High Molecular Weight Polyphenylene Vinylene

F. E. Karasz [a] , J. D. Capistran [a] , D. R. Gagnon [a] & R.W. Lenz [a]

[a] Polymer Science and Engineering Department, Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts, 01003
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HIGH MOLECULAR WEIGHT POLYPHENYLENE VINYLENE

F.E. KARASZ, J.D. CAPISTRAN, D.R. GAGNON and R.W. LENZ
Polymer Science and Engineering Department, Materials
Research Laboratory, University of Massachusetts,
Amherst, Massachusetts   01003

Abstract   High molecular weight films, fibers and foams of
poly(p-phenylene vinylene), (PPV), have been prepared via a
water soluble polyelectrolyte precursor. p-Type chemical
doping of these materials with AsF_5 and H_2SO_4 leads to high
conductivity and to high electrical anisotropy in oriented
films and fibers. n-Doping with sodium naphthalide is also
possible giving a semiconducting material. PPV synthesis,
processing, and conductivity results are reported.

INTRODUCTION

Conducting polymers, based upon a conjugated backbone structure,
have enjoyed considerable research focus from both the application
and theoretical points of view. However, the underlying dif-
ficulty of these systems is that the materials offering the
highest conductivities are insoluble, infusible, and intractable;
attempts to increase processibility by pendant substitution have
typically resulted in decreased conductivity (1-4). The solution
to this problem may lie in the use of a precursor polymer which
can be converted to the desired conducting polymer after the
appropriate processing steps have been performed. One of the
earliest precursor approaches towards conducting polymers is the
work of Edwards and Feast whereby polyacetylene was synthesized by
the thermal pyrolysis of films of a substituted polymer with the
elimination of 1,2-bis(trifluoromethyl)benzene (5). The precursor
polymer is soluble in toluene, and the film can be stretched
during the pyrolysis step to induce high chain orientation (6).

High molecular weight poly(p-phenylene vinylene), PPV (II),
can be synthesized via a water soluble precursor polyelectrolyte,
poly(p-xylene-α-dimethylsulfonium chloride) (I) (7). The conver-
sion is accomplished either by base-induced or thermal elimination
of dimethylsulfide and HCl. Casting films of I by evaporation,
followed by thermal elimination, yields strong flexible films of
PPV of controllable thickness. The degree of conversion to PPV is
controlled by the elimination temperature and the time of exposure
to that temperature.
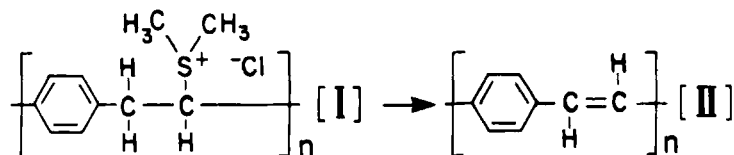
The most important advantage of this route to PPV is that the film softens during the thermal elimination allowing stretching of the film to draw ratios of up to 15 times the initial length. This induces a very high degree of molecular orientation of the polymer chains. Doped PPV, oriented in this manner, exhibits highly anisotropic electrical behavior with markedly increased conductivity in the chain axis direction (8). Since a full range of orientation is available through this process, PPV shows promise as an important theoretical and practical conducting polymer. By heating the sample instantaneously without stress, open celled foams can also be blown. These foams can similarly be doped to high conductivity.

EXPERIMENTAL

The monomer, p-xylene-bis(dimethylsulfonium chloride), is prepared by the reaction of α,α'-dichloro-p-xylene (Aldrich) with excess dimethylsulfide (Aldrich) in methanol at 50°C for 12 hrs, followed by concentration and precipitation in cold acetone to give a 93% yield of highly hydroscopic white crystals (m.p. = 149-151°C). Polymerization is carried out by mixing equal volumes of N_2 flushed 0.4M aqueous monomer and 0.4M aqueous NaOH at 0°C with stirring. The resulting clear, colorless solution is viscous and exhibits UV fluorescence after a reaction time of ~45 min. The reaction is then quenched to pH 6.8 with dilute HCl, and then dialyzed against deionized water for three days in a "Spectropor" dialysis tube (MWCO = 3500). This procedure is outlined in greater detail by Capistran et al. (9).

