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# Temperature dependence of the electrical conductivity of $AsF_5$-doped poly(*p*-phenylene vinylene)

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The electrical conductivity $\sigma(T)$ in poly(*p*-phenlyene vinylene) (PPV) heavily doped with $AsF_5$ has been measured as a function of temperature for $4.2 < T < 300$ K. Films which can be oriented were prepared by a soluble-polymer precursor route and were investigated in the as-doped state and after aging by exposure to air. PPV with $\sigma(300\ \mathrm{K}) < \sim 100\ (\Omega\,\mathrm{cm})^{-1}$ has a temperature dependence given by $\sigma(T) \sim \sigma_0 \exp[-(T_0/T)^\alpha]$, $\frac{1}{4} \le \alpha \le \frac{1}{2}$, independent of the sample history. For samples with higher room-temperature conductivity, the temperature dependence for $T < 100$ K is well represented by a power law of the form $\sigma = a_0 + bT^{1/2}$; $a_0$ generally decreases with decreasing $\sigma(300$ K) and becomes negative for $\sigma(300\ \mathrm{K}) < \sim 300\ (\Omega\,\mathrm{cm})^{-1}$. The latter results are consistent with a metal-insulator transition.

## I. INTRODUCTION

Highly conjugated poly(*p*-phenylene vinylene) (PPV) is a member of the class of polymers which display greatly enhanced electrical conductivity when oxidized or reduced. Previous studies have shown PPV to obtain room-temperature electrical conductivities on the order of $10^3\ (\Omega\,\mathrm{cm})^{-1}$ when chemically oxidized with group-V pentaflouride oxidizing agents or concentrated sulfuric acid,[1-3] or electrochemically oxidized.[4] Oriented PPV films also demonstrate a large anisotropy with the conductivity parallel to the chain direction being up to 2 orders of magnitude greater than that in the transverse direction.[5] In the present communication the temperature dependence of the dc conductivity is investigated to further illustrate the character of the charge carriers.

## II. EXPERIMENTAL PROCEDURES

PPV films were synthesized according to the soluble precursor route described previously.[6] The poly(xylelene tetrahydrothiophenium chloride) precursor films can be stretch oriented during elimination to obtain varying degrees of alignment of the molecular axis in the draw direction.[7] Films of original length $L_0$ were stretched in a heated zone apparatus operated at 100–120 °C to a length $L$ giving a final draw ratio $\lambda = L/L_0$ in the range $1 < \lambda < 10$. The conversion to fully conjugated PPV was conducted by subsequently annealing the films at 250 °C in vacuum for 4 h.[8]

For doping, the samples were attached to a four-terminal probe with a conductive paste (electrodag). Two mounted samples with typical dimensions of $2\ \mathrm{cm} \times 0.4\ \mathrm{cm} \times 10\ \mu\mathrm{m}$, together with a free-standing film, were then loaded into a glass vessel which was subsequently evacuated to $10^{-4}$ Torr. High conductivities were achieved by exposing the PPV films to $AsF_5$ vapor at several hundred Torr which was purified prior to doping by three freeze-pump-thaw cycles. The doping was stopped when a limiting room-temperature conductivity was reached as determined by measurements on a reference sample in the doping cell. Usually 5–10 d were required, and the samples were bright gold in color after doping. The vessel was then again evacuated to a pressure below $10^{-4}$ Torr for 24 h to remove any residual dopant and to equilibrate. At this point the evacuated vessel was transferred to a helium-filled dry box where the weight uptake of the free-standing film was measured and the conductivity samples were loaded into the low-temperature apparatus. The dimensions of the free-standing film were also measured and it was found that the thickness of the doped samples had increased 25–100 % depending on the doping level, with the other dimensions essentially unchanged. The doping level $y$, defined as the molar ratio $[AsF_6^-]/[C_8H_6^+]$, was calculated assuming that the entire weight increase was due to the incorporation of the $AsF_6^-$ anion in the polymer lattice. This calculation neglects any surface oxide layer of $As_2O_5$ which has been observed in other doped films.[9]

