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Processability and Order in Conducting Polymers

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INTRODUCTION

Processability and intrinsic anisotropy in electrical and optical properties are of fundamental and technological importance in the area of conducting polymers. Investigation of both aspects has seen unprecedented advances in the last two years. Focusing on conducting polymers at the molecular level (chain) experimentally and theoretically has contributed to such advances, and only by combining both efforts could that occur. On the one hand, intrinsic anisotropy constitutes a unique aspect that derives from the weak inter-chain interaction and from the π-electron delocalization along the polymer backbone. On the other hand, processability is of importance for it allows (i) the study of the polymers' intrinsic properties and their doped derivatives; and (ii) the polymers tractability is crucial in many technological applications. Combining both aspects in a conducting polymer constitutes an important achievement for it allows to obtain for example, fiber-forming materials (for structural purposes) with anisotropy and conductivity. Both aspects are strongly influenced by the polymer's morphology which is a very important parameter in this study:

- Solution-processability consists of the solubilization of individual chains accompanied by a weak inter-chain interaction, and therefore, aggregation into *i.e.*, fibrillar, globular or lamellar forms is inhibited.
- Order could be achieved at the initial stage of forming the chains resulting in orderly aggregation, or by desentanglement and orientation of the already formed randomly oriented aggregates. The des-

entanglement process accompanied by a weak inter-chain interaction adds anisotropy to macroscopically ordered materials.

Various methods could be utilized to accomplish processability and/or order in conjugated rigid polymers. Processability depends upon the intrinsic properties of the polymer backbone such as its structure and the extent to which its molecular weight and its distribution can be controlled. Order in conducting polymers can be accomplished in several ways:

Externally, some conducting polymer films can be stretch-oriented resulting in most cases in a macroscopic orientation; that is aggregate orientation. If the nature of the polymerization reaction is such that extended, parallel chains are formed, the result is naturally a microscopic and macroscopic orientation. Polymers can also be oriented in the solution form. Extension of the rigid chains in diluted solutions can be achieved by *i.e.*, elongation flow using double suck jets creating uniaxial stretching flows or through a cross-slot device or a four-roller mill producing simple shear flows. In the present case, order is microscopic and macroscopic.

Intrinsically, order can be achieved by (i) polymerization in ordered media, *i.e.*, by using a nematic liquid crystal as the polymerization solvent; and (ii) by direct synthesis of conjugated liquid crystal polymers.

External effects and intrinsic features can be combined leading to polymers with higher order.

Conjugated, rigid chains, in their aggregated or soluble forms exist in various geometrical configurations depending on the degree of their orientation and extension as schematically shown in Scheme 1.

SCHEME 1

The degree of extension determines the extent of the π-electron delocalization and the extension direction of the chain aggregates influences the intrinsic anisotropy of the polymer properties.

Although, the aspects of processability and order are related by chain and/or aggregate morphology of the polymers, this paper deals with the two aspects in two separate parts, only for reasons of clarity. Specific examples are discussed in detail in both parts.

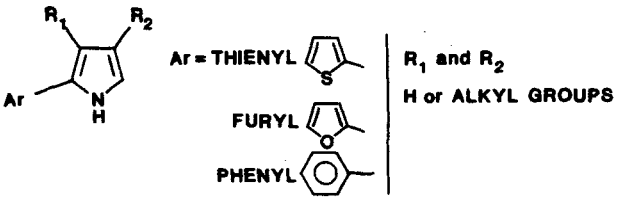
PART I—SOLUTION PROCESSABILITY

Overview

Because of the rigid nature of their backbones, crosslinking, and the aggregate character of their morphology, processing of most of the initial undoped conjugated polymer systems was unsuccessful. For doped polymers, the difficulties were greater because doping causes further aggregation, interchain interaction and certain local geometry changes of the chain, *i.e.*, chain relaxation to accommodate the formation of the charge transfer complex. The first processable, highly conductive polymer was poly(phenylene sulfide). When it is doped, it becomes intractable owing to structural changes.[1] It was found later that only by doping the polymer in AsF_3 solution with AsF_5 could a blue solution of the doped polymer be formed.[2] However, this technique was not successful with other polymers. Only by direct polymerization (oxidative coupling) of acetylenic and aromatic monomers, using a similar combination of AsF_3 and AsF_5, could soluble polymers be obtained.[3,4]

Poly(arylpyrrole)s

Our focus has been on newly synthesized polyheterocycles in which the repeating unit is an arylpyrrole moiety of the general formula shown in Scheme 2, for the following reasons:



SCHEME 2

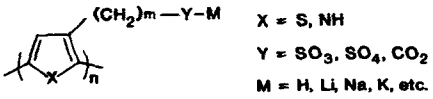
- The decrease in disorder by reducing the number of coupling sites during the electrosynthesis, and therefore, the decrease of the amorphous character that dominates known polyheterocycles.
- The π system in arylpyrroles is such that their electron density is higher than in pyrrole. The electron delocalization causes the polymerization to occur easily resulting in soluble materials necessary for studying the single chain behavior.
- Arylpyrroles could lead to conjugated "diatomic" polymers with theoretically well defined excitations.

