

TITLE MOLECULAR AND SUPRAMOLECULAR ORIENTATION IN CONDUCTING POLYMERS

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. MOLECULAR AND SUPRAMOLECULAR ORIENTATION IN
CONDUCTING POLYMERS

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Abstract

Intrinsic anisotropy in electrical and optical properties of conducting polymers constitutes a unique aspect that derives from π -electron delocalization along the polymer backbone and from the weak inter-chain interaction. To acquire such an intrinsic property, conducting polymers have to be oriented macroscopically and microscopically (at the chain level). A review of the various techniques, including stretch-alignment of the polymer and of precursor polymers, polymerization in ordered media, i.e. in a liquid crystal solvent, and synthesis of liquid crystalline conducting polymers will be given.

Introduction

The initial polymeric systems discovered about ten years ago as conducting materials lacked processability and easy manipulation and therefore, the field was materials-limited and the use of processing techniques known in the case of conventional flexible or rigid chain polymers was not attempted. It is only in the last few years that a renewal of efforts and redirection in research in the area of conducting polymers has occurred. These efforts focused on (i) technologically important areas such as processability, orientation and stability; and (ii) fundamentally crucial aspects to the development of new systems that consist of defining the various non-linear excitation states responsible for conduction and a good understanding of the charge storage mechanism. A recent review [1] discusses various aspects including a materials survey, processability and stability aspects

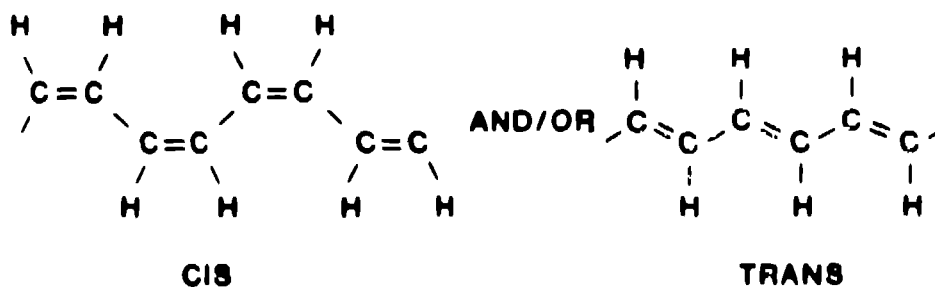
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and electronic states responsible for conduction in the various doped and undoped materials. Another recent review [2] discusses some of the potential application areas. The classic picture of the morphology observed in most as-grown polymer films has been characterized by randomly oriented fibrils. This generates many inter-fibril contacts yielding various conduction pathways and creating barriers for the charge carriers to move freely in the system. Orientation of conducting polymers is a very important aspect of the development in this field and is being investigated actively. It is closely related to processability and responsible for introducing intrinsic anisotropy in the optical and electrical properties of conducting polymers. Anisotropy in these systems derives from the existence of an extended π system on parallel chains and a weak inter-chain interaction. The high conductivities that resulted in some cases represent a strong motivation to pursue efforts in this direction. Therefore, this paper is devoted to orientation of polymer aggregates and chains, and discusses the various techniques and materials used for such a purpose.

Stretch-Orientation

Polyacetylene films whose morphology consist of randomly oriented fibrils are commonly obtained by Ziegler-Natta catalysis as shown in scheme 1.

