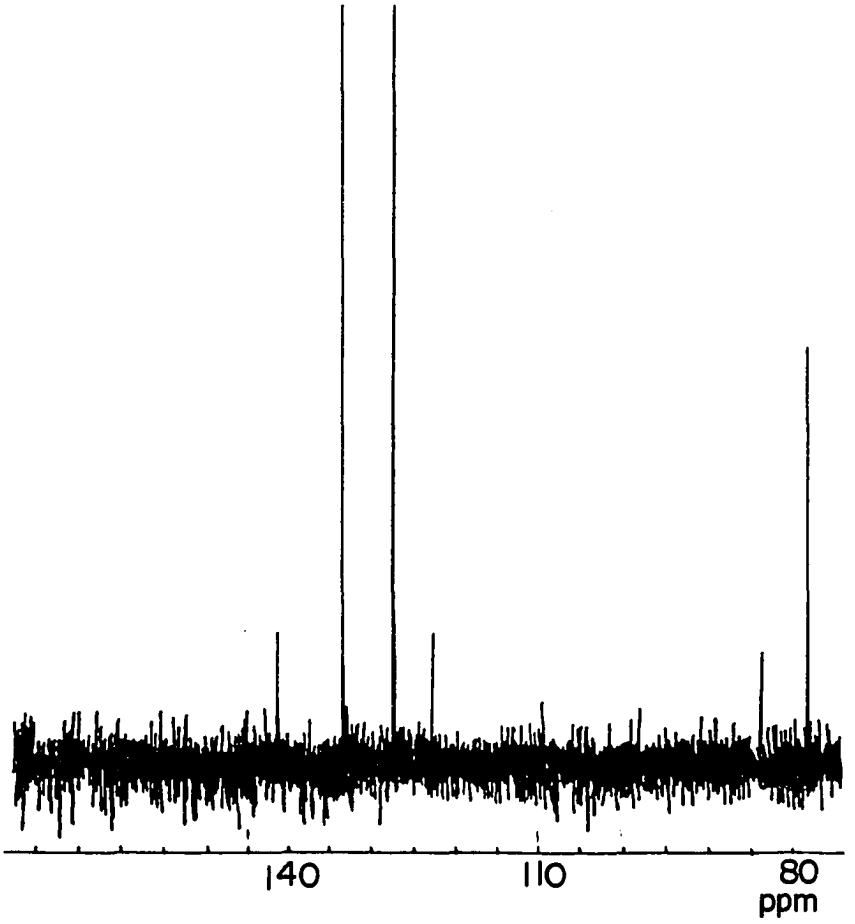
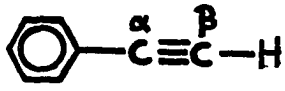
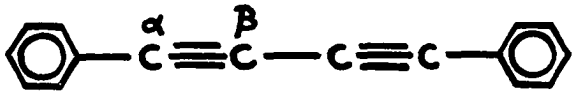
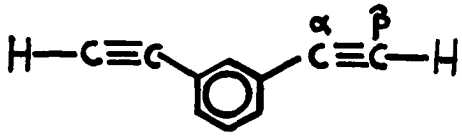
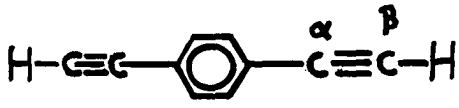
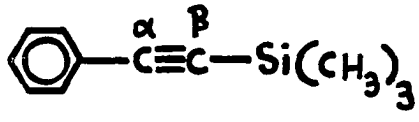
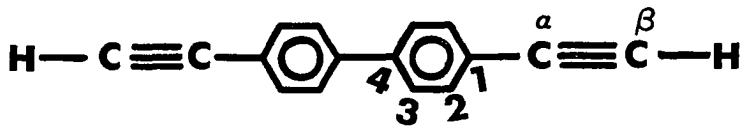


Figure 30. ^{13}C NMR spectrum of 4,4'-diethynylbiphenyl. Conditions: 15%(w/v) in CS_2, C.S. relative to TMS at room temperature, 450 transients, 45° pulse angle, 4 seconds between pulses.

Table 4. ^{13}C NMR chemical shifts for alkyne carbons in phenyl acetylenes(41).

Compound	α	β
	83.3	77.7
	81.7	74.0
	85.7	79.8
	82.5	78.9
	82.9	80.6
	104.0	92.5

Based on this, the acetylenic signals of product VII at 83.55 ppm and 78.17 ppm can be assigned to α and β carbons of the structure VII, respectively.



VII

Out of the acetylenic carbons of VII, the β carbons connected to protons, should be affected by NOE(43). The β carbons may also have shorter spin lattice relaxation times compared to the α carbons. The observed peak height ratio, 1:4.4, for the carbons α : β of VII, suggests that the higher signal intensity for β carbon arise as a combination of NOE and relaxation effects under the experimental conditions.

The assignment of the ^{13}C chemical shift values for the aromatic carbons of VII was done by a comparison of the theoretical chemical shift values with those of the observed ones. The theoretical chemical shift values were obtained by the following calculation using reported values(44), (table 5) for the substituent effects on benzene. Considering the acetylene and phenyl substitutions of the phenyl rings of VII, the chemical shift values of the carbons in phenyl rings could be calculated as follows:

C_1 ppm = 128.5 - 6.1 - 1.2

= 121.2

Table 5. ^{13}C substituent effects of substituted benzene.

Benzene ^{13}C chemical shift = 128.5 ppm(43)

Substituent	C_1	ortho	meta	para
—C≡C—H	- 6.1	3.8	0.4	- 0.2
	13.1	- 1.1	0.4	- 1.2

C_2 ppm = 128.5 + 3.8 + 0.4

= 132.7

C_3 ppm = 128.5 + 0.4 - 1.1

= 127.8

C_4 ppm = 128.5 + 13.1 - 0.2

= 141.4

The observed ppm values 121.99, 132.63, 126.74 and 140.44 were in close agreement with the calculated ppm values and have been assigned to C_1, C_2, C_3 and C_4 carbon atoms respectively.

3. Characterization of poly(4,4'-diethynylbiphenyl)

The IR spectrum of product VIII showed no absorption band at 3260 cm^{-1}(Fig.31), indicating that the acetylenic bonds of the monomer are converted into some other structural units during the polymerization process. The absorption band at 2920 cm^{-1} usually indicates aliphatic C-H bonds(36). However, the aromatic C-H vibrations also could appear at this wavenumber, if aromatic units are in a more extensively conjugated system. Since there was no peak observed for the sp^3 carbons in the ^{13}C NMR spectrum of the polymer (vide infra), the absorption band at 2920 cm^{-1} was assigned to the aromatic C-H vibrations of the phenyl units which are in a more extensively conjugated system. The absorptions at 2130 cm^{-1} and 2200 cm^{-1} are indicative of C≡C triple bonds of the di-substituted and mono-substituted acetylene, respectively(41), (Fig.32). The observed change in the intensity ratio of the peaks at 1480 cm^{-1} and 1595 cm^{-1}(compare Fig.32 with Fig.28) of the phenyl C=C

Figure 31. IR spectrum of poly(4,4'-diehtynylbiphenyl) in KBr mull, 2600-4000 cm^{-1}.

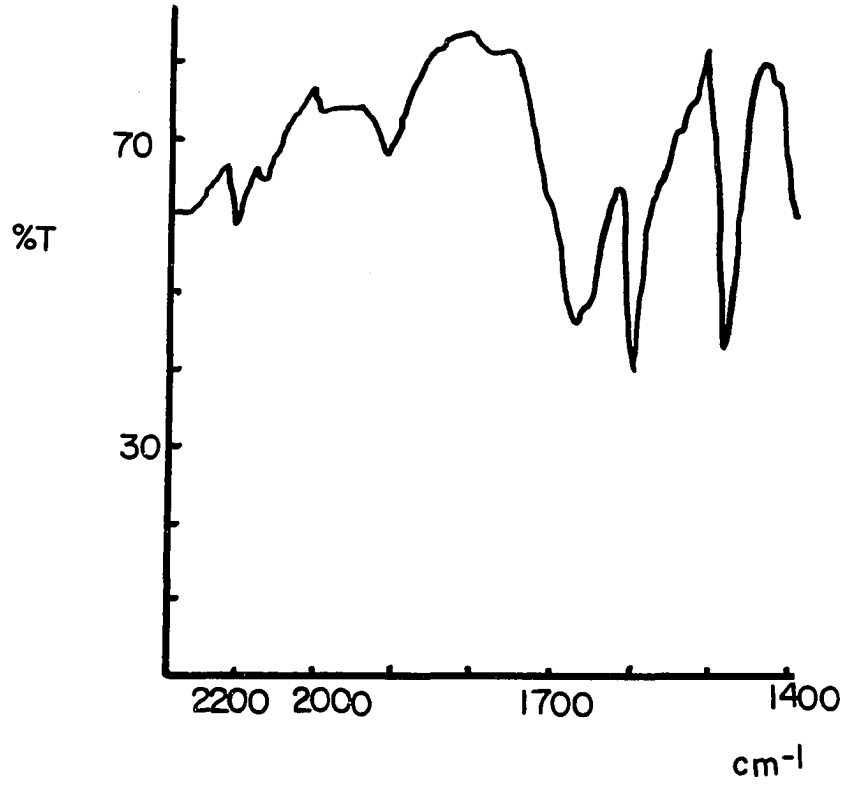
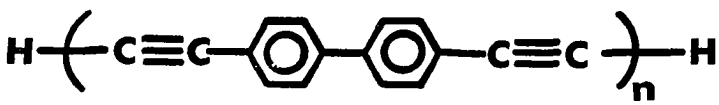


Figure 32. IR spectrum of poly(4,4'-diethynylbiphenyl) in KBr mull, 1400-2400 cm^{-1}.

vibrations by this polymerization process is indicative of strong interactions of acetylene groups with phenyl units of the polymer probably due to formation of a more highly conjugated system. The substitution pattern of the phenyl rings could be identified by the C-H out of plane vibrations in the region of 740-900 cm^{-1}(37). The observed absorption band at 815 cm^{-1} is indicative of 1,4 para disubstitution in the phenyl groups(Fig.33). The infrared data are consistent with a polymer structure containing the repeat units of structure VIII.