We have shown for the first time that arylpyrroles can be polymerized electrochemically leading to alternating copolymers[5] and therefore could be the first synthetic conducting A-B polymer which could be used to test the theoretical predictions on the particle excitations: solitons or polarons in the bleached state and polarons and/or bipolarons in the doped (oxidized) state. Their electrochemical synthesis is performed in the same way as for polypyrrole or polythiophene. Due to the electron delocalization in the monomer units the polymerization occurs easier than in the latter two compounds. In fact, an applied potential of 0.25 V vs $Ag/AgNO_3$ is enough to initiate the polymerization of thienylpyrrole or furylpyrrole at the surface of an anode. The potentials needed for polymerizing thiophene or pyrrole are higher. The cyclic voltammograms of thienylpyrrole exhibit one oxidation peak and a corresponding reduction peak at potentials different from those of thiophene and pyrrole separately. One important feature of poly(arylpyrrole)s is their solubility in the organic medium in which they are prepared, particularly THF, propylene carbonate (PC) or acetonitrile. The color of the solutions varies with the solvent. Preliminary studies indicate that the molecular weights are higher than 20,000. However, low molecular weight fractions and large aggregates are obtained in each case. Polymer films could also be obtained along with the polymer solution, particularly when a poor solvent is used. Conductivities of films in the range $1-10\ (\Omega cm)^{-1}$ are generally obtained. The optical spectra of the various synthesized materials show peaks that correspond to polaronic and bipolaronic species at energies that depend upon the electrolyte system used and the repeat unit. Optical absorption characteristics are shown in Table I.

Note that some of the sub-gap states characteristic of doped polypyrrole are not observed in some of the polymers.

Water-soluble polyheterocycles

It was found recently that conducting polymers can be made water-soluble by attaching a surfactant or soap molecule to the structure of the polymer.[6,7] In this process alkyl-sulfonates and -carboxylates are substituents on the β carbon atom of a thiophene or a pyrrole monomer. The general formula is shown in Scheme 3.



SCHEME 3

The water-soluble polymers are synthesized chemically or electrochemically by known procedures. The dopant is covalently bonded to the chain. Therefore, intrinsic or self-doping occurs when a charge is ejected from the π system, leading to the formation of a charge transfer complex between the anion and the defect on the conjugated chain. Conductivities of about 10^{-2} $(\Omega cm)^{-1}$ are obtained for the various materials. The conductivity can be increased by doping the polymers, up to 10^{2} $(\Omega cm)^{-1}$, with oxidizing agents such as AsF_5 or H_2SO_4. The water-soluble polymers synthesized in this study are characterized by a highly conjugated chain similarly to that of polythiophene or poly(3-alkylthiophene)s as can be seen in Figure 1, with perhaps a slight difference in the distribution of the conjugated segments.

PART II—MACROSCOPIC AND MICROSCOPIC ORDER

Overview

Stretch-alignment of a polyacetylene film to a maximum of three times its original length resulted in a modest optical and electrical aniso-

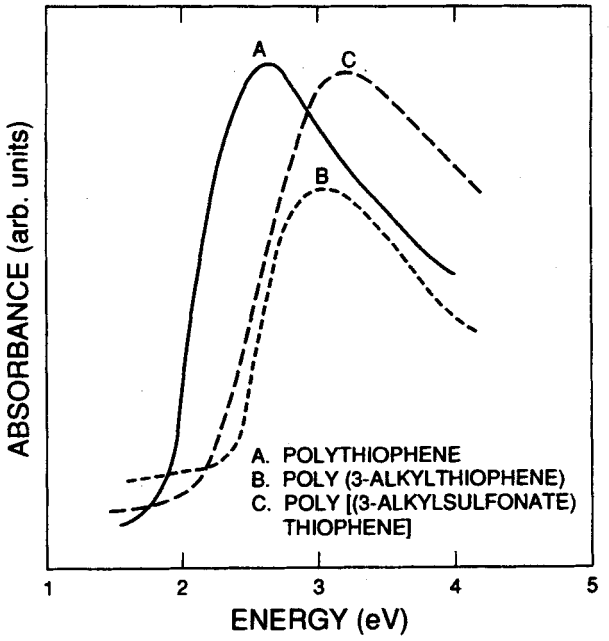


FIGURE 1 Optical absorption spectra of polythiophene, poly(3-butylthiophene) and poly(3-butylsulfonatethiophene).