ZIEGLER-NATTA: $Ti(OBu)_4 + AlEt_3$ IN TOLUENE $\xrightarrow{C_2H_2}$



Scheme 1

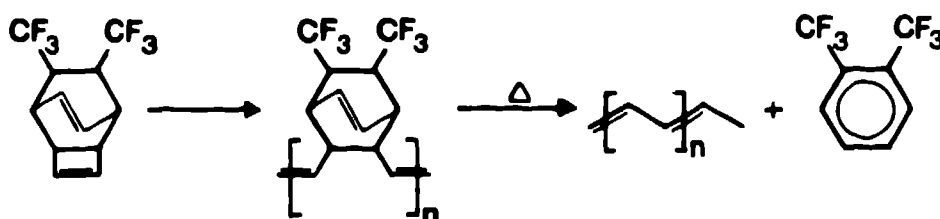
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Stretch-orientation was the first attempt to aligning polyacetylene fibrils [3,4]. The technique consisted of an initial drawing of cis-polyacetylene films, synthesized at -78°C . The drawing is then continued at increasing temperatures up to 150°C . A modest draw ratio of 3 could be obtained using this process. The resulting morphology of the film exhibited a somewhat oriented material with partially aligned fibrils along the drawing axis. Polarized IR reflectance studies showed that the reflectance parallel to the orientation direction as a function of frequency behaves similarly to semiconductors while the perpendicular component behaves like an insulator, and therefore, the material exhibits an intrinsic optical anisotropy [5]. The anisotropy is maintained after doping. Electrical anisotropy also resulted from orientation and was translated by an increase in conductivity of the heavily doped samples with AsF_5 along the orientation direction. The $\sigma_{\parallel}/\sigma_{\perp}$ ratio is higher than 10 and the maximum σ_{\parallel} obtained was approximately 2.8×10^3 S/cm. An improved synthetic technique of highly oriented polyacetylene films developed at BASF (Ludwigshafen, W. Germany) has been reported recently [6]. The method consisted of a thermal treatment of the Ziegler-Natta catalyst and drawing was realized during the polymerization reaction rather than a post-polymerization orientation. Improved optical anisotropy compared to the previous case is obtained, but the most impressive result is that of the electrical anisotropy. The highest $\bar{\sigma}$ ever obtained is approximately 1.5×10^5 S/cm which is only 5 times less than that of copper. With $\bar{\sigma}$ of 100 S/cm this constitutes the highest electrical anisotropy ever recorded on conducting polymeric systems ($\sigma_{\parallel}/\sigma_{\perp} = 1.5 \times 10^3$). The resulting material is highly dense and consists of almost perfectly aligned fibrils. Because the polymer chains are oriented along the fibril axis in polyacetylene films, the orientation of the chains in BASF polyacetylene must be extremely high. Although, high chain orientation is obtained the crystallinity of the polymer as a whole is almost unchanged [7]. Transparent polyacetylene exhibiting a parallel conductivity of 5000 S/cm was also prepared at BASF using the same catalyst treatment, but the polymer was formed on a thin polyethylene film that was stretched and doped afterwards [6]. The enormous increase in conductivity, as justified by BASF authors is due to reduction of the sp_3 defects to a minimum or to the total absence of such defects by a careful aging of the catalyst.

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Precursor Polymers

The Durham route to polyacetylene was the first technique that proceeded via a precursor polymer [8]. This technique offers the advantage of solution processing at the precursor polymer level which then by thermal conversion yields trans-polyacetylene. The reaction sequences are shown in scheme 2.



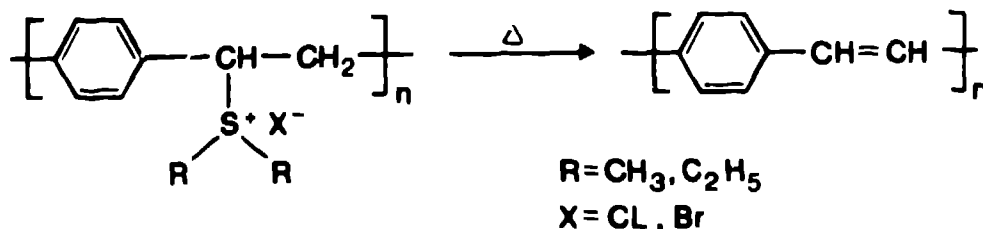
Scheme 2

It has been found that highly oriented dense films of polyacetylene can be obtained by stretching the precursor polymer during the thermal conversion and that the morphology of these films can be controlled by varying the conditions of the transformation step. Draw ratios up to 20 can be achieved [9,10]. This orientation leads to longer straight-chain sequences and motionally narrowed spins rather than immobile spins characterized by a broad ESR line in the unstretched polymer [11]. Although, high draw ratios are achieved, conductivities similar to those of the initially stretched Ziegler-Natta polyacetylene (draw ratio = 3) are obtained on the doped material. However, the intrinsic optical anisotropy is very high. In fact, the optical properties of the doped oriented Durham-polyacetylene are similar to those of a one-dimensional metal [12,13]. For example, the parallel reflectance is that of a metal and the perpendicular one is that of an insulator.

Poly(phenylenevinylene) was prepared using the precursor technique [14,15]. The technique consists of pyrolysis of the a water-soluble precursor polymer of a

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sulfonium salt. The reaction sequences are shown in scheme 3.



