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Conducting Polymers

Conductivity Anisotropy in Oriented Poly(p-Phenylene Vinylene)

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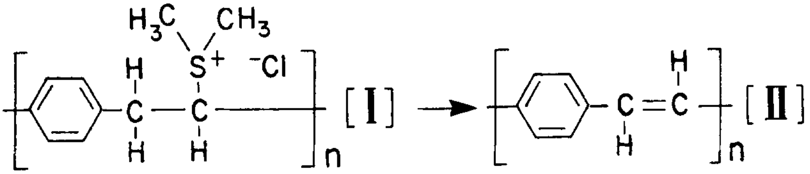
SUMMARY

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 AsF_5 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-α-dimethylsulfonium chloride)[I] by the method of WESSLING and ZIMMERMANN (1968).



AsF_5 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 CAMPBELL, 1960) or by dehydrohalogenation of p-xylidene dihalides (HORHOLD et al. 1977) have yielded only insoluble and infusable oligomeric powders which when pressed into pellets, and AsF_5 doped, gave a conductivity close to 1 S/cm. Preparation of high 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 $(CH_3)_2S$ and HCl. Such PPV films are strong and flexible and can be doped with AsF_5 to a conductivity of at least 500 S/cm. Doping with H_2SO_4 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 anistropy σ^* $(= \sigma_{\parallel}/\sigma_{\perp})$ 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 presum-ably 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 and the air stream temperature the final draw ratio ($\lambda = L/L_0$) could be varied from $1<\lambda<15$. The elimination was completed by placing a stretched film in a 280°C sandbath in the test tube under N_2 for 2 hours.

Wide angle x-ray scattering was used to characterize the molecular order of the oriented films. A CuK_α x-ray source was used with a Statton camera to obtain flat film diffraction patterns. Spacings were internally calibrated for each difraction pattern by a dusting of Al_2O_3 on the sample.

Film samples, measuring about 5x5x0.01 mm, were mounted on two platinum electrodes with colloidal graphite in MEK (electrodag). Contact resistance (~8Ω) was negligible for most of these measurements because the lowest resistance across the samples was of the order of 100Ω. More accurate 4-probe measurements gave calculated conductivities only about 5% higher. The dopant vessel and the vacuum manifold were evacuated to $<10^{-4}$ torr prior to introduction of the dopant, AsF_5 (Ozark Mahoning Co.). The vapor pressure of AsF_5, kept at -78°C in a cold finger, was 200 torr. A "skin effect" had been reported previously for oligomeric PPV pellets which had prevented further dopant diffusion (WNEK et al. 1981). In our films, however, no skin effect was noted, probably because the skin thickness was larger than the film thickness. Doping was carried out until a steady minimum electrical resistance was obtained, usually about 2 days. The color of doped samples ranged from a deep metallic purple for unstretched samples to a bright brassy color for stretched samples. The samples retained most of their flexibility after doping.

RESULTS AND DISCUSSION

The thermal elimination of dimethylsulfide and HCl proceeds via an ElcB mechanism giving a trans configuration of the double bond as evidenced by the strong IR absorbance at 970 cm^{-1}. The rate of this elimination is maximized at about 180°C in an N_2 atmosphere shown by TGA and DSC techniques. During the elimination the color of the film changes from the initially colorless precursor film to the deep yellow PPV. The film remains transparent throughout the conversion process.

The residual sulfur (<2%) in the film indicates that some saturated units still remain (i.e. >90% of the units are unsaturated). Further studies show that by optimizing the elimination temperature this residual sulfur can be more completely removed, and the conjugation length increased to give higher conductivities than those reported here.

Wide angle x-ray diffraction (WAXD) of unoriented PPV shows diffuse rings at spacings of 4.5 and 3.3 Å indicating a close packed amorphous type morphology. These rings have the same spacing as the equatorial spots which develop with uniaxial orientation of the films. Two orders of meridional layer lines appear in the WAXD patterns of the oriented PPV at a spacing of 6.6 Å which corresponds to the PPV c-axis monomer repeat distance. Samples oriented to $\lambda>7$ show a third order layer line indicating highly aligned chains. These diffraction patterns show only hk0 and 001 reflections; the lack of any hkl reflections is interpreted as showing a 1-dimensional nematic orientation with no 3-dimensional crystallinity. A measure of the degree of orientation can be obtained from the angular sharpness of the equatorial reflections which narrows to less than 10° at high draw ratios.