tropy ($\sigma_{\parallel}/\sigma_{\perp} \approx 3 - 5$).[8] The stretch-orientation was improved later by improving the synthesizing method and the highest parallel conductivity resulting from that process was 1.5×10^5 $(\Omega cm)^{-1}$, which is only four times less than that of copper.[9] With a perpendicular conductivity of 100 $(\Omega cm)^{-1}$, this constitutes the highest electrical anisotropy ever obtained. The resulting material is highly dense and consists of almost perfectly aligned fibrils. Although the Durham technique for the synthesis of oriented polyacetylene yielded a highly oriented material by stretch-alignment of the precursor polymer, the highest conductivity reached at an ultimate draw ratio of 20 is comparable to that of the initial stretch-aligned Ziegler-Natta polyacetylene. However, the material exhibited a high optical anisotropy.[10–12] A similar technique was used to synthesize highly oriented poly(phenylenevinylene). The electrical anisotropy was 100 at a draw ratio of 10 with a parallel conductivity of approximately 2.8×10^3 $(\Omega cm)^{-1}$.[13,14]

Polymerization of acetylene in ordered media

In this section, we discuss a unique approach that was described earlier[15,16] utilizing nematic liquid crystals as ordered solvents for polymerizing acetylene. In our approach, microscopic (chain) and macroscopic (fibril) orientation is obtained due to the orientation of the active catalyst sites along the liquid crystal molecules under a magnetic field which is maintained during the polymerization. This approach was later used by others with success. Araya *et al.* showed that by using a nematic liquid crystal under flow in the absence of a magnetic field,[17] conductivities approaching 1×10^4 $(\Omega cm)^{-1}$ are obtained. Akagi *et al.*[18] have shown recently that similar conductivities are obtained when a magnetic field is used to orient the liquid crystal instead of using its flow properties. By combining both techniques, Rolland *et al.*[19] obtain conductivities of approximately 2×10^4 $(\Omega cm)^{-1}$ thus doubling the values obtained above.

The experimental details of the preparation of the polymer films and the techniques used are described elsewhere.[20]

Morphology of the films is examined by scanning electron microscopy (SEM). As seen in Figure 2, a fibrillar structure is obtained in which the fibril alignment is very high and is observed in the direction of the magnetic field. A noticeable difference from conventional polyacetylene is that of the fibril length which is increased using this alignment process. Thin films examined by TEM (Figure 3) show the microfibrillar structure within the large fibrils observed in SEM. Here

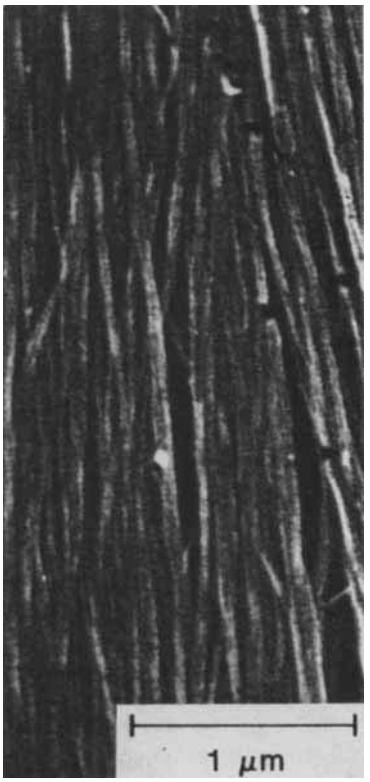


FIGURE 2 Scanning electron micrograph of a stretch-oriented, ordered polyacetylene film.

again, the orientation is quite high aside from very thin microfibrils that tend to spread throughout the structure. The stretch-alignment, which can not be observed by TEM on the stretched thick film, must improve the over-all orientation since electrical anisotropy is improved as will be mentioned later.