VIII

The polymer exhibited an ESR singlet (Fig.34) having a linewidth, ΔH_{msl} of 9.4 G and spin density of 5.41 x 10^{15}spins/gram. These results are also consistent with the polymer structure, VIII.

The structure of the polymer was confirmed by the ^{13}C NMR results. The ^{13}C NMR spectrum of the polymer(Fig.35) exhibited 6 peaks for two different types of carbons; acetylenic sp in the region of 65-90 ppm and aromatic sp^2 in the region of 115-155 ppm. The assignment of these six peaks was done by comparing the ppm values for the polymer with those for its monomer(Table 6). The observed chemical shift values of the polymer were in close agreement with the chemical shift values of the monomer and hence the polymer structure was assigned to structure VIII.

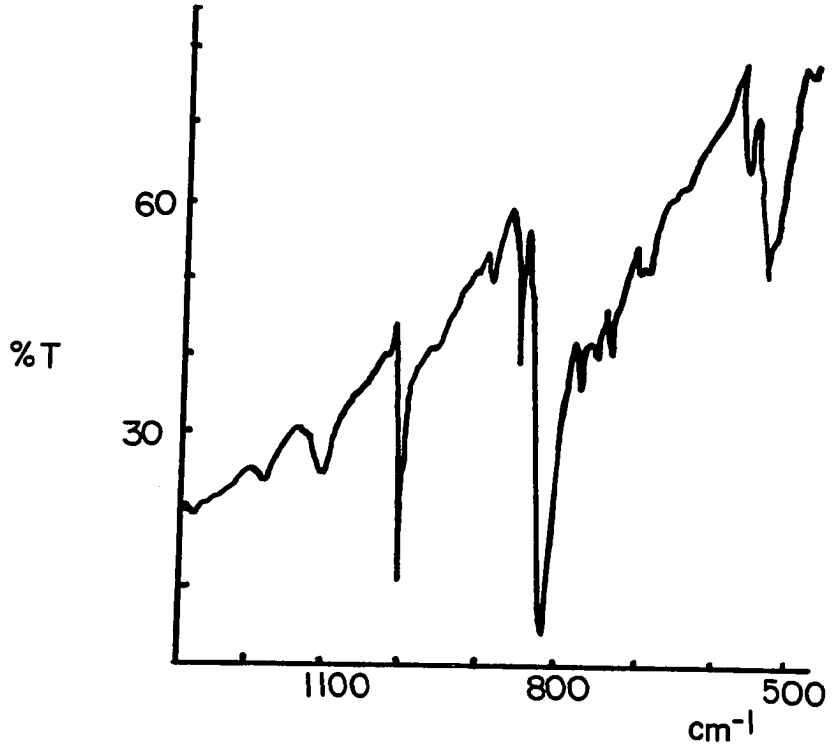


Figure 33. IR spectrum of poly(4,4'-diethynylbiphenyl) in KBr mull, 500-1300 cm^{-1}.

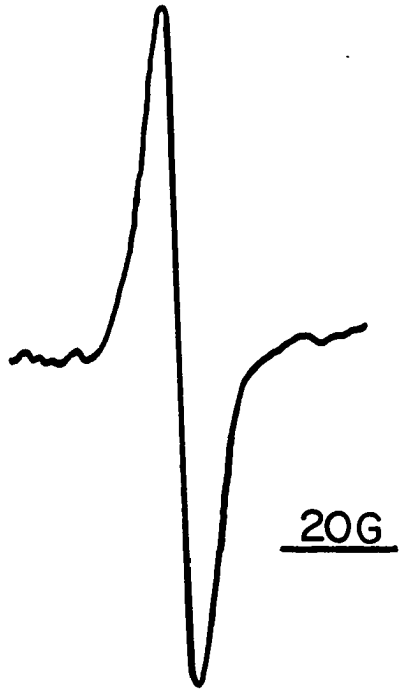


Figure 34. Room temperature ESR spectrum of poly(4,4'-diethynylbiphenyl).

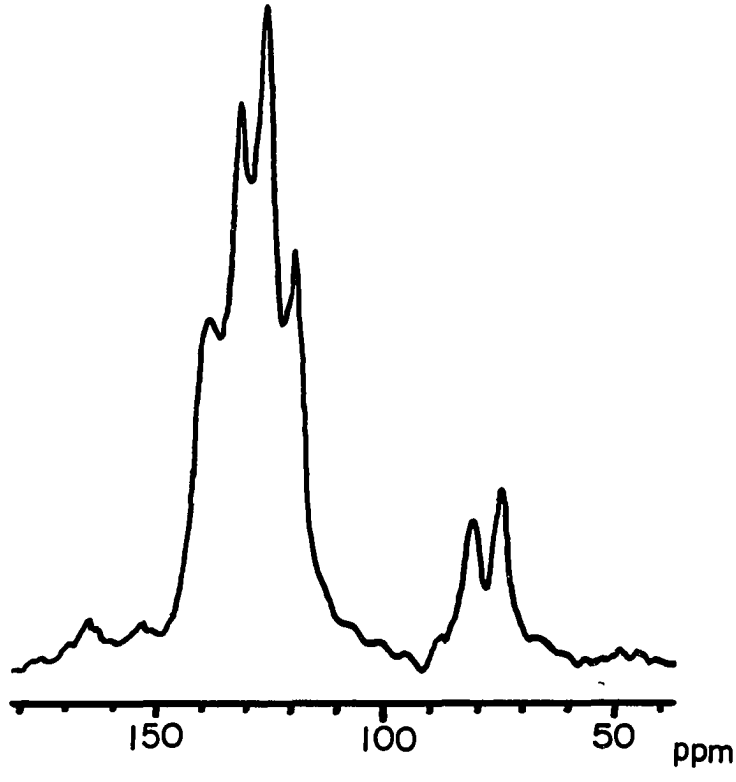
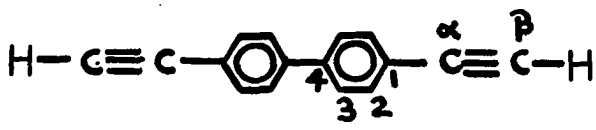


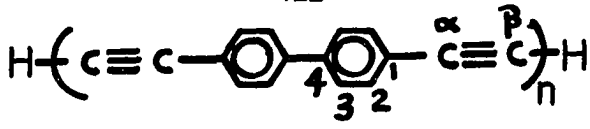
Figure 35. CPMAS spectrum of poly(4,4'-diethynylbiphenyl)
Conditions: 2 m second cross polarization time, 801 scans, 3 seconds between scans.

Table 6. Correlation of ^{13}C chemical shift values of 4,4'-diethynylbiphenyl with its polymer.

Compound	α	β	C_1	C_2	C_3	C_4
VII	78.17	83.55	121.99	132.63	126.74	140.94
VIII	74.20	81.30	120.00	132.40	126.50	139.40



VII



VIII

A comparison of the chemical shift values of the α and β carbons of 4,4'-diethynylbiphenyl with its polymer showed that the above carbons of the polymer are shielded compared to those of the monomer. However, this effect was higher for the α carbon atom (3.97 ppm difference) compared to β carbon atom (2.25 ppm difference).

F. Poly(1,4-diphenyl-1,3-butadiyne)

1. Characterization of the soluble part

The soluble portion of poly(1,4-diphenyl-1,3-butadiyne) in the solid state exhibited an ESR singlet having a line width, ΔH_{msl}, of 6.8 G(Fig.36). The spin density of the solid polymer under vacuum was 6.3×10^{16} spins/gram and these unpaired electrons were stable towards water and solvents, suggesting a conjugated backbone in the polymer structure. The number-average molecular weight of the polymer was 1.8×10^{3}. This value was higher than the reported number-average molecular weights of the thermal(19) and Ziegler-Natta catalyst(45) polymerized 1,4-diphenyl-1,3-butadiyne, 1110 and 1250, respectively. The elemental analysis results showed that the polymer contains a minute amount of aluminum from the catalyst:

C	H	Cl	Al	O
85.21%	5.09%	6.87%	0.03%	2.18%

Similar to poly(diphenyl acetylene) (Section IIID2), the soluble part of poly(1,4-diphenyl-1,3-butadiyne) also contains oxygen and chlorine. However, the amount of chlorine in the polymer was much larger and suggests the possibility of partial hydrochlorination of triple bonds during the polymerization.

The ^{1}H NMR spectrum of this polymer showed a very broad peak at 7.3 ppm for sp^{2}protons (Fig.37). The IR spectrum of this polymer (Fig.38) showed the formation of a new absorption band at 2925 cm^{-1} which normally indicates aliphatic sp^{3} C-H vibrations (36). However, the aromatic C-H vibrations also could appear at this wavenumber

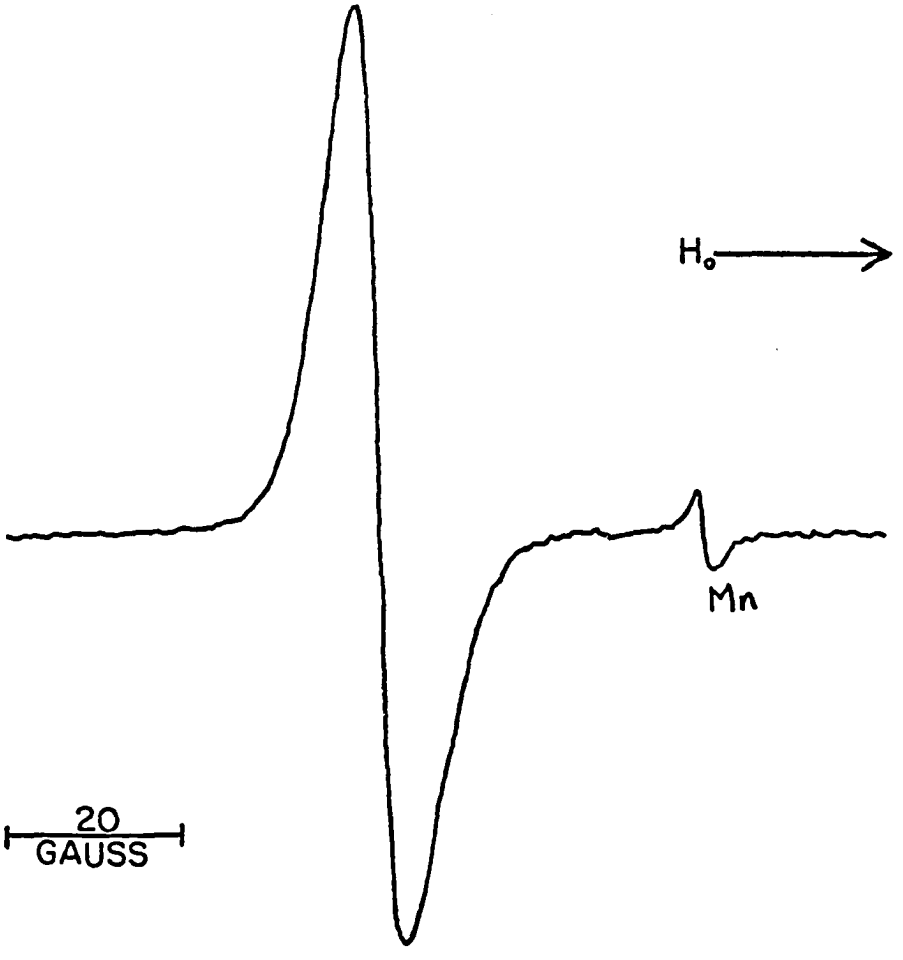


Figure 36. Room temperature ESR spectrum of the soluble part of poly(1,4-diphenyl-1,3-butadiyne) in solid state.