Films of the polyelectrolyte precursor, cast in vacuo from this solution, were strong, and flexible; their color ranged from clear to light green. The films used in this study were typically 0.01 mm thick, but this could be varied depending on the volume of solution evaporated. Differential scanning calorimetry (Perkin Elmer DSC-II), thermogravimetry (Perkin Elmer TGS-2) and elemental analysis were used to characterize and optimize the elimination of $(CH_3)_2S$ and HCl from the polyelectrolyte films. IR and UV

spectroscopy was also performed to follow the elimination. Utilizing these results, it was determined that samples for doping should be heated to above 200°C for at least 2 hrs to complete the elimination.
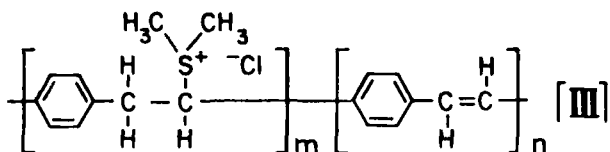
Uniaxially oriented fibers were obtained by clamping the polyelectrolyte film at two ends and performing the elimination under a uniaxial load in a hot air stream at temperatures of from 100°-200°C. This caused rapid elimination of dimethylsulfide and HCl thus "plasticizing" the film to allow stretching 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 $1 < \lambda < 15$. 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$_\alpha$ x-ray source was used with a Statton camera to obtain flat film diffraction patterns. Spacings were internally calibrated for each diffraction 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, synthesized by Wittig condensation, which had prevented further dopant diffusion (10). In our films, however, no skin effect was noted, probably because the skin thickness exceeded 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 loss of methylsulfide and HCl proceeds via an ElcB elimination mechanism (11) giving a trans double bond configuration, confirmed by the strong IR absorbance at 970 cm^{-1}. Elemental analysis of samples eliminated for 1 hour at various temperatures shows that the ratio of substituted units to unsubstituted units increases until a temperature of about 200°C is reached where the residual sulfur content is about 2.5%, corresponding to structure (III) where the ratio of m:n is ~1:11. More recent studies of samples eliminated at >300°C

$$\left[\begin{array}{c} \underset{H}{\overset{H}{\bigcirc}} - \underset{H}{\overset{H_3C}{\underset{|}{C}}} - \underset{H}{\overset{S^+ \;\; ^-Cl}{\underset{|}{C}}} \end{array} \right]_m \left[\begin{array}{c} \bigcirc - \underset{H}{\overset{H}{C}} = \underset{H}{\overset{H}{C}} \end{array} \right]_n \quad [\text{III}]$$

indicate that even lower sulfur contents are attainable. Thermal analysis of the elimination reaction by TGA and DSC shows three major coinciding weight loss and endotherm transitions centered at $102°C$, $124°C$ and $184°C$, probably corresponding respectively to the loss of water and two stages of the elimination reaction which have yet to be characterized fully. The only other defined TGA transition noted in these samples is the final decomposition point at between $575°$ and $600°C$.

As mentioned above, the film is "plasticized" during the elimination process, thus when uniaxial stress is applied during heating, the film can be stretched up to 15 times the initial length. Fibrillation, however, occurs above a draw ratio (λ) of ~10. By varying the elimination temperature and the initial m:n ratio of the film, a complete range of draw ratios with proportional degrees of molecular orientation can be obtained. This orientation is nematic (one-dimensional) in nature as shown by the wide angle x-ray diffraction showing only 00ℓ and $hk0$ reflections; $hk\ell$ reflections are absent (12).

Doping with AsF_5 of the unstretched PPV films, eliminated above $220°C$, gave limiting conductivities on the order of $\cong 10$ S cm^{-1}. By changing the elimination temperature to result in various degrees of conversion, the final conductivity could be varied over 4 orders of magnitude (Fig. 1). Improvement of the ultimate conductivity may be realized by using higher elimination temperatures (possibly by increasing the conjugation length). H_2SO_4 doping gave a conductivity of 100 S cm^{-1}, however the conductivity was demonstrated to be partially ionic in nature by observing a slight increase in resistance as DC current was passed through the sample. n-Doping with sodium naphthalide resulted in a conductivity of 2×10^{-4} S cm^{-1}; but this material is extremely unstable.