Four-probe conductivity measurements were performed on the various samples at room temperature and at liquid nitrogen. The samples were doped with iodine or AsF_5 vapors to doping levels of approximately 15% molar and 10% molar respectively. The best results are obtained with AsF_5. The conductivity measured in the direction of the orientation parallel to the magnetic field ($\sigma_{\|}$) is approximately 1.5×10^4 $(\Omega cm)^{-1}$ and the conductivity perpendicular to the orientation direction ($\sigma_{\perp}$) is 5×10^2 $(\Omega cm)^{-1}$. The electrical anisotropy ($\sigma_{\|}/\sigma_{\perp}$) is 30. The stretch-orientation with a modest draw ratio of

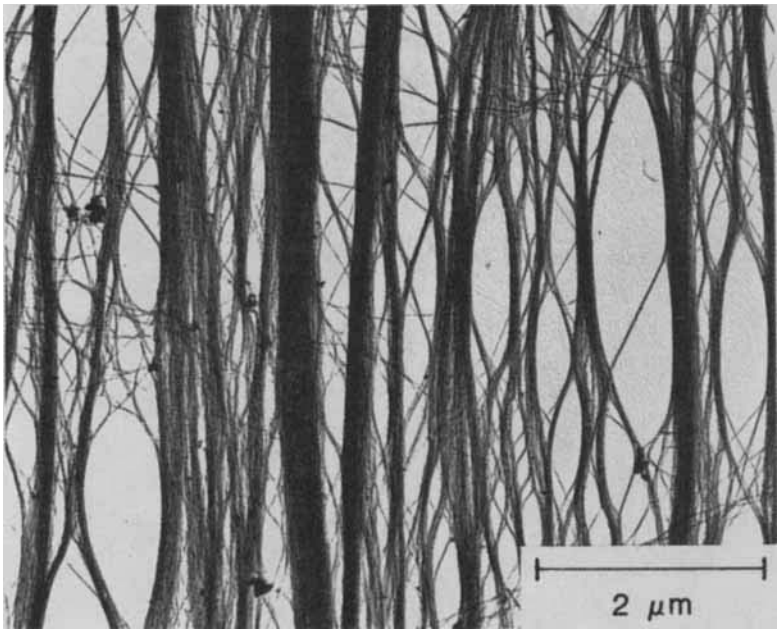


FIGURE 3 Transmission electron micrograph of a thin film of ordered polyacetylene.

2.0 affects directly only the supramolecular orientation which is translated by a higher alignment of the fibrils and possibly of the microfibrils. In fact, while $\sigma\perp$ of the stretched material and doped with AsF_5 is unchanged, $\sigma_{||}$ is approximately doubled approaching 3×10^4 $(\Omega cm)^{-1}$ with a $\sigma_{||}/\sigma_\perp$ ratio of 60. Another interesting result is that the doped polymer stays metallic at the liquid nitrogen temperature without an appreciable decrease in $\sigma_{||}$. We have recently improved slightly the technique used by Rolland *et al.*[19] (magnetic field and flow of the nematic solvent) by adding thermal treatment of the catalyst as described in the experimental section and drawing of the polymer film twice the original length. Therefore, the high order obtained in the polymer film is due to the molecular orientation obtained by a flowing liquid crystal under the influence of a magnetic field and a supramolecular orientation enhanced by drawing. The conductivity results on the AsF_5-doped film (10% molar) are impressive. While $\sigma_\perp$ is almost unchanged, $\sigma_{||}$ is increased to 6×10^4 $(\Omega cm)^{-1}$ which results in a very high electrical anisotropy ($\sigma_{||}/\sigma_\perp \approx 120$). Due to the low catalyst concentration, a low-density film is generally obtained (0.25 g/cm^3). Therefore, if the conductivity of such

a film is extrapolated to that of the highly conducting polyacetylene developed at BASF whose density is approximately 1 g/cm^3, a conductivity higher than that of the latter could be obtained. In fact, the normalized parallel conductivity of our polymer to that of BASF is 2.4×10^5 $(\Omega cm)^{-1}$, and our normalized electrical anisotropy is 480.

Polarized infrared (IR) absorption spectra of the stretch-oriented films shown in Figure 4 were recorded in an IR cell under vacuum. The absorbances in both directions, $A_{\parallel}$ and $A_{\perp}$, indicate clearly the high optical anisotropy of these films. For example, the out-of-plane *cis* and *trans* vibrations at 745 and 1015 cm^{-1} respectively exhibit high intensities in the perpendicular absorbance mode compared to that of the parallel mode. As shown on the spectra, in-plane vibrations such as those in the 3000 cm^{-1} region exhibit the opposite effect. Also, the absorbance spectra show no evidence of Csp3 defects in the structure which in principle act as barriers for the free movement of the charge carriers.