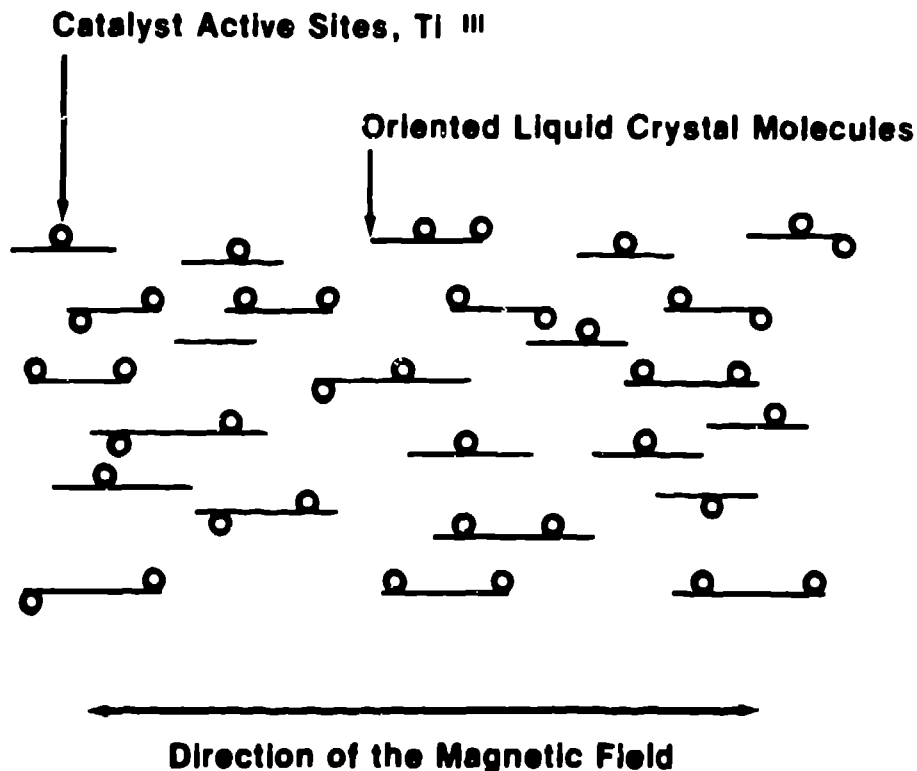
Scheme 3

Draw ratios up to 10 of the precursor polymer during the thermal conversion can be achieved resulting in a highly oriented polymer. The highest conductivity achieved on the H_2SO_4 -doped oriented polymer is approximately 4×10^3 S/cm and the electrical anisotropy is approximately 100 [16]. The optical anisotropy is also high. It is however, lower than that of stretched Durham-polyacetylene.

Polymerization in Ordered Media

The polymerization of acetylene in an ordered solvent, ie, a nematic liquid crystal, has become an area of interest. This method differs from the previous ones in that the orientation exists already at the molecular level. For example, a certain degree of order of the active sites of the Ziegler-Natta catalyst $\text{Ti}(\text{OBu})_4 \cdot \text{Al}(\text{Et})_3$ can be obtained if dissolved in a nematic liquid crystal that is subjected to a magnetic field as shown in scheme 4.

The first polymerization attempt [17-19] was made using N(p-methoxybenzylidene)p-butylaniline (MBBA) which has a nematic range of 19-30°C in a magnetic field ≥ 2500 gauss. The polymerization of acetylene using a catalyst concentration of 0.1 mol/l was carried out under a magnetic field of 4000 gauss. In these conditions the liquid crystal molecules are oriented with respect to an externally defined axis along the catalyst molecules. This process resulted in a noncrosslinked polymer with a

Scheme 4

minimum of sp_3 defects on the conjugated chains. The electrical anisotropy was higher than 4 with $\sigma_{||}$ of approximately 2×10^{-3} S/cm for the iodine-doped polymer. The X-ray diffraction patterns indicated that a preferred orientation compared to conventional stretched or unstretched polyacetylene is obtained. The morphology, as seen by SEM, showed some oriented features and a more regular structure than in conventional polyacetylene. These results indicated that orientation at the molecular level is possible, i.e., initiator and propagating species. This led to considering the alignment of the liquid crystal itself which is supposed to be perfectly aligned under the experiment conditions. Adding an impurity to a liquid crystal is known to disturb its order with or without a magnetic field, particularly if the volume fraction of the impurity is $\geq 10\%$. Since the catalyst in this case acts as an impurity, the alignment of the medium and therefore of the polymer can not reach its maximum. Therefore, a smaller amount of catalyst than in