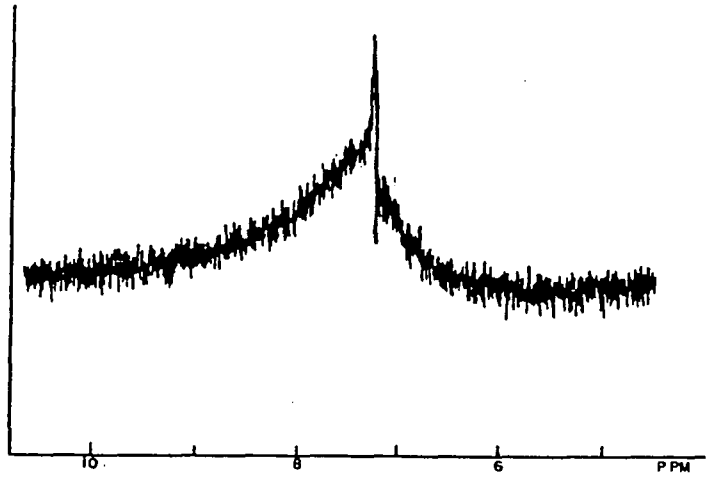


Figure 37. ^{1}H(CW) NMR spectrum of poly(1,4-diphenyl-1,3-butadiyne). Conditions: 10%(w/v) in $CDCl_3$, chemical shifts relative to TMS at room temperature.

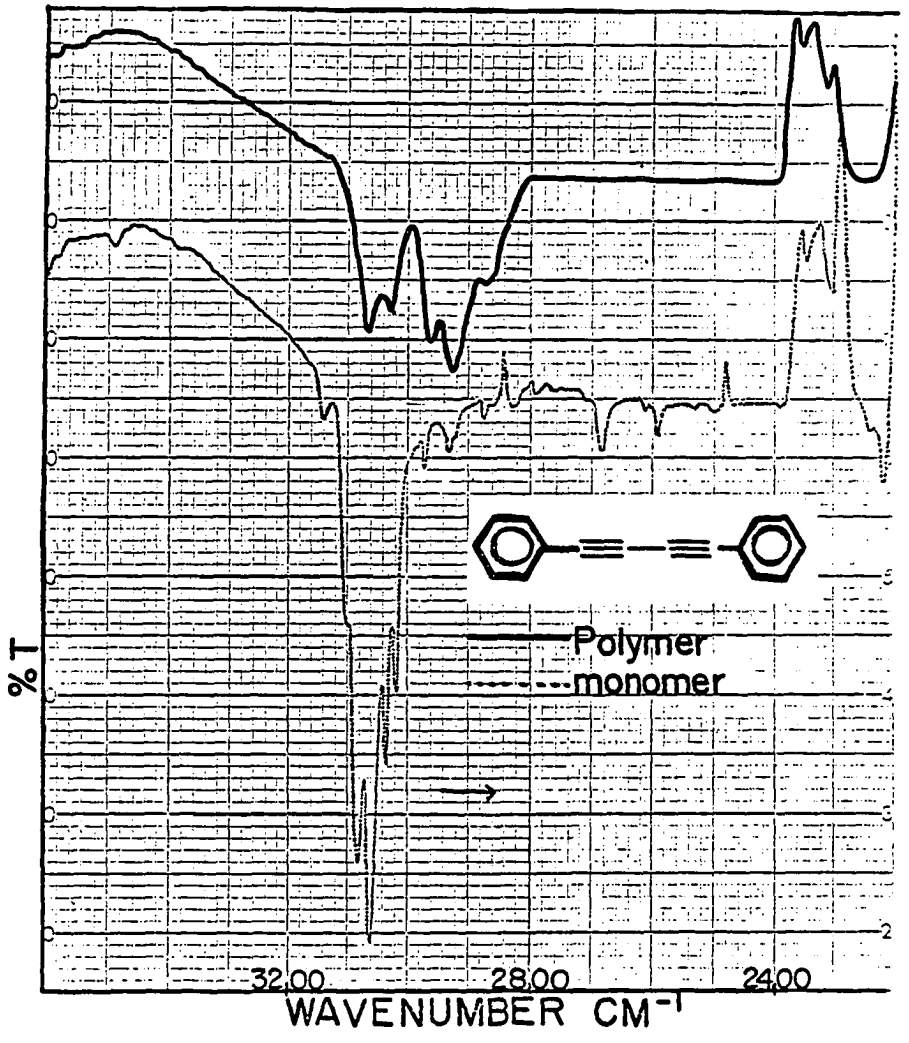
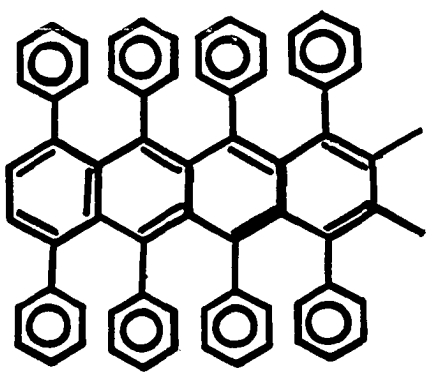


Figure 38. IR spectra of 1,4-diphenyl-1,3-butadiyne monomer and polymer in CS_2, 2200-4000 cm^{-1}.

if the aromatic units are part of a long conjugated system(Fig.31 and section III E3). Since there was no peak observed for sp^3 protons in the proton NMR spectrum, the above absorption band was assigned to C-H vibrations of the phenyl rings located in a conjugated system. Similar situations have been observed for poly(diphenyl acetylene) and poly(4,4'-diethynylbiphenyl), (Sections III D2 and III E3). We have not observed the above unusual IR band at 2925 cm^{-1} for the thermally-polymerized 1,4-diphenyl-1,3-butadiyne(Fig.39). The thermally polymerized 1,4-diphenyl-1,3-butadiyne was proposed(19) to be a polyacene structure(XXXVIII).



XXXVIII

Based on the above IR data, the structure XXXVIII cannot be the structure of the soluble part of poly(1,4-diphenyl-1,3-butadiyne).

The UV-VIS spectrum of poly(1,4-diphenyl-1,3-butadiyne), (Fig. 40) showed that it differs from the reported UV-VIS spectrum(45) of the Ziegler-Natta catalyst polymerized 1,4-diphenyl-1,3-butadiyne (Fig.41). Compared to the Ziegler-Natta catalyst polymerized

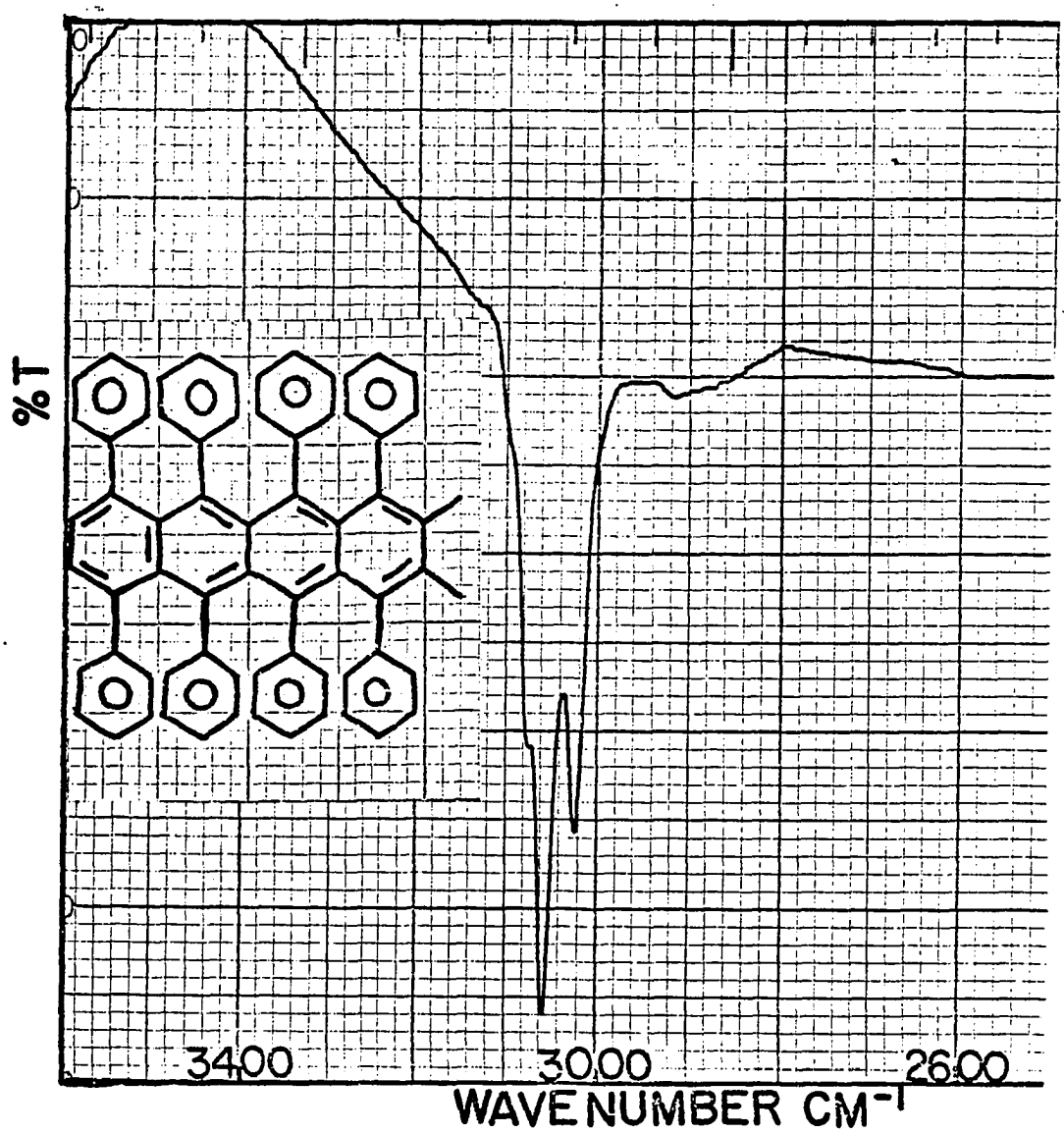


Figure 39. IR spectrum of thermally polymerized 1,4-diphenyl-1,3-butadiyne in CS_2, 2200-4000 cm^{-1}.