Liquid crystalline behavior of water-soluble polymers

When the alkyl chain length (m) in the water-soluble derivatives of polythiophene is long enough, a fatty acid or a cholesteric behavior is observed. In fact, the cloudy blue solution of the electrochemically formed polythiophene derivative consists of typical mesophases of a

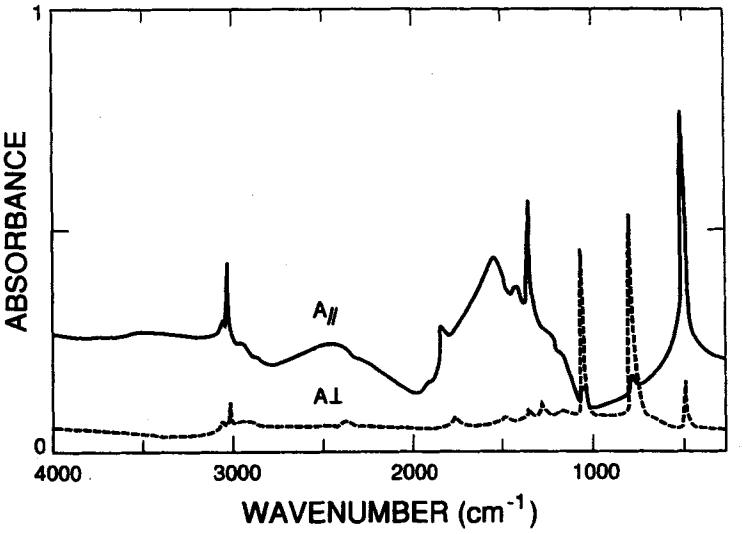


FIGURE 4 Polarized infrared absorption spectra of ordered polyacetylene in parallel and perpendicular directions to the orientation axis.

lyotropic phase.[21] However, the mesophases are observed only by using a polarizing film under a microscope (× 100 times). The clear blue phase is an indication of a liquid crystalline phase most likely nematic that can be schematized as in Figure 5.

When the cloudy blue solution is subjected to a magnetic field of 9 KGauss, the mesophases are observed without the use of a polarizing film or a microscope and the liquid crystalline phase is quite clear. Removal of the solvent from the liquid crystalline layer results in a highly conducting film with a parallel conductivity of 10^4 $(\Omega cm)^{-1}$ and an electrical anisotropy of 10^3.

CONCLUSIONS

It is quite clear that the morphology of conducting polymers, as demonstrated in the few examples studied here, plays a crucial role in the order and processability of the materials. On the one hand, we have seen that by changing the structure of well known heterocycles such as thiophene and pyrrole solubility is introduced into the polymers. In fact, the increase of the electronic density in arylpyrrole monomers not only makes the polymerization easier but also yields solution processable polymers as in poly(3-alkylthiophene)s. If a polar group is joined to the alkyl substituent the resulting material is a water-soluble polymer. In both types of material the aggregation is minimized but not totally absent which is typical of rigid backbone polymers. On the other hand, order in conducting polymers is best when introduced at the molecular level. Polymerization of acetylene

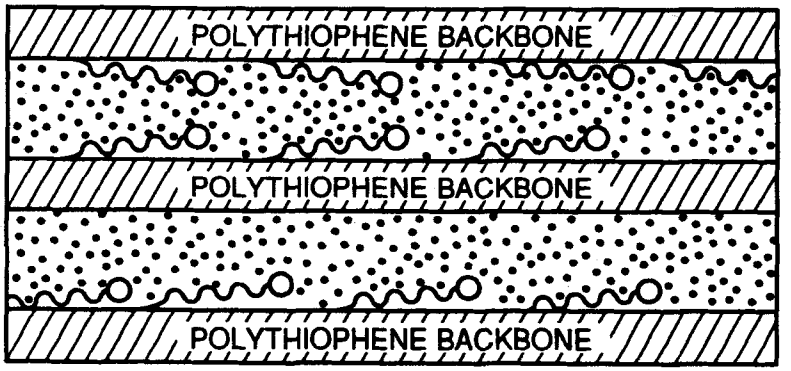


FIGURE 5 Schematic representation of the liquid crystalline phase of poly(3-alkylsulfonatethiophene).

in nematic liquid crystals demonstrates that very well and the liquid crystalline behavior of polymers such as the water-soluble polthiophene derivatives is an intrinsic property which results due to the dynamics of the various segments of the polymer backbone. Therefore, by combining liquid crystalline properties and conductivity in conjugated polymers, a new class of polymers is born which presents a real challenge in this area of research. The high conductivity and anisotropy obtained in this class of material demonstrates clearly that what has been achieved by us and BASF researchers with polyacetylene can be achieved with other conducting polymers as well.

Acknowledgments

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