Conducting Polymers

Conductivity Anisotropy in Oriented Poly(p-Phenylene Vinylene)

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SUMMARY

The study of charge transport mechanisms in highly conjugated conducting polymers has historically been hampered by the complex and invariant morphologies of the best conductors. We have prepared amorphous and uniaxially oriented films of poly(p-phenylene vinylene) (PPV) which exhibit a large conductivity anisotropy proportional to the degree of molecular orientation. The conductivity of the AsF₅ doped PPV, together with wide angle x-ray and IR characterization of these samples is reported.

INTRODUCTION

To study the structure/property relationships of conducting polymer charge transport, the material should consist of a known, homogeneous morphology that can be systematically varied. Ideally the morphological range should extend from an amorphous state to a single crystal. This ideal cannot be attained with a real polymer which invariably contains numerous chain defects and other larger scale inhomogeneities. In this context, one of the more promising materials from both the scientific and applications standpoint is poly(p-phenylene vinylene), PPV [II], as prepared from the water soluble precursor polyelectrolyte poly (p-xylene-a-dimethylsulfonium chloride)[I] by the method of WESSLING and ZIMMERMANN (1968).

\[
\text{H}_3\text{C} \quad \text{CH}_3
\]

\[
\text{H} \quad \text{S}^+ \quad \text{Cl}
\]

\[
\left[ \text{I} \right] \rightarrow \left[ \text{II} \right]
\]

AsF₅ doped poly(p-phenylene vinylene), PPV, has been shown to be a good electrical conductor (WNEK et al. 1979, 1981). However, attempts to synthesize a film forming material of high molecular weight by methods such as Wittig condensation of p-xylene bis (triphenylphosphonium chloride) and terephthaldehyde (McDONALD and CAMPBEIL, 1960) or by dehydrohalogenation of p-xylidene dihalides (HORHOLD et al. 1977) have yielded only insoluble and infusible oligomeric powders which when pressed into pellets, and AsF₅ doped, gave a conductivity close to 1 S/cm. Preparation of high mole-
molecular weight PPV films has been realized by first synthesizing the water-soluble precursor, poly (p-xylene-α-dimethylsulfonium chloride), followed by solution casting and thermal elimination of (CH₃)₂S and HCl. Such PPV films are strong and flexible and can be doped with AsF₅ to a conductivity of at least 500 S/cm. Doping with HgSO₄ also leads to high conductivity, although it is partially ionic in nature. n-Doping with sodium naphthalide results in a conductivity of 10⁻⁴ S/cm (GAGNON et al., 1984).

The significant advantage of this precursor method of PPV synthesis is that during the thermal conversion from films of [I] to PPV the film can be uniaxially stretched to draw ratios of up to 15 times the initial length (WESSLING and ZIMMERMANN, 1972) thus nematically orienting the polymer chains in the draw direction to a degree proportional to the draw ratio. This allows conductivity anisotropy studies over a large morphological range: from that of an amorphous matrix to that of a one-dimensionally ordered matrix. It is found that conductivity increases in the draw direction and decreases perpendicular to the draw direction giving a conductivity anisotropy $\sigma^* = \sigma_1/\sigma_\perp$ proportional to the draw ratio.

**EXPERIMENTAL**

The monomer, p-xylene-bis(dimethylsulfonium chloride), was prepared from methyl sulfide and α,α′-dichloro-p-xylene. Polymerization to the polyelectrolyte precursor was carried out by mixing equal volumes of $N_2$ flushed 0.4 M aqueous solutions of the monomer and of NaOH at 0°C for about 40 minutes. This polyelectrolyte solution was dialyzed against deionized water for 3 days in a Spectropor Dialysis Tube (MW cutoff = 3500) to remove low molecular weight ionic species. The result was a clear, slightly viscous solution exhibiting blue fluorescence presumably due to the partial base induced elimination to occasional phenylene vinylene sequences. This procedure is outlined in more detail elsewhere (CAPISTRAN et al., 1984).

Films were cast from this solution in a flat glass dish which had been thoroughly cleaned in a base bath and then treated with dichlorodimethylsilane to facilitate film removal. Casting was carried out in vacuo over a 3-day period resulting in a tough clear colorless film of the polyelectrolyte. Film thickness could be varied depending upon the solution volume evaporated. Films about 10 μm thick were typically used for most of this study.

The conversion of this polyelectrolyte film to PPV was accomplished by heating to above 180°C for 2 hours in a test tube under $N_2$ flow. The optimum temperature required for this thermal elimination was determined by a combination of thermogravimetry, differential scanning calorimetry and IR using Perkin Elmer TGS-2, DSC-2, and a PE Model 283 IR spectrometer. The final product was a clear yellow flexible film which was stable to air for over 1 month. Elemental microanalysis (U. Mass Microanalysis Lab) showed that less than 2% sulfur remained and that no chlorine was detectable.

Uniaxially oriented fibers were obtained by clamping the polyelectrolyte film at two ends and performing the elimination under a uniaxial load in a hot air stream at temperatures of from 100°-200°C. This caused rapid elimination of dimethylsulfide and HCl thus "plasticizing" the film to allow stretching up to 15 times the initial length. By varying the load...