Doped stretched samples possess a pronounced anisotropy of conduction proportional to their draw ratio. Conductivity perpendicular to the draw direction σ decreases with draw, and conductivity parallel to the draw direction σ increases with draw. Figure 2 shows anisotropy for samples eliminated at $220°C$. More recent results in our laboratory give a parallel conductivity of

the order of 500 S cm^{-1}, for $\lambda = 7$ with samples having a final elimination to temperature of 380°C. This confirms qualitatively the independent results of Murase and coworkers of $\sigma_{max} = 2800$ cm^{-1} for a higher draw ratio (13).
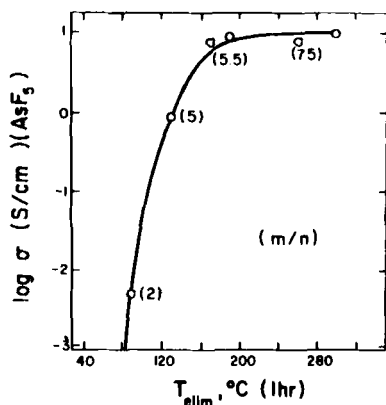

FIGURE 1:
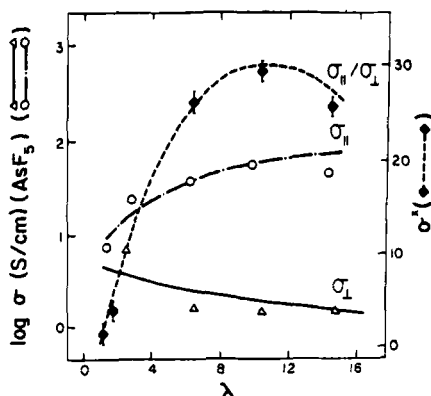Conductivity as a function of elimination temperature and structure (see text).

FIGURE 2:
Conductivity and aniso-
tropy versus draw ratio.

CONCLUSIONS

High molecular weight PPV, a promising conducting polymer, can be synthesized through a soluble and thermally processible precursor polymer to give films, foams and fibers. Samples possessing various degrees of uniaxial molecular orientation are easily obtained which show high electrical anisotropy, and hence will be of significant importance towards the goal of understanding and applying conducting polymers.

ACKNOWLEDGEMENT

REFERENCES

1. P. Cukor, J.I. Krugler and M.F. Rubner, ACS Polymer Prepr., 21, 161 (80).
2. H.W. Gibson, F.C. Bailey and J.M. Pochan, Org. Coat. Plast. Chem., 42, 603 (80).
3. M.J. Kletter, T. Woerner, A. Pron, A.G. MacDiarmid, A.J. Heeger and Y.W. Park, J. Chem. Soc., Chem. Comm., 426 (80).
4. G.W. Wnek, J. Capistran, J.C.W. Chien, L.C. Dickinson, R. Gable, R. Gooding, K. Gourley, F.E. Karasz, C.P. Lillya and K.D. Yao, Conductive Polymers, R.B. Seymour, Ed., Plenum Press, N.Y., 1981, p. 183.
5. J.H. Edwards and W.J. Feast, Polymer, 21, 595 (80).
6. H. Kahlert and G. Leising, ICSM Abstracts, Abano Terme, Italy, 1984, p. 21.
7. R.A. Wessling and R.G. Zimmermann, U.S. Pat. #'s 3,401,152 and 3,706,677.
8. D.R. Gagnon, J.D. Capistran, F.E. Karasz and R.W. Lenz, ACS Polymer Prepr., 25(2), 284 (84).
9. J.D. Capistran, D.R. Gagnon, R.W. Lenz, F.E. Karasz and A. George, ACS Polymer Prep., 25(2) (84).
10. G.W. Wnek, J.C.W. Chien, F.E. Karasz and C.P. Lillya, Polymer, 20, 1441   (79).
11. P. Sykes, A Guidebook to Mechanism in Organic Chemistry, Longman Group Ltd., London, 1975, p. 244.
12. D.R. Gagnon, J.D. Capistran, F.E. Karasz and R.W. Lenz, Polymer Bull., in press.
13. I. Murase, T. Ohnishi, T. Noguchi, M. Hirooka and S. Murakami, ICSM Abstracts, Abano Terme, Italy, 1984, p. 56.