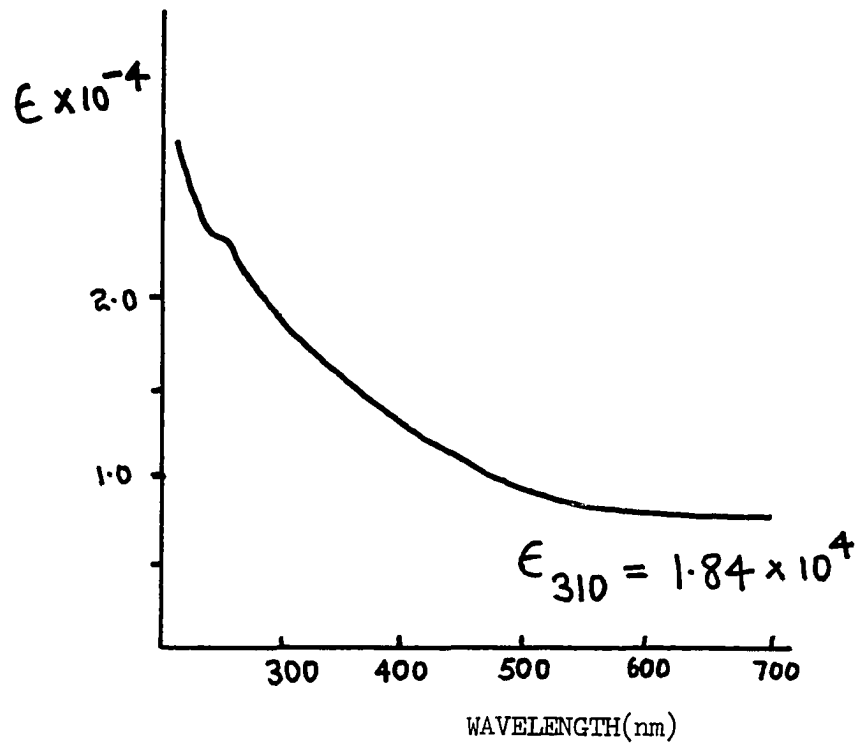


Figure 40. UV & VIS spectrum poly(1,4-diphenyl-1,3-butadiyne).

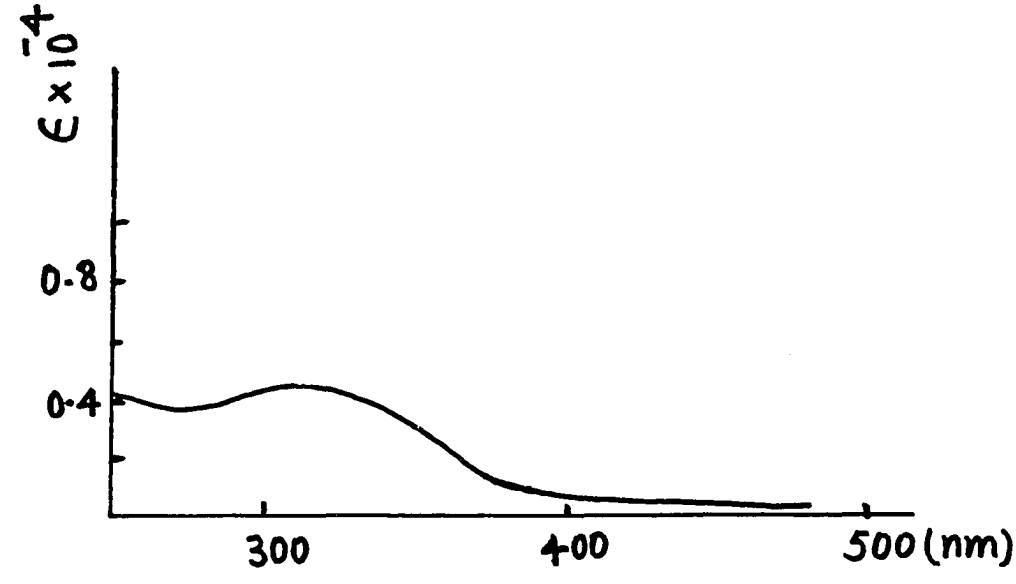
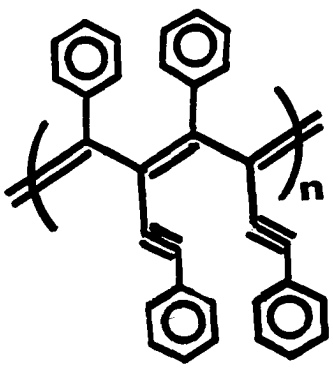
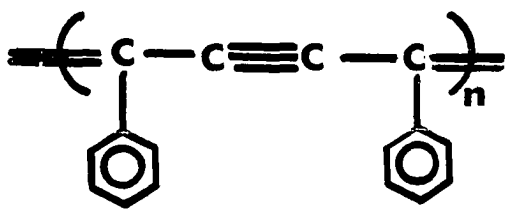


Figure 41. Reported UV spectrum (45) of the Ziegler-Natta catalyst polymerized 1,4-diphenyl-1,3-butadiyne.

1,4-diphenyl-1,3-butadiyne, poly(1,4-diphenyl-1,3-butadiyne) has higher molar absorptivity coefficients. The proposed structures XXXIX and XL(45) for the Ziegler-Natta catalyst polymerized 1,4-diphenyl-1,3-butadiyne do not contain any disubstituted phenyl rings. Based on the IR and UV-VIS spectral data of the soluble part of poly(1,4-diphenyl-1,3-butadiyne), the structures XXXIX and XL can be ruled out.



XXXIX



XL

The structure of the soluble part of poly(1,4-diphenyl-1,3-butadiyne) contains disubstituted phenyl rings which are located in a conjugated system as observed through IR spectroscopy. However, the exact structure of this polymer can not be defined based on the structural evidence available at present.

2. Characterization of the insoluble part

The insoluble part of poly(1,4-diphenyl-1,3-butadiyne) also exhibited an ESR singlet having a linewidth, ΔH_{msl}, of 6.2 G and spin density of 5.41 x 10^{15} spins/gram (Fig.42). These unpaired electrons were stable towards water and solvents, suggesting a conjugated backbone in the polymer structure. The IR spectrum of the insoluble part of poly(1,4-diphenyl-1,3-butadiyne) was very similar to the IR spectrum of the soluble part(compare Fig.43 with Fig.38 in section III F1). The new absorption band at 2920 cm^{-1} may again correspond to C-H vibrations of aromatic groups which are located in a conjugated system. The IR absorption bands at 2200 cm^{-1}(very weak) and 1950 cm^{-1} correspond to C≡C triple bonds and C=C=C units respectively(Fig.44). The observed absorptions at 700 and 760 cm^{-1} suggests that the substitution pattern of the phenyl rings are non-para(37), (Fig.45).

A comparison of the above IR data with that of poly(4,4'-diethynylbiphenyl), (Section III E3) showed that the structure of the insoluble part of poly(1,4-diphenyl-1,3-butadiyne) does not contain repeat units given in structure VIII(Section I). However, based on the above IR data, the structure of the insoluble portion of poly(1,4-diphenyl-1,3-butadiyne) should contain the following structural units, XLI, XLII and XLIII.

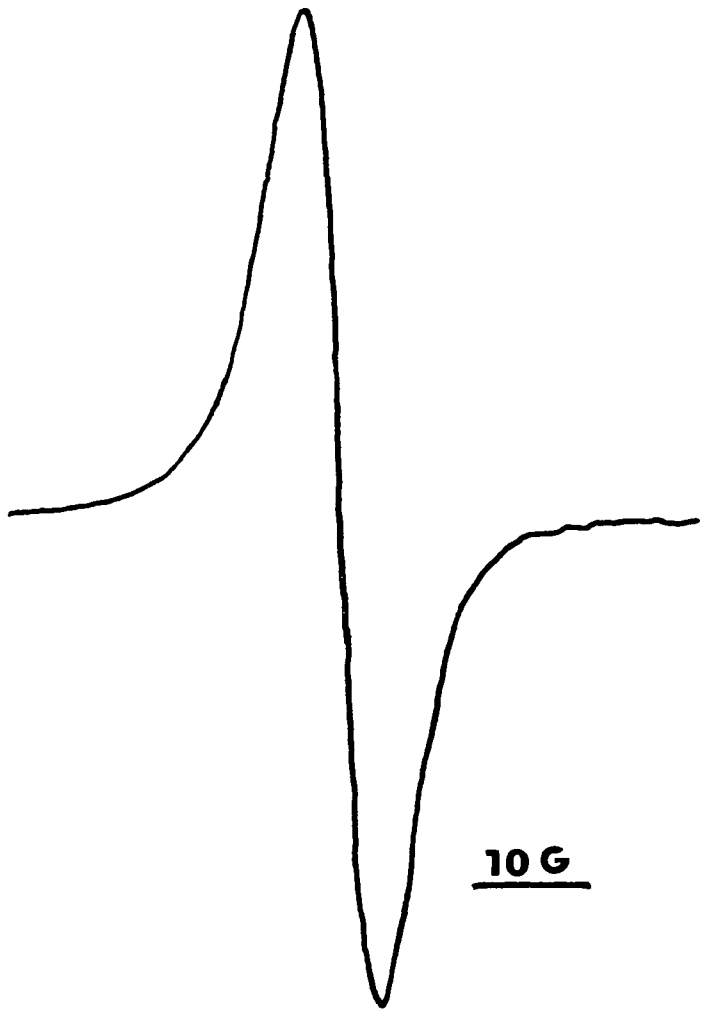


Figure 42. Room temperature ESR spectrum of the insoluble part of poly(1,4-diphenyl-1,3-butadiyne) in solid state.

