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EFFECT OF CHAIN RIGIDITY ON CONDUCTIVITY OF CONJUGATED POLYMERS

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ABSTRACT

There are several ways to introduce processability to conjugated polymers, and one of them is discussed here. The basic approach involves the introduction of flexible centers in a conjugated backbone with a periodicity that allows the existence of conjugated sequences characterized by an electron mobility high enough to result in electronic conduction upon oxidation or reduction. The process consists of the use of AsF_5 as a polymerization catalyst, and AsF_3 as a non-conventional medium for the reaction. The Lewis acid coupling reactions, via which the polymerization occurs, result in soluble materials. Characteristics of the materials obtained by polymerizing acetylene and some aromatic compounds are discussed.

INTRODUCTION

Although conjugation, to a certain extent, of the polymer backbone is necessary for electronic conduction in organic polymers, it is also responsible for the intractability of most of these materials, a characteristic which is one of the drawbacks in the field. The introduction of flexible centers in the backbone was found to be a good approach towards processability. An incentive for this work is the example illustrated in the cases of polyphenylene [1] which is an insoluble polymer and poly(phenylenesulfide) [2] which melts at 270°C and is soluble in diphenylether at 220°c. In addition to introducing flexibility to the polymer backbone the sulfur atom provides for a continuous overlap of orbitals along the chain. Can this example be used to synthesize processable and dopable conjugated polymers? The answer is yes, and the following consists of the discussion of the results obtained. The experimental procedures are described in ref. 3.

RESULTS

The average number (M_n) and weight (M_w) molecular weights and polydispersity (M_w/M_n) of various materials were determined using GPC. These parameters vary with the experimental conditions. Molecular weights of up to 5,000 are obtained in the case of polyacetylene, and up to 1,000 for the polyaromatic materials. In most cases, these values are affected by the treatment time of the compounds with AsF_5, which acts as a catalyst and a doping agent. Elemental analyses of Lewis acid coupling polymers showed that C/H ratios are different than one. This is due to side reactions during the polymerization, such as partial saturation and/or crosslinking, or after the polymerization such as oxidation during handling. The structure is expected to consist of arsenic incorporated in the chain with As-C linkages and bound to three fluorine atoms. Up to 25 weight % of arsenic is found in the materials suggesting that arsenic insertion in the chain occurs during polymerization. Such results are in agreement with what was observed in the oxidative polymerization of diethynyl compounds [4].

By combining GPC and elemental analysis results, the number of repeating units in polyacetylene has been found to exceed 50 (CH) units but be below 10 monomer units in the aromatic polymers.

The visible absorption of soluble polyacetylene (Fig. 1) shows a maximum at 500 nm (2.5 eV), which indicates that a higher bandgap than for conventional polyacetylene is obtained. By fitting this result in data obtained for polyenes [5], the length of the conjugated sequences is estimated at 15 C=C. Such a length could be sufficient for the charge carrier to move along the chain under appropriate conditions, i.e., doping.

The fibrillar morphology of conventional polyacetylene no longer exists in the soluble materials, but a smooth amorphous-like structure is obtained. This might be due to the chain length and interchain interaction, which is reduced as compared to the insoluble materials. The amorphous character is evidenced by a very diffuse Raman band profile.

The thermogravimetric analyses of various polyacetylenes are displayed in Fig. 2. While Ziegler-Natta polymer starts to decompose at 420°C, the weight loss for the "arsenic" polymers is observed much earlier: 175°C for the insoluble material prepared in absence of AsF_3, and 125°C for the soluble one.

The room temperature conductivity of the polymers is increased by several orders of magnitude upon doping with iodine or AsF_5 (Table 1). Such an increase depends upon the experimental conditions of the polymerization. While polyaniline is a conducting system as-synthesized, since the polymerization medium is acidic, the slightly yellow powder of poly(phenylenesulfide) becomes conducting by further treatment with AsF_5, turning into a dark blue material.

TABLE 1

Colors and room temperature conductivities of "arsenic" polymers doped with iodine or AsF_5.