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previous experiments, $\leq 10\%$ volume fraction, was used for the polymerization. The higher order of the solution was translated by, at the same magnetic field, by an improved intrinsic anisotropy. In fact, with a $\sigma_{||}$ of approximately 10^4 S/cm and a $\sigma_{||}/\sigma_{\perp} \approx 50$ were obtained on the AsF_5 -doped polymer.

Polyacetylene films synthesized using this technique can be stretched mechanically in a similar manner to that used for conventional polyacetylene. The stretch-orientation (draw ratio $\approx 1.5-2$) combined with the neat process that involves polymerization in a nematic liquid crystal resulted in an increase of $\sigma_{||}$ of the AsF_5 -doped film by approximately 2.5 times, up to 2.5×10^4 S/cm. With $\sigma_{\perp} \approx 10^4$ S/cm, a high electrical anisotropy is obtained ($\sigma_{||}/\sigma_{\perp} \approx 250$). This result can be explained as follows:

O A high orientation of the polymer chains is achieved via the oriented liquid crystal molecules which also leads to a high orientation of the fibrils with respect to the externally applied magnetic field.

O Stretching enhances the orientation of the fibrils by aligning those that were not formed in the direction of the field and increases the density of the films, thus reducing the inter-fibril resistance.

Other experiments followed using 4-(trans-4-n-propylcyclohexyl)-ethoxybenzene or -butoxybenzene as the nematic liquid crystal [20]. Parallel conductivities of 10^4 S/cm and electrical anisotropies ($\sigma_{||}/\sigma_{\perp}$) of approximately 50 were obtained. In other experiments [21], using the same liquid crystals, the polymerization of acetylene was carried out under a flow of the nematic catalyst solution in the absence of a magnetic field. The polymer obtained in these conditions was oriented but exhibited lower conductivities and anisotropies than those obtained on the films synthesized under the influence of a magnetic field.

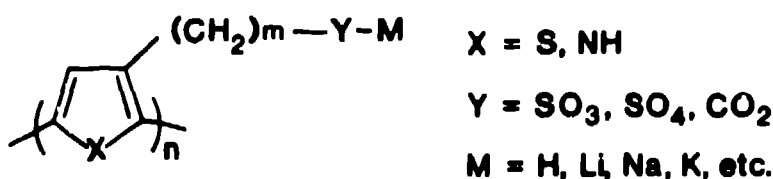
By combining the two techniques, flow properties and use of a magnetic field of 47000 gauss with the latter two solvents, Rolland et al. [22] were able to reach conductivities of $2-3 \times 10^4$ S/cm and a morphology that consists of almost perfectly aligned fibrils. In fact, X-ray diffraction studies showed that the mosaic spread of the fibrils is approximately 20° . Electron diffraction studies on thin samples prepared on a grid showed that

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the mosaic spread of the microfibrils that form the fibrils seen by SEM is 7° . The results of Rolland et al. indicate that the orientation of the polymer chains is not perfect and that there is room for improvement. The optical anisotropy is also very high due to the high order of the polymer chains.

Conducting Liquid Crystal Polymers

Liquid crystal polymers constitute a very important class of material for their modulus strength and therefore for their structural applications. This class of material represents an advantage in that a certain order exists already in the polymer structure and exhibit various ordered phases. Structural order is therefore what makes it different from the polycrystalline or amorphous conducting polymers that possess a fibrillar morphology. Combining liquid crystalline properties and high conductivities is a very exciting approach to making conducting polymers. 3-Alkylsulfonate and 3-alkylcarboxylate derivatives of thiophene or pyrrole can be polymerized electrochemically yielding water-soluble polymers that are intrinsically conducting due to self-doping by the polar group or the soap molecule [1,23]. The synthesis reactions of monomers and details of the polymerization are mentioned elsewhere [24]. The general formula of such compounds is shown in scheme 5.



Scheme 5

When $m \geq 10$ a liquid crystalline polymer in the lyotropic phase can be obtained due to the presence of the polar group pending from the main backbone which is rigid by definition.