The low-temperature apparatus consisted of a copper sample cell which, after mounting of the doped films in the helium-filled dry box, was sealed using an indium o-ring. The sample cell was then removed from the dry box and attached to a cryostat so that conductivity measurements could be made as a function of temperature. The sample cell was slowly immersed in liquid $^4$He and allowed to come into thermal equilibrium. To reach temperatures between 4 and 80 K, the sample cell was raised above the liquid $^4$He. For temperatures greater than 80 K the cell was removed from the cryostat and allowed to warm slowly to room temperature. The sample temperature and resistance were measured simultaneously. Temperatures were measured with reference to two thermometers: a commercially calibrated germanium thermometer for the range $4 < T < 70$ K, and a silicon diode for $70 < T < 300$ K. The dc resistance was measured using the standard four-terminal technique with a typical dc current $I$ in the range $\sim 1 < I < \sim 3$ mA, yielding a current density of the order 2 A/cm$^2$. This is more than 2 orders of magnitude below the maximum current density we have observed for $AsF_5$-doped PPV in similar configurations. For a given sample, the resistance was typically measured in the as-doped state and after aging by deliberate exposure to air.

The undoped oriented PPV films consist of equiaxed approximately 50 Å crystallites. In films with $\lambda = 9$, the maximum misorientation from the draw direction is no more than 9°. These crystallites make up about 50% of the film and are distributed in a cylindrically symmetric manner about the draw direction.[10] Characterization of the grain boundaries is less certain but preliminary neutron scattering results on isotropic polycrystalline films of PPV suggest a high degree of connectivity with single chains traversing many crystallites.[11]

Direct observation of the crystallites in $AsF_5$-doped PPV was not possible because of an electron-dense surface layer attributed to $As_2O_5$. In sulfuric-acid-doped PPV, which did not suffer from this problem, the unit cell was modified but the crystallite structure was maintained after doping.[10] Wide-angle x-ray diffraction indicates that sulfuric acid and $AsF_5$ dopants are incorporated similarly in PPV.[12]

## III. RESULTS

Representative results which characterize the conductivity for a number of samples are given in Table I. The parameters in the table are relevant to the explicit functional dependences to be discussed shortly. Conductivities of many samples were measured in the as-doped state, with no exposure to air, and then remeasured after exposure to air. These samples are designated with an A following the sample number; multiple A's designate multiple measurements and exposures to air on the same sample. There was variability in the conductivity of the samples, some of which is attributable to subtle variations in the thermal, mechanical, and chemical histories of the materials. Thus $\sigma$(300 K) cannot be predicted solely from the draw ratio and doping level; however, in the as-doped state, the general trend observed was that $\sigma$(300 K) increased with draw ratio and dopant level as expected.

We show in Fig. 1 that for samples with $\sigma(300\ \mathrm{K}) \lesssim 100\ (\Omega\ \mathrm{cm})^{-1}$, the data are in good agreement with

$$\sigma(T) = (\sigma_0/\sqrt{T})\exp[-(T_0/T)^{\alpha}] \qquad (1)$$

for $\alpha = \frac{1}{4}$. This result is independent of the history of the sample. In particular, the draw ratio, sample preparation, original dopant level, and as-doped room-temperature conductivity apparently have no influence on the conduction mechanism for samples measured parallel to the stretch direction with $\sigma(300\ \mathrm{K}) \lesssim 100\ (\Omega\ \mathrm{cm})^{-1}$. Reasonable fits could be obtained for some of the samples for $\frac{1}{4} \le \alpha \le \frac{1}{2}$, especially if the temperature dependence of the prefactor is modified or eliminated.