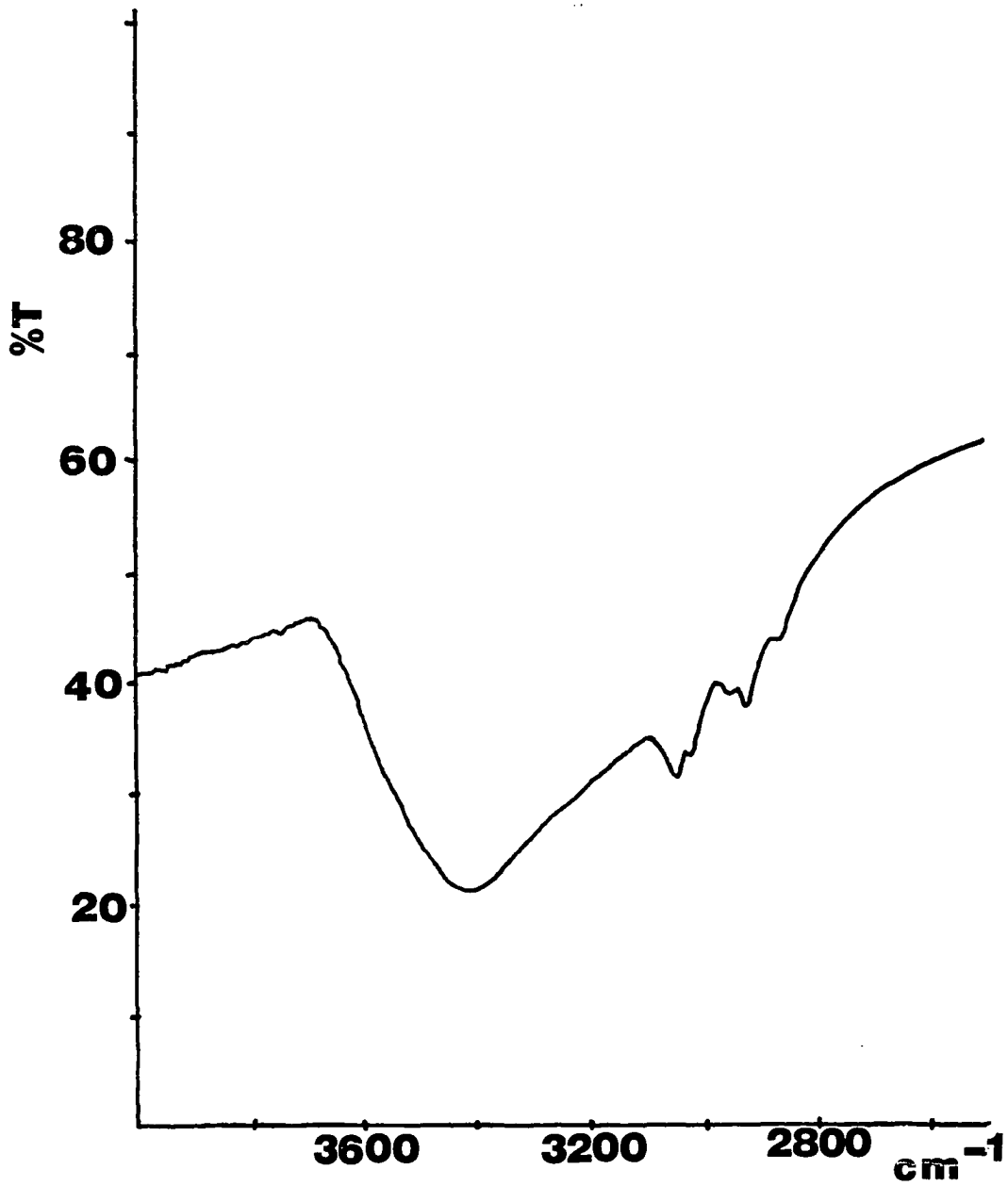


Figure 43. IR spectrum of the insoluble part of poly(1,4-diphenyl-1,3-butadiyne) in KBr mull, 2400-4000 cm^{-1}.

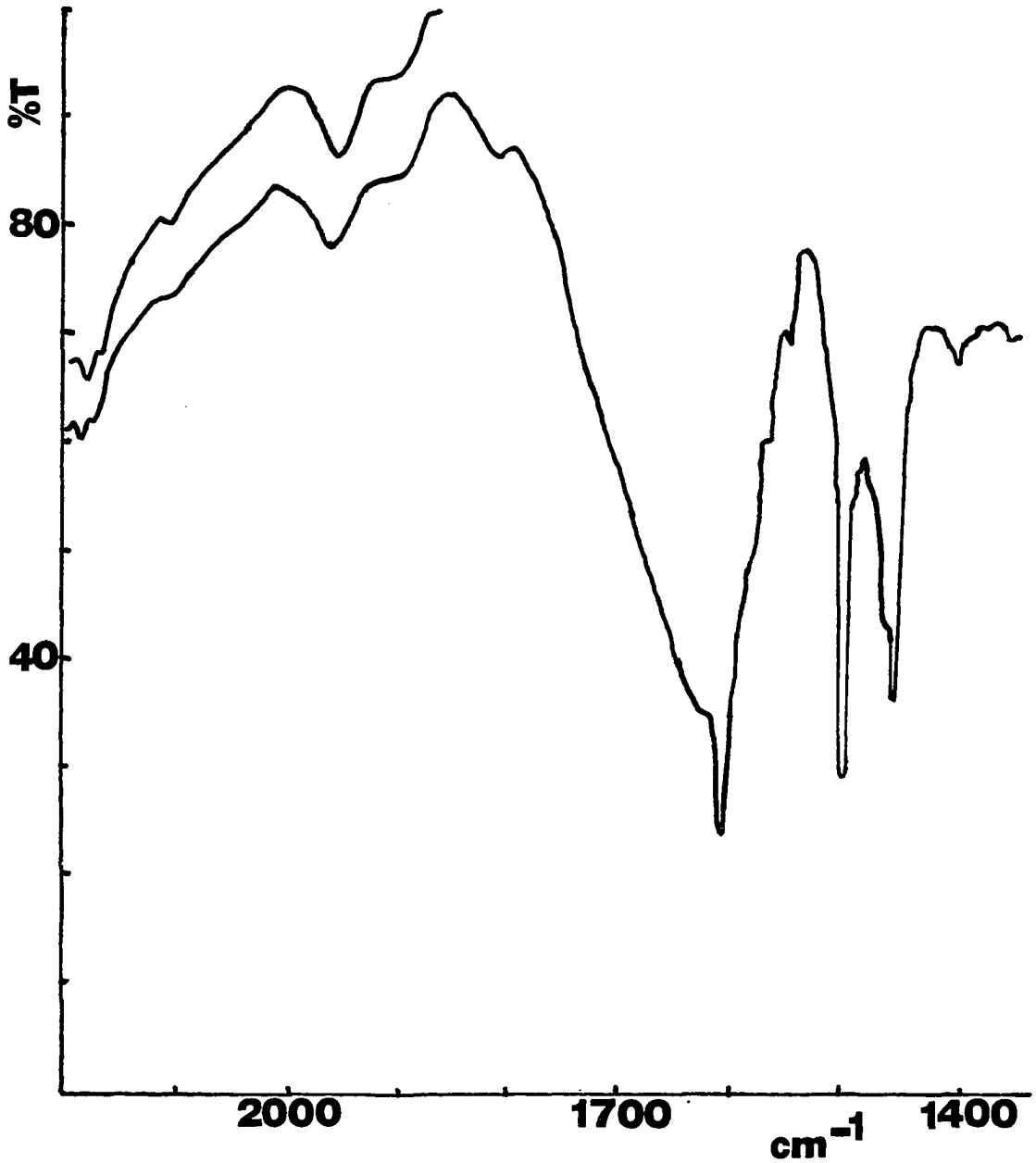


Figure 44. IR spectrum of the insoluble part of poly(1,4-diphenyl-1,3-butadiyne) in KBr mull, 1300-2400 cm^{-1}.