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The possibility of phase separation and ordering in solutions of rigid rodlike polymeric particles has been thoroughly investigated in theory. For example, Flory [25] demonstrated, by application of the lattice model for polymer solutions, that concentrated solutions of rodlike particles should show phase separation even in the absence of interactions between rods.

The behavior of these polymers is similar to that of fatty acid salts in water. The latter type of molecule was studied by various authors [26-28]. Several equilibrated mesophases exist in the lyotropic solutions that could consist of isotropic micellar solutions and other more ordered phases. These phases exist because of the amphiphilic property of the substituted thiophene repeat unit which has a hydrophilic polar group and a hydrophobic hydrocarbon molecule composed of unsaturated and saturated components. Because the thiophene backbone is of a rigid nature, the mesophases could consist of uniformly elongated cylinders of uniform diameter or micelles arranged in parallel sheets with solvent in between or linear aggregates of spherical micelles. Small angle neutron scattering and electron microscopy studies will be undertaken to study the various phases in the various systems and correlate their morphologies with transport properties. Over-all conductivities similar to those with shorter alkyl groups are obtained. The high conductivity is maintained when m is increased due to the high conjugation of the chain and therefore the highly delocalized character of the electrons. This is the result of the absence of interference of the alkyl group with the chain planarity. Conductivities of approximately 10^{-2} S/cm are obtained on films cast from their aqueous solutions, which can be increased by 3-4 orders of magnitude upon doping with H_2SO_4 or AsF_5 . Also, doping of the polymer can be performed in solution in water. Homogeneous films can be obtained by evaporation of the solvent. When the sulfonic acid polymers are oxidized, a loss of a proton occurs and a self-doped polymer is obtained. The sulfonate ion (SO_3^-) acts as the counter anion to the polycation which is the polythiophene backbone.

Conclusions and Outlook

The progress made in the area of conducting polymers within the last 2-3 years with respect to manipulating their morphology and introducing some order in the

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structure is impressive. With a conductivity almost that of copper and the high electrical and optical anisotropies obtained in various cases, conducting polymers are becoming more and more the materials of choice for near-future applications.

Stretch-orientation of the polymer or of precursor polymers provides an orientation of the macroscopic aggregates, ie, fibrils, in which the chains are believed to be oriented along the fibril axis.

Polymerization in ordered media under the influence of a magnetic or electric field constitutes a much more exciting approach to perfection of the chain or fibril alignment since order is introduced already at the initiation reaction level and that order is maintained during polymerization by maintaining the field. Also, an increase in order of the already oriented films is obtained by mechanical stretching. One possibility for the improvement of the over-all orientation involves a thermal treatment history similar to that used at BASF and the use of the flow properties of a nematic liquid crystal under a magnetic or electric field as the polymerization solvent. Use of low polymerization temperatures by choosing the appropriate liquid crystal is also a parameter of importance for high order. Such an approach should result in a perfectly or almost perfectly oriented polymer which is totally defect-free and whose conductivity should exceed that of copper on a volume and weight basis.

Liquid crystalline polymers that are synthesized in their intrinsically conducting form represent a new class of material that combines two technologically important properties which are strength and conduction. Order exists here in the as-synthesized polymer. Due to their solubility in water, the study of the single chain behavior and the inter-chain interaction in functionalized poly(alkylthiophene)s becomes quite possible and therefore it opens up a number of possibilities for the study of conducting polymers in general.

There are other ways for orienting conducting polymers. For example, epitaxial growth of polyacetylene is possible on single crystals such as biphenyl [29]. However, the orientation is limited to the first layer or few layers of the polymer. Also, fiber spinning of a soluble conducting polymer could be achieved from a blend

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solution of the conducting polymer and a conventional polymer that is known for its fiber spinning properties. This could be very useful for fiber formation, particularly, when strong, highly crystalline materials are used. This technique would result in conducting polymer composites of a high modulus strength.

The interest in oriented conducting polymers is in part due to the increase in the extent of the uninterrupted π -electron delocalization for which the length of the straight-chain sequences is maximized. This leads to the possibility of studying the intrinsic anisotropic properties of the polymers which can provide detailed information on the microscopic nature of transport mechanisms and the importance of inter-chain and intra-chain interaction for transport.

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