TABLE I. A summary of the samples reported here. An A (or $A$'s) after the sample number denotes a sample that has been remeasured after deliberate exposure (or exposures) to air. Here $\lambda$ is the draw ratio, and $Y$ is the number of $AsF_6^-$ ions per PPV monomer. The parameters $T_0$ and $\sigma_0$ are defined in Eq. (1), and were obtained by fitting data for $4 < T < 300$ K. the variables $a_0$ and $b$ are defined in Eq. (2), and data were fit for $T < 100$ K. For the samples denoted by a +, the thickness of the weight uptake sample was not measured after doping; these results use the thickness before doping. An * indicates measurements made perpendicular to the stretch direction.

| No. | $\lambda$ | $Y$ | $\sigma$(300 K) $\left[\frac{1}{\Omega\ \mathrm{cm}}\right]$ | $\sigma$(4 K) $\left[\frac{1}{\Omega\ \mathrm{cm}}\right]$ | $T_0$ ($10^4$ K) | $\sigma_0$ $\left[\frac{10^4\sqrt{K}}{\Omega\ \mathrm{cm}}\right]$ | $a_0$ $\left[\frac{1}{\Omega\ \mathrm{cm}}\right]$ | $b$ $\left[\frac{1}{\Omega\ cm\ \sqrt{K}}\right]$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 0.85 | 106 | 4.27 | | | −12.1 | 7.37 |
| 2A$^+$ | 9.2 | 0.20 | 142 | 10.1 | | | −9.97 | 9.59 |
| 3$^+$ | 1 | 0.49 | 263 | 47.8 | | | 10.5 | 17.8 |
| 3A$^+$ | 1 | 0.49 | 89.0 | 0.269 | 8.85 | 9.53 | | |
| 4 | 1 | 1.1 | 107 | 1.36 | 4.02 | 5.31 | | |
| 5 | 8.4 | 0.33 | 562 | 325 | | | 237 | 20.9 |
| 6A | 8.4 | 0.33 | 75.4 | 1.70 | 2.84 | 2.72 | | |
| 7 | 7.8 | 1.0 | 1400 | 560 | | | 433 | 58.5 |
| 7A | 7.8 | 1.0 | 381 | 21.0 | | | −35.1 | 26.0 |
| 8 | 7.8 | 1.0 | 1090 | 325 | | | 192 | 68.2 |
| 10 | 10 | 0.25 | 409 | 212 | | | 178 | 17.1 |
| 10A | 10 | 0.25 | 318 | 88.2 | | | 46.5 | 19.5 |
| 10AA | 10 | 0.25 | 80 | 0.455 | 6.83 | 6.66 | | |
| 11* | 10 | 0.25 | 14.2 | 7.37 | | | 6.21 | 0.510 |
| 11AA* | 10 | 0.25 | 2.81 | 0.0205 | 5.84 | 0.193 | | |
| 12 | 10 | 1.0 | 2360 | 1840 | | | 1650 | 81.8 |

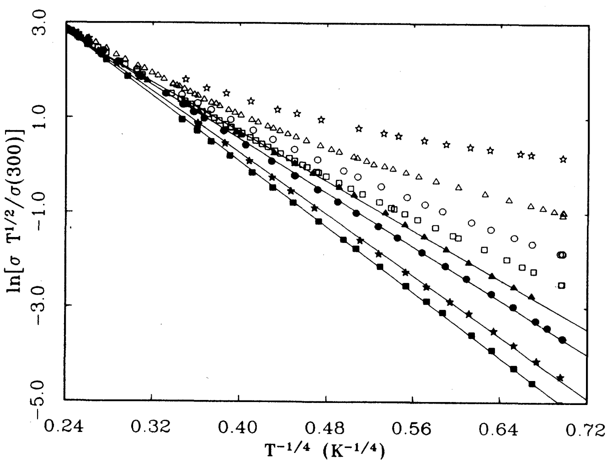

FIG. 1. The linearization $\ln[\sigma(T)\sqrt{T}/\sigma(300\text{ K})]$ vs $T^{-1/4}$ are shown for the conductivities of samples 1 (□), 2A (○), 3 (△), 3A (■), 4 (●), 5 (☆), 6A (▲), and 10AA (★). Data for samples with $\sigma(300\text{ K}) < 100\ (\Omega\,\text{cm})^{-1}$ are linear while those with $\sigma(300\text{ K}) > 100\ (\Omega\,\text{cm})^{-1}$ are not.