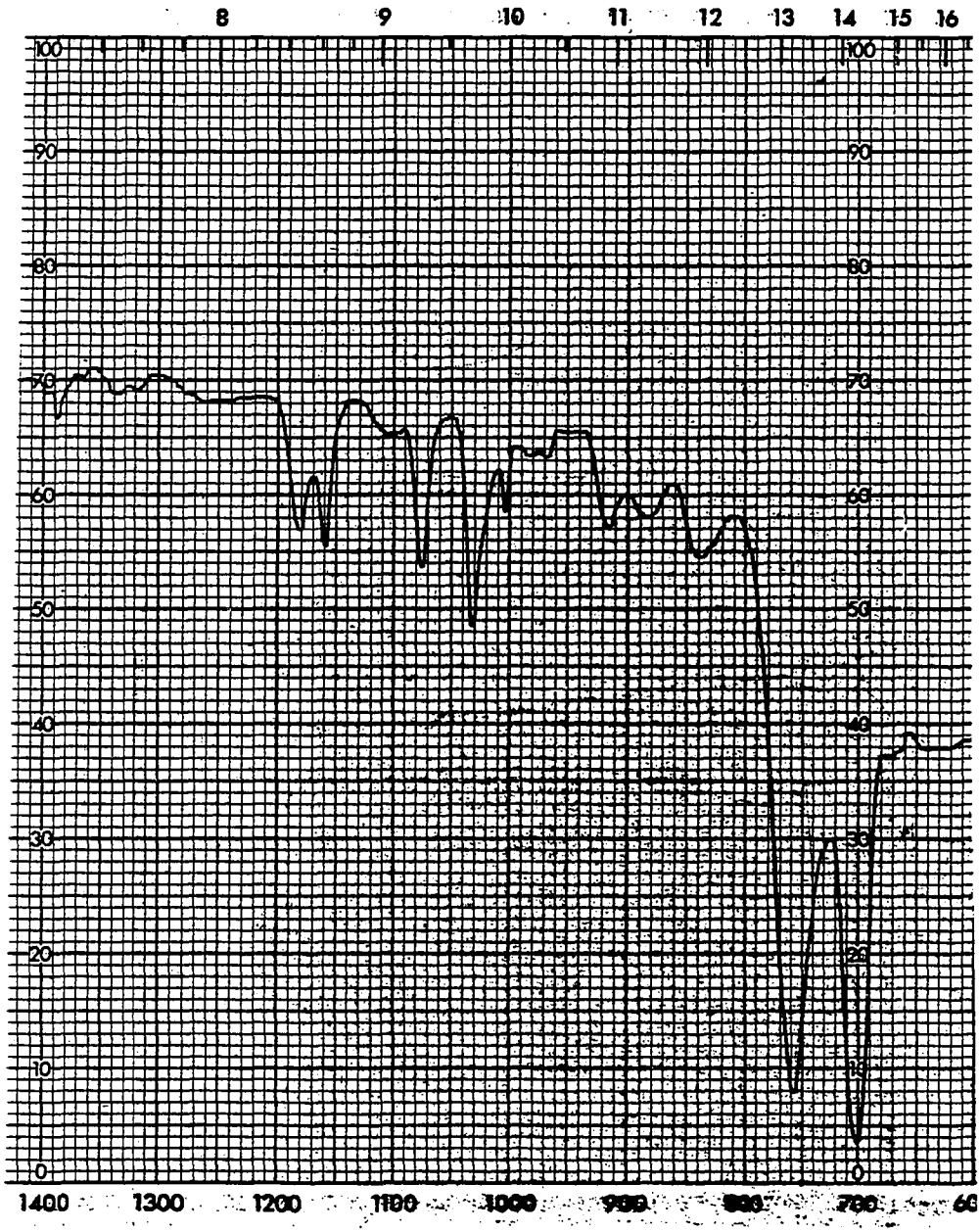
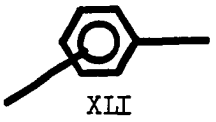


Figure 45. IR spectrum of the insoluble part of poly(1,4-diphenyl-1,3-butadiyne) in KBr mull, 600-1400 cm^{-1}.



XLI

disubstituted phenyl rings

with non-para substitution

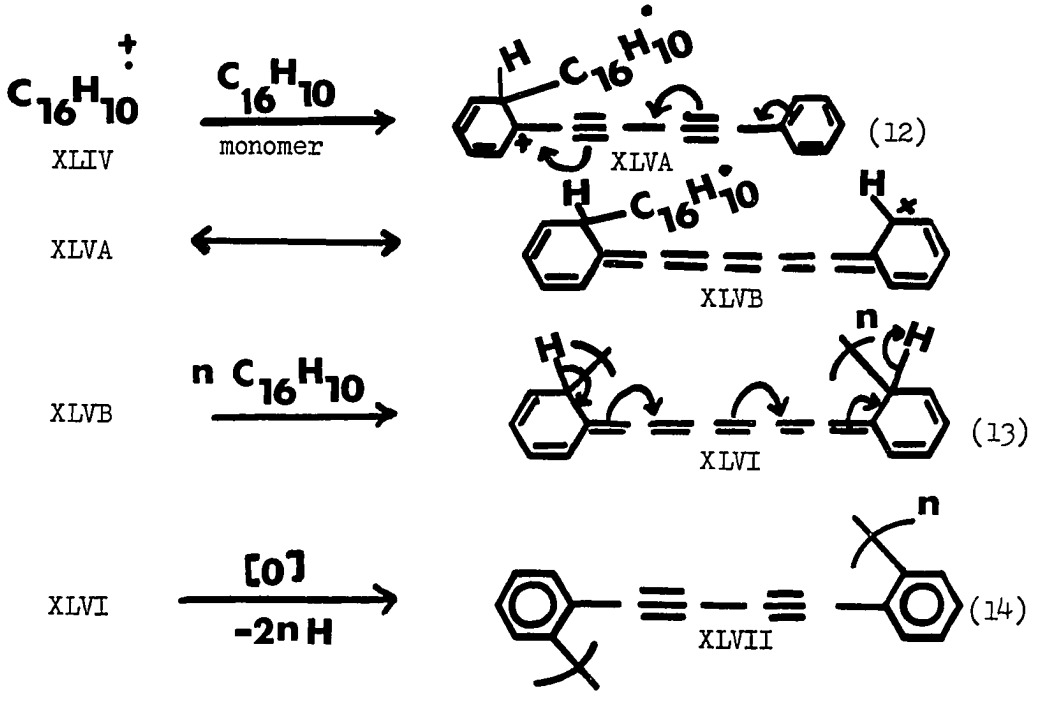
XLII

carbon-carbon triple bonds

XLIII

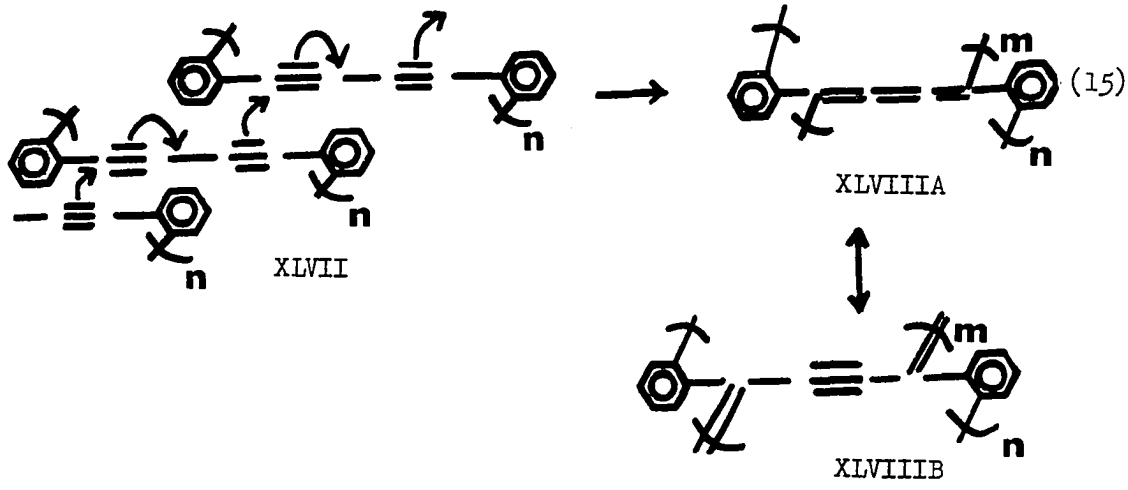
cumulated double bonds

A mechanism involving aromatic nuclear coupling could generate disubstituted phenyl rings as well as triple bonds:



Similar to the initiation step of the polymerization of trans-stilbene(Section IIIC), 1,4-diphenyl-1,3-butadiyne could form its radical cation XLIV, with $AlCl_3$. Attack of the radical cation XLIV on a phenyl ring of the monomer could lead to formation of XLVA. Ortho attack was considered here, based on the phenyl ring substitution patterns of the observed IR spectra of the polymer. Cation XLVB, after successive additions on 1,4-diphenyl-1,3-butadiyne, will generate the structure XLVI. The oxidation of XLVI could lead to formation of XLVII, containing triple bonds and disubstituted phenyl rings.

The structures containing cumulated double bonds could be generated by the polymerization of XLVII through their triple bonds:



(15)

Reaction 15 is a concerted reaction involving triple bonds, leading to formation of a crosslinked product, XLVIII A. The structure of the product contains cumulated double bonds and disubstituted

phenyl rings.

The polymerization of 1,4-diphenyl-1,3-butadiyne via one of its triple bonds could form structure XXXIX(Section IIIF1), which is identical to the proposed structure(45) of the Ziegler-Natta catalyst polymerized 1,4-diphenyl-1,3-butadiyne. However, unlike the insoluble part of poly(1,4-diphenyl-1,3-butadiyne), the Ziegler-Natta catalyst polymerized 1,4-diphenyl-1,3-butadiyne is a soluble polymer and has little or no thermal stability above 600°C(vide infra). Based on the IR data and also by comparing the solubility characteristics and thermal properties of the above two polymers, the structure XXXIX cannot be considered for the total structure of the insoluble part of poly(1,4-diphenyl-1,3-butadiyne). However, the polymerization of XXXIX via its phenyl rings could form three dimensional networks. Such structures cannot be ruled out.

Polymerization of 1,4-diphenyl-1,3-butadiyne via both of its triple bonds could form structures XXXVIII and XL(Section IIIF1). These structures do not have disubstituted phenyl rings and are not in agreement with the IR spectral data of poly(1,4-diphenyl-1,3-butadiyne). However, structures XXXVIII and XL could further polymerize via their phenyl rings to form 3 dimensional structures. Such structures cannot be ruled out.

The repeat units in structures XLVII, XLVIIIA, XLVIIIB, XL, XXXVIII, XXXIX and the above discussed 3 dimensional structural units may be present in different proportions in the structure of the insoluble part of poly(1,4-diphenyl-1,3-butadiyne). The

exact structure of the polymer cannot be established based on the structural evidence available at present. However, our observations make it clear that nuclear coupling produces non-para catenated disubstituted phenyl groups. It also shows that the nuclear coupling process is complicated by the presence of triple bonds.

G. Comparison of synthetic routes

We have used two synthetic routes, aromatic nuclear coupling and oxidative coupling, to prepare modified polyphenylenes. Oxidative coupling produced tailor-made structures free from structural irregularities. Unlike oxidative coupling, aromatic nuclear coupling was complicated by the presence of carbon-carbon double and triple bonds.

The proposed structure VIII of poly(4,4'-diethynylbiphenyl) (Section IIIE3) shows that the oxidative coupling of 4,4'-diethynylbiphenyl is not complicated by the presence of phenyl groups. The biphenyl moiety of the monomer (Structure VII, section IIIE2) remains intact in the oxidative coupling. Phenyl groups of the other monomers with terminal acetylenes such as m-diethynylbenzene do not participate actively in oxidative coupling polymerization (15). Apparently, copper ions are not sufficiently effective in removing an aromatic proton from a phenyl ring to form a copper salt. Weak acetylenic C-H bonds are selectively broken to form a copper-acetylene salt complex required for the coupling process.