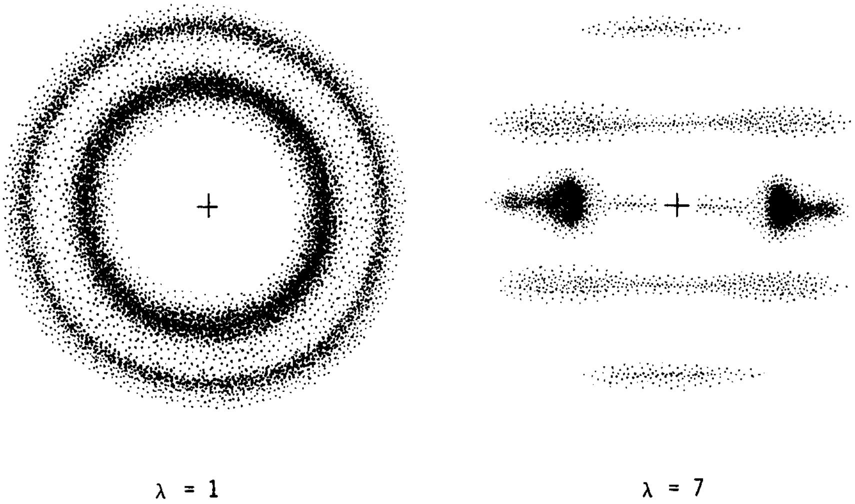


Fig. 1 Wide Angle Diffraction Patterns of Undrawn and Drawn PPV

AsF$_5$ doping of unstretched PPV films results in a dark lustrous purple material with a conductivity of 7.5 S/cm with a weight uptake of about 50%. Latest studies (MURASE et al. 1984) show that extremely long doping times (i.e. more than 2 weeks) can lead to higher conductivities, however for the purpose of this anisotropy study, doping times of two days were routinely used. Drawn samples with comparable AsF$_5$ weight uptake show greatly increased conductivity when measured parallel to the orientation (draw) direction and decreased conductivity perpendicular to the orientation direction. For example PPV with $\lambda = 10$, showed parallel and perpendicular conductivities $\sigma_\parallel = 50$ S/cm, $\sigma_\perp = 1.5$ S/cm, and a conductivity anisotropy $\sigma^*(\sigma_\parallel/\sigma_\perp) = 33$. Other samples gave anisotropies proportionally greater or smaller according to the draw ratio (Figure 2).

CONCLUSIONS

High molecular weight films of PPV can be doped to high conductivity with AsF$_5$. Uniaxially oriented films of PPV show greatly enhanced conductivity along the chain direction. Further studies of the electrically anistropic behavior of these materials coordinated with morphological characterization will be important in the advancement of both the theoretical interpretation of electrical charge transport and in the advancement of the state-of-the-art of conducting polymers.

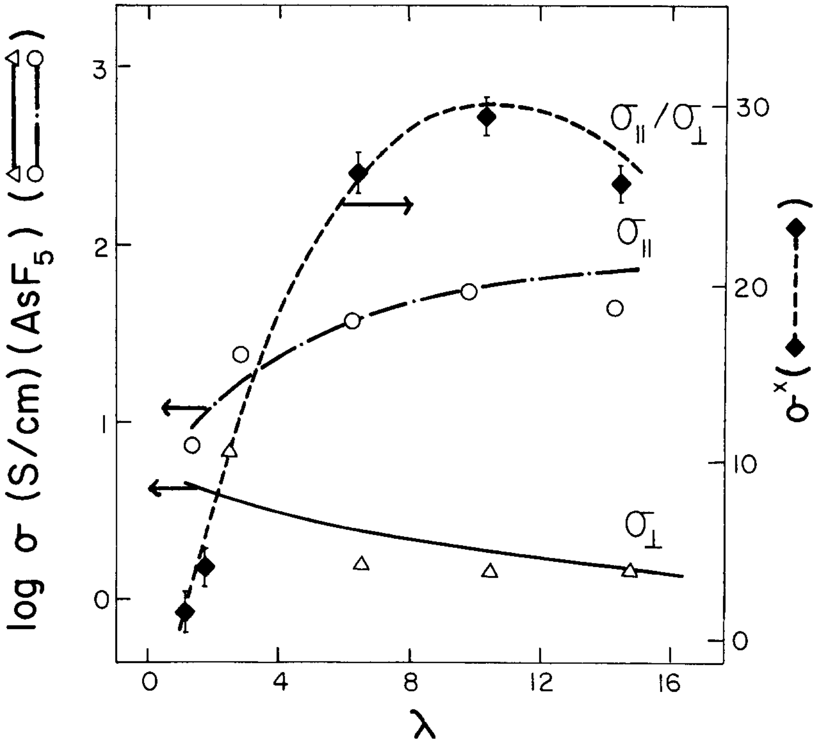


Fig. 2 Conductivity and Anisotropy with Draw

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