Polymer	Color	Conductivity/$(\Omega cm)^{-1}$
polyacetylene #1	red-brown	10^{-3}-10^{-4}
polyacetylene #2	red-brown	10^{-2}
polyacetylene #3	red-brown	10^{-3}-10^{-4}
poly(phenylene)	brown	10^{-3}-10^{-4}
polynaphthalene	dark red	---
polyanthracene	dark red	---
poly(phenylenesulfide	dark blue	1
polyaniline	green	1

Note: Polyacetylenes #1, 2, and 3 are prepared by using $[AsF_5]/[C_2H_2]$ ratios of 1, 0.5, and 0.08 respectively.

In view of the materials properties discussed in this paper, it is interesting to study the spin resonance to help understand the intrinsic properties of these materials. A temperature-dependent study in the range -180°C-250°C was carried out. The linewidth of the soluble material is quite large (18 G at room temp.) which indicates a very low spin mobility. This might be due to short conjugated sequences in the chain, large contents of cis configuration in which mobile defects do not exist, or partial localization of the spin on the arsenic atoms incorporated in the chain. The linewidth stays constant between 180°C and 60°C as opposed to a narrowing upon warning in conventional polyacetylene. The line becomes narrower above 60°C and reaches a minimum at ∿ 150°C. At this point the line consists of two distinct signals. Above 150°C, a single peak signal is observed with a slight increase in its width. These variations could be explained by structural changes such as cis-trans isomerization and crosslinking, and a change in the chain morphology. Since the linewidth does not change when the sample is cooled from 250°C to room temperature, it can be concluded that motional narrowing does not exist. The number of spins measured at room temperature is of the order of 5×10^{16} spins/gram of material. The Dysonian lineshape is an indication of the existence of conduction electrons. As observed in Fig. 3, the line is slightly asymmetric at room temperature (A/B ∿ 0.86) due to impurities, i.e., AsF_5 from the polymerization process. The symmetry changes when the temperature changes, i.e., A/B ∿ 0.95 at -180°C, and also when the material is exposed to iodine (A/B ratio is 0.86 and 1.0 before and after exposure to the dopant respectively). This slight change could be due to the fact that the conductivity is not in the metallic regime, and therefore, the esr lineshape is not a good indication of how conductive the system is in these conductivity ranges.

CONCLUSIONS

The use of AsF_3 as a non-conventional solvent introduces a new process which takes place during the polymerization initiated with AsF_5, leading to soluble polymers [3]. This process might be explained as follows:

1. A new arsenic species resulting from the interaction between AsF_5 and AsF_3 could be the initiator of the polymerization as suggested for poly-(phenylenesulfide) synthesized in a conventional way [2] and doped with AsF_5 in the presence of liquid AsF_3 [6].

2. The role of AsF_3 could be that of a plastifying agent resulting in the solvation of the propagating species during the polymerization, a process which might limit side reactions such as chain transfer and crosslinking reactions. This possible solvation might be associated with the highly polar character of AsF_3 [7].

The polymer chain synthesized using this process contains arsenic which introduces flexibility to the chain. As a result of this, the chain conformation is expected to be different from that of the insoluble material. The results obtained so far with the various materials showed that in order to achieve solubility, materials with lower conductivities are obtained as compared to insoluble ones. The amorphous character of the oxidative polymerization compounds could be correlated with their conductivities, suggesting that a certain crystallinity is needed to achieve high conductivities.