A comparison of the proposed structure VIII of poly(4,4'-diethynylbiphenyl) with the possible structures of the insoluble portion of poly(1,4-diphenyl-1,3-butadiyne)(XLVII, XLVIIIA, XLVIIIB, XXXVIII, XXXIX, XL or their 3-dimensional phenyl linked structures) shows that those two polymers are not the same. If aromatic nuclear coupling is not interrupted by the triple bonds of 1,4-diphenyl-1,3-butadiyne, then those two polymers, poly(1,4-diphenyl-1,3-butadiyne) and poly(4,4'-diethynylbiphenyl), should have the same

polymer structure except the end groups. However, the above situation has not been observed, indicating that complications do occur in aromatic nuclear coupling due to the presence of triple bonds. Both the phenyl and acetylene groups are involved in the polymerization.

A similar situation has been observed for the aromatic nuclear coupling of diphenyl acetylene. The proposed possible structures XXXIV, XXXV, XXXVI, XXXVII(Section IIID3) of poly(diphenyl acetylene) also show that triple bonds and a certain amount of aromatic groups are involved in the polymerization of diphenyl acetylene.

Aromatic nuclear coupling is also complicated by the presence of C=C bonds. The proposed mechanism for the polymerization of cis and trans-stilbenes (Section IIIC) shows that both the phenyl and double bonds are simultaneously involved in a concerted type of reaction leading to formation of a polymer structure consisting of phenanthrene repeat units. The observed data for poly(trans-stilbene) also show that the polymerization involving only double bonds does not propagate to the observed degree of polymerization of poly(trans-stilbene).

In general, aromatic nuclear coupling is complicated by the presence of carbon-carbon double or triple bonds. These complications may vary from one monomer to another depending on the structure of the monomer. However, the oxidative coupling of terminal acetylene groups is not complicated by the presence of aromatic groups.

H. Thermal properties

1. Thermal properties of poly(trans-stilbene)

Poly(trans-stilbene) did not melt even when it was heated to the point of becoming red-hot, providing further circumstantial evidence for its highly rigid polyphenylene backbone (Structure XV, section IIIA2). The differential scaning calorimetry curve of poly(trans-stilbene) showed an endothermic drift up to 335°C leading to a broad endothermic peak around 400°C(Fig.46). The continuous endothermic drift could be attributed to the thermal energy absorbed due to relative movements(less than 180° movements) of phenanthrene units. Random or higher degree of movements(> 180° angle) of phenanthrene units are sterically not possible unless the cleavage of chemical bonds takes place. The endothermic peak around 400°C could be due to higher degree movements of phenanthrene units leading to cleavage of certain chemical bonds. The thermogravimetric analysis, TGA, of poly(trans-stilbene) shows that the polymer starts to partially degrade at the same temperature, 400°C, as the endothermic peak in the DSC and confirms the cleavage of certain chemical bonds at 400°C (Fig.47). After the partial cleavage of chemical bonds, a certain fraction of products may have the correct structure required for the recombination to produce a more stable graphite like system. The stable portion of the TGA curve above 600°C may correspond to graphatized products.

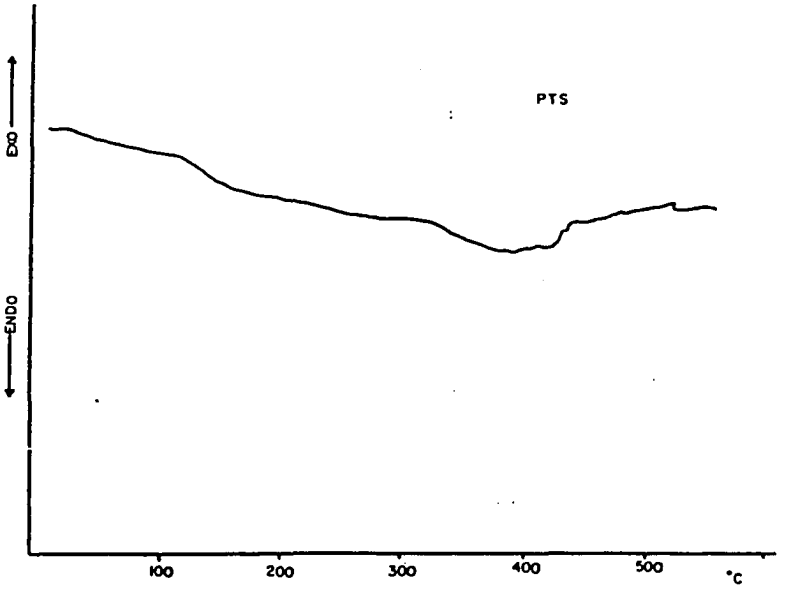


Figure 46. Differential Scaning calorimetry curve of poly(trans-stilbene). Conditions: 20° C per minute; in N_2 gas.

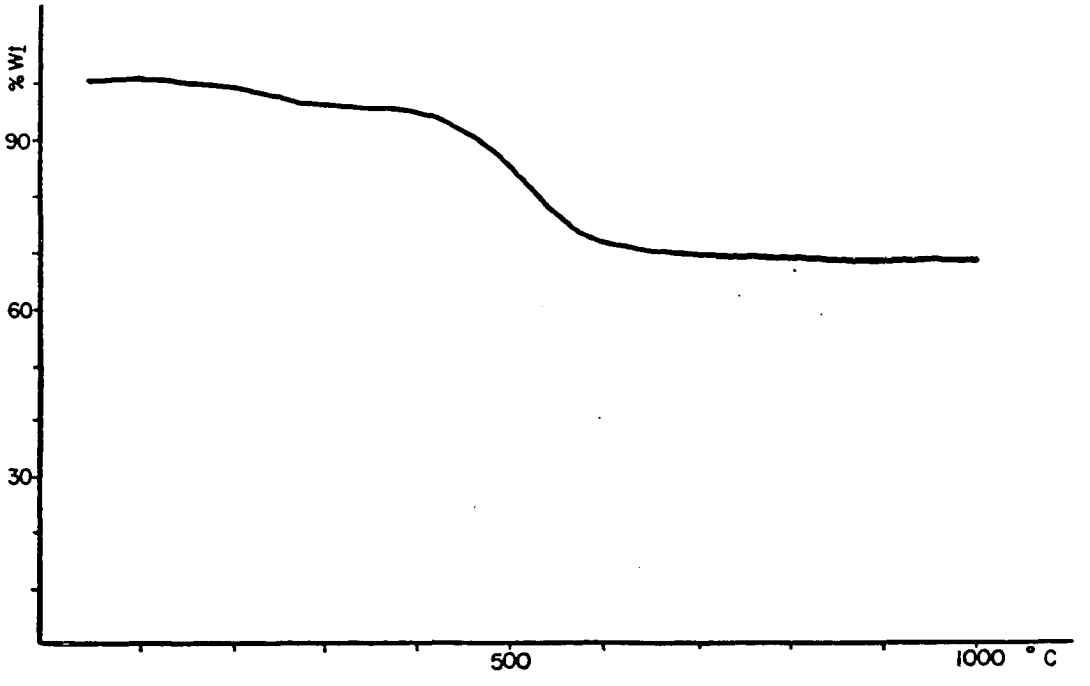


Figure 47. Thermal gravimetric analysis curve of poly(trans-stilbene). Conditions: 50°C per minute in N_2 gas.

2. Thermal properties of poly(4,4'-diethynylbiphenyl)

This polymer also did not melt even when it was heated to the point of becoming red-hot, providing further circumstantial evidence for its highly rigid rod-like backbone(Structure VIII, section I). The polymer structure does not contain any flexible units which could accumulate large amount of kinetic energy at higher temperatures leading to cleavage of chemical bonds. This was clearly reflected in its thermogram (Fig.48A). The polymer lost 16% of its weight when it was heated to 1000°C in nitrogen. The 16% weight loss could probably be due to lower molecular weight fractions and residual catalyst impurities. Compared to other conjugated polymers such as poly(trans-stilbene), this polymer has a much higher thermal stability and could be attributed to its highly rigid rod-like polymeric backbone with no pendant groups.

3. Thermal properties of the polymers of 1,4-diphenyl-1,3-butadiyne

The insoluble portion of poly(1,4-diphenyl-1,3-butadiyne) exhibited better thermal stability compared to thermally polymerized and Ziegler-Natta catalyst polymerized polymers of 1,4-diphenyl-1,3-butadiyne(Fig.48,B,C,D). The Ziegler-Natta catalyst polymerized polymer completely decomposes above 600°C (45). This thermal instability of the Ziegler-Natta catalysed polymer could arise from its -C≡C-Ph and Ph pendant groups and the flexibility of its backbone(Structure XXXIX, section III F1).

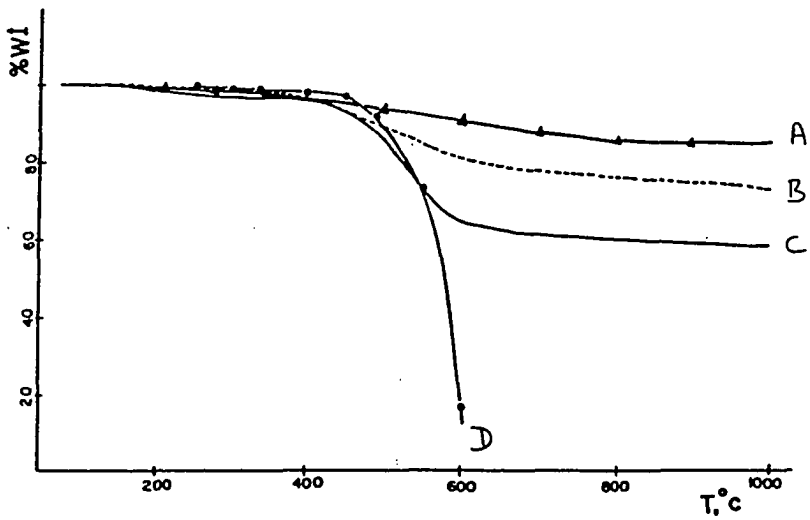


Figure 48. Thermal gravimetric analysis curves: A, poly(4,4'-diethynylbiphenyl); B, insoluble part of poly(1,4-diphenyl-1,3-butadiyne); C, thermally polymerized 1,4-diphenyl-1,3-butadiyne; D, Ziegler-Natta catalyst polymerized 1,4-diphenyl-1,3-butadiyne (45).