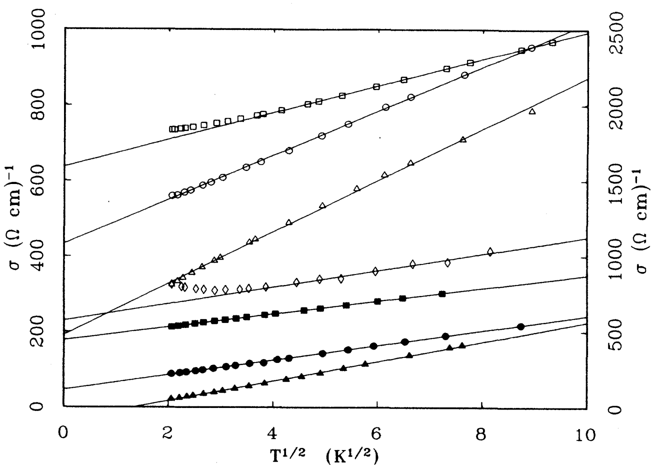

FIG. 2. The conductivities of samples 7 (○), 7A (▲), 8 (△), 10 (■), and 10A (●) are well represented by the function $a_0+b\sqrt{T}$. The deviations for samples 5 (◇) and 12 (□) are noted in the text. Note that the data for sample 12 (□) go with the right-hand axis; all other data were plotted using the left-hand axis.

The $\ln[\sigma(T)\sqrt{T}\,]\propto T^{-1/4}$ temperature dependence for the electrical conductivity observed is predicted by the three-dimensional variable-range-hopping model (3DVRH).[13] For our data, the slopes $T_0$ from the $\ln[\sigma(T)\sqrt{T}\,]$ versus $T^{-1/4}$ fit are too small to be interpreted in terms of the 3DVRH model.[14] Recent work on polyacetelyne has shown after a limited amount of aging that $\alpha=\frac{1}{4}$ to a high degree of accuracy.[15] The origin of this temperature dependence remains unexplained. An exponent $\alpha=\frac{1}{3}$ has been obtained for a model of nearest-neighbor hopping occurring at chain terminations.[16] While the analytic function should be valid only for $T>100$ K, our data are consist with this expression to much lower temperatures. Only one sample had data which could be reasonably fit using $\alpha=\frac{1}{2}$, which is the exponent predicted by the metallic island model.[17] Given the morphology of our samples, which consist of dispersed crystallites, it is perhaps surprising that more samples do not have behavior consistent with this model.

Ambiguity in the exact value of the exponent is not limited to measurement on conducting polymers. A study of the metal-insulator transition in niobium nitride thin films showed a crossover from behavior consistent with 3DVRH to a power-law dependence at $\sigma(300\text{ K})=100\ (\Omega\,\text{cm})^{-1}$.[18] Agreement with the 3DVRH model for niobium nitride was limited to $2.5<T<35$ K; the niobium nitride data for $T>35$ K could be equally well represented by $\alpha=\frac{1}{2}$, $\frac{3}{7}$, $\frac{1}{3}$, or $\frac{1}{4}$.

For our samples with $\sigma(300\text{ K})>100\ (\Omega\,\text{cm})^{-1}$, the conductivity is generally well represented by an expression of the form

$$\sigma(T)=a_0+bT^{1/2}\ . \qquad (2)$$

(Two exceptions are samples 12, the highest conductivity sample, and 5, whose conductivity actually began to *increase* below ~6 K. See Fig. 2.) The extrapolated zero-temperature conductivity $a_0$ generally decreases with decreasing room-temperature conductivity, and is negative for $\sigma(300\text{ K})\lesssim 300\ (\Omega\,\text{cm})^{-1}$.

This $T^{1/2}$ dependence is observed in studies of the metal-insulator transition in amorphous alloys[19] and at much lower temperatures in heavily doped semiconductors.[20] Metallic samples are defined as having a finite conductivity at zero temperature, corresponding to a positive $a_0$ in Eq. (2). The metal-insulator transition can proceed in ordered systems due to Coulomb correlations[21] and in disordered systems due to fluctuations in the random potential resulting from the disorder.[22] Measurements on polyacetylene give a coefficient $b$ which is very near the quasiuniversal value of 7 $(\Omega\,\text{cm})^{-1}\,\text{K}^{-1/2}$ predicted and observed in a variety of disordered materials.[23] Our data are generally not consistent with this scaling theory result.