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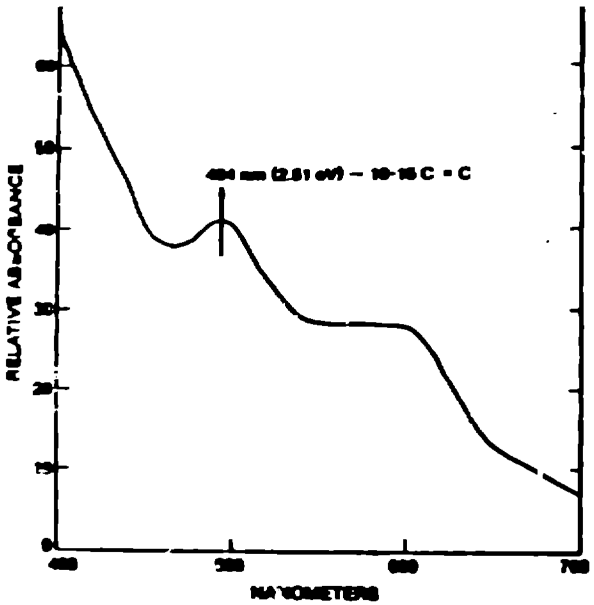

Fig. 1. Visble absorption of polyacetylene #1 in acetone.

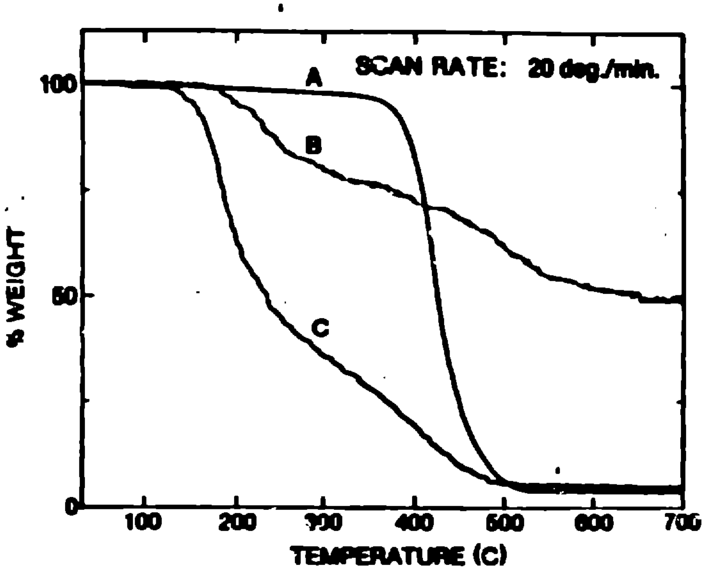

Fig. 2. Thermogravimetric analysis of Ziegler-Natta polyacetylene (A), insoluble (B), and soluble (C) "arsenic" polyacetylene.

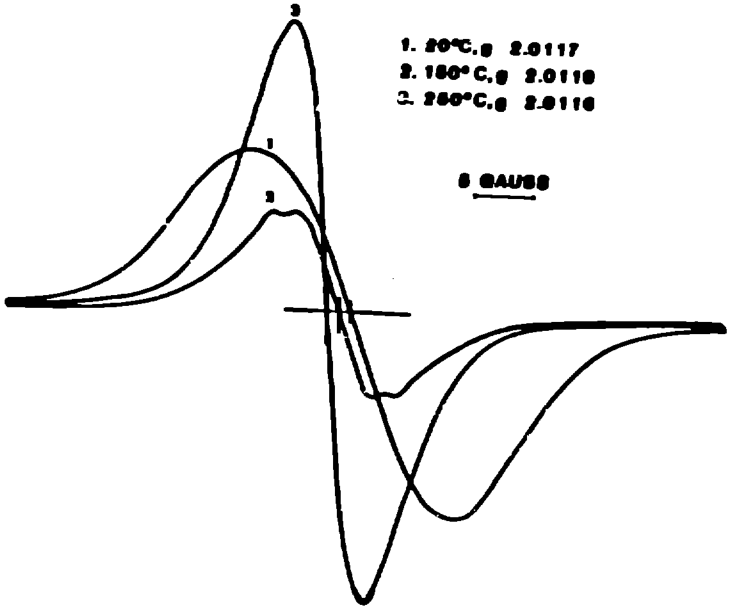

Fig. 3. ESR signals of soluble polyacetylene #1 at 20°C, 150°C, and 250°C recorded at microwave frequencies of 9.125, 9.123, and 9.119 GHz respectively.