The thermally polymerized 1,4-diphenyl-1,3-butadiyne has a rigid polyacene backbone(19) and exhibited better thermal stability compared to the Ziegler-Natta catalysed polymer. The thermal polymer lost 40% of its weight when it was heated to 1000°C. This could probably be due to the combined effect of its low molecular weight ($\bar{M}_n$ = 1110) and the pendant phenyl groups.

Compared to the above two polymers, the insoluble portion of poly(1,4-diphenyl-1,3-butadiyne) has a much better thermal stability. It lost 26% of its weight when it was heated to 1000°C. The higher thermal stability of this polymer could be due to its connected phenyl rings which could reduce its flexibility and number of pendant groups. However, compared to poly(4,4'-diethynyl-biphenyl), this polymer has a lower thermal stability and this provides further circumstantial evidence for its non-para catenation and possible structural irregularities formed due to the complicated nature of the aromatic nuclear coupling.

I. Electrical properties

1. Electrical properties of poly(trans-stilbene)

The proposed structure for poly(trans-stilbene) contains a polyphenylene backbone and is basically a modified polyphenylene system (Structure XV, section IIIA2). Compared to polyphenylene, this polymer has a greater non-planar barrier for the electronic transport. This situation is not favourable for electronic transport. However, by doping with iodine it underwent a transition from insulator to semiconductor. The electrical conductivity of the iodine doped polymer was much higher than that of the iodine doped commercial polyphenylene (Table 7). The higher conductivity of the iodine doped poly(trans-stilbene) could be rationalised in terms of its ability to undergo charge transfer complex formation. Compared to polyphenylene, poly(trans-stilbene) consists of higher membered aromatic units. Higher-membered aromatics such as pyrene and perylene have lower ionization potentials compared to lower-membered aromatics and readily form charge transfer complexes with iodine having good electrical properties (46). In certain iodine charge transfer complexes (eg. N,N'-diphenyl-p-diaminobenzene/I_2) it has been shown that the contribution of electronic transport along the polyiodine chains would be a large factor to its electrical conductivity (47,48,49). A similar situation may be present in doped poly(trans-stilbene). Molecular iodine by charge transfer complex formation could form polyiodine chains. Unlike molecular iodine, polyiodine ion chains could participate in electronic conduction. The electrical

Table 7. Room temperature powder average electrical conductivities of doped polymers.

Polymer	Weight% of iodine	D.C. Conductivity
Poly(trans-stilbene)	65	1.5×10^{-4} ohm^{-1}cm^{-1}
Commercial polyphenylene	55	4×10^{-6} ohm^{-1}cm^{-1}
Poly(4,4'-diethynylbiphenyl)	53	9.5×10^{-7} ohm^{-1}cm^{-1}

conductivity due to polyiodine ions in doped poly(trans-stilbene) probably exceeds the electronic conductivity due to the charge transport along polymer chains.

The formation of charge transfer complexes by iodine doping was established through ESR studies. Iodine doping of poly(trans-stilbene), increased the spin density by a factor of 58 and changed its ESR spectrum line shape from Gaussian to a Dysonian shape(Fig. 49). This reveals that poly(trans-stilbene) undergoes an electron transfer process with iodine. The change from the original Gaussian shape to a Dysonian shape indicates a change in electronic state and such changes have been observed for other conjugated polymers when they assume conducting states by charge transfer complex formation (50).

2. Electrical properties of poly(4,4'-diethynylbiphenyl)

The iodine doped system of this polymer did not exhibit good conducting properties (Table 7). Compared to iodine doped polyphenylene, this doped polymer has a lower electrical conductivity, probably due to its higher ionization potential. Higher ionization potentials have been observed for structurally similar systems. For example, by introducing C≡C triple bonds into p-polyphenylene to form an alternating co-polymer, its theoretical ionization potential increases from 5.5 eV to 5.6 eV(6).

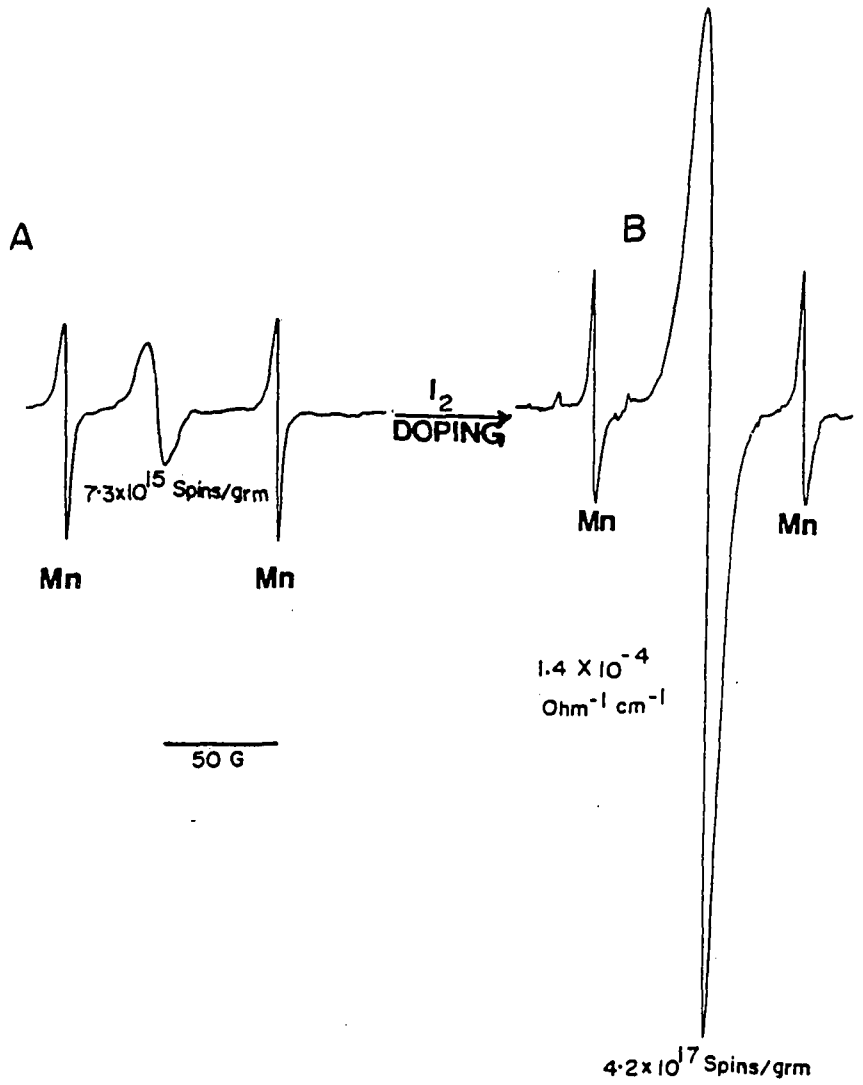


Figure 49. Room temperature ESR spectra : A, poly(trans-stilbene) ; B, iodine doped poly(trans-stilbene) in solid state.

3. Electrical properties of poly(diphenyl acetylene).

The AsF_5 doped poly(diphenyl acetylene) did not exhibit good conducting properties(Table 8). The maximum conductivity obtained for the above doped system was $1.6 \times 10^{-6} ohm^{-1} cm^{-1}$. Compared to the conductivity value of the corresponding polyphenylene system, the above polymer has a very poor conductivity. The lower electrical conductivity of this polymer could probably be due to its non-planar backbone with non-para catenated phenyl units.

4. Electrical properties of the insoluble part of poly(1,4-diphenyl-1,3-butadiyne).

The AsF_5 doped system of the above polymer did not exhibit good electrical properties(Table 8). It has a slightly higher electrical conductivity compared to that of AsF_5 doped poly(diphenyl acetylene). However, this conductivity was much lower than the reported conductivity of AsF_5 doped polyphenylene(10) and could be attributed to its cumulated carbon-carbon double bonds with perpendicular orbitals which do not participate in electronic conduction. The higher ionization potential of the C ≡ C triple bonds and non-para catenated phenyl rings could also be reasons for its low electrical conductivity.

Table 8. Room temperature powder average electrical conductivity (D.C) of AsF_5 doped polymers.

Polymer	D.C. Conductivity
Poly(diphenyl acetylene)	$1.6 \times 10^{-6} ohm^{-1} cm^{-1}$
Insoluble part of poly(1,4-diphenyl-1,3-butadiyne)	$2.5 \times 10^{-5} ohm^{-1} cm^{-1}$
Polyphenylene(10)	$500\ ohm^{-1} cm^{-1}$

IV. CONCLUSIONS

We have attempted to extend the scope of aromatic nuclear coupling polymerization to more complicated monomers such as cis- and trans-stilbenes, diphenyl acetylene and 1,4-diphenyl-1,3-butadiyne. The process can be complicated by the interaction of functional groups such as carbon-carbon double bonds and triple bonds with the phenyl rings if they are present in the monomer as a conjugated system. Hence reactions for such monomers could produce polymers with very complicated structures (Section IIIF, 1 and 2). Unlike the above reaction, oxidative coupling of 4,4'-diethynylbiphenyl produced well defined tailor-made polymer structures free from structural irregularities. In this reaction, coupling of acetylene groups is not affected by the presence of phenyl groups.

Polyphenylene, polyacetylene and their alternating co-polymer (50) are insoluble materials. However, poly(trans-stilbene) is a soluble polymer, with a modified polyphenylene structure and exhibits better electrical properties compared to polyphenylene. This clearly shows that tractability and electrical conductivity are not mutually exclusive and suggests the possibility of having tractable polymers exhibiting good electrical properties.

We have obtained experimental evidence that higher ionization potential, non-planar structures, and cumulated double bonds with perpendicular π orbitals are major barriers for the electrical conductivity of a doped polymer.

Oxidative stability is also a very important property of the doped polymer systems. The effect of various oxidizing agents including oxygen on these doped polymer systems may reveal important information on the stability of doped systems.

The conjugated polymers in general enjoy high thermal stability. Flexibility of the polymer backbone, large pendant groups and non-planar or non-linear structures could remarkably lower their thermal stability.

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