The temperature dependence predicted by the Sheng model[24] of fluctuation-enhanced tunneling between highly conducting regions separated by insulating barriers has been observed in measurements of pristine polyacetylene.[15] This model has a physical appeal based on the morphology of our samples. We could not obtain satisfactory fits using the predicted $\sigma(T)=\sigma_0\exp[-T_1/(T+T_0)]$ temperature dependence, however. Also, heavily doped PPV films have been found to be Ohmic conductors. Varying the current over 3 orders of magnitude at room temperature had no effect on the measured resistance. This is also contrary to the non-Ohmic behavior expected in the fluctuation-enhanced tunneling model.[24]

The conductivity has also been measured perpendicular to the stretch direction. Samples 10 and 11 were cut from the same large piece of film, mounted, doped, and the conductivities measured simultaneously in the same sample cell. The conditions were as identical as possible.

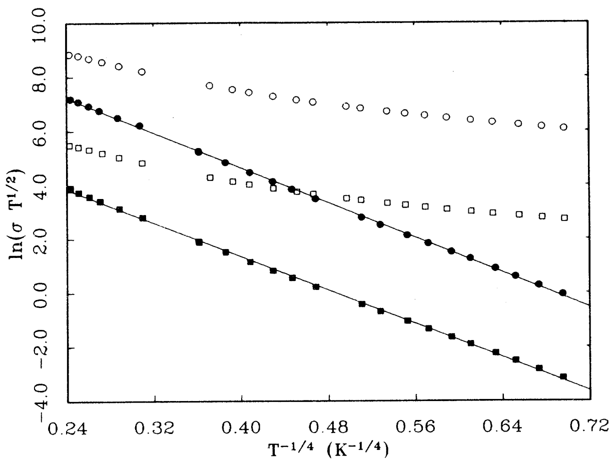

FIG. 3. The tests for consistency with the $\ln[\sigma(T)\sqrt{T}]$ vs $T^{-1/4}$ behavior are shown for the data from samples 10 (○), 10AA (●), and for measurements made perpendicular to the stretch direction on samples 11 (□) and 11AA (■). In the as-doped state, the data are not consistent with this temperature dependence.

Sample 10 was measured parallel to the stretch direction, while sample 11 was measured perpendicular to it. From Table I, for sample 11 $\sigma(300\text{ K})=14.2\ (\Omega\,\text{cm})^{-1}$, about 30 times smaller than for sample 10. For measurements made parallel to the stretch direction, and also in the unstretched samples, all samples aged by exposure to air until $\sigma(300\text{ K})\lesssim 100\ (\Omega\,\text{cm})^{-1}$ have conductivities consistent with Eq. (1), independent of any other sample parameter such as dopant level, stretch ratio, or as-doped conductivity. However, for sample 11, even though $\sigma(300\text{ K})\ll 100\ (\Omega\,\text{cm})^{-1}$, the as-doped conductivity data are not consistent with Eq. (1). This is shown in Fig. 3, where the conductivities in the as-doped state and after aging by exposure to air are shown. In the as-doped state, both samples 10 and 11 follow the $T^{1/2}$ power law and, after sufficient aging, the conductivities of both samples are well described by Eq. (1).

The magnitudes of the conductivities differ greatly in the two orthogonal directions. In particular, the conductivity threshold for agreement with Eq. (1) appears to be much lower in the perpendicular direction. However, the similarity of $\sigma(T)$ in these two samples suggests that the conduction mechanism is the same for the parallel and perpendicular directions in the as-doped state and after aging. This is expected if stretching increases the degree of alignment of the molecular axis in the draw direction and if the intrinsic conductivity of PPV is highest along the molecular axis. Stretching would increase the amount of intrachain conductivity in the draw direction while decreasing the amount of intrachain conductivity perpendicular to the draw direction. The limiting conductivity in both directions would be the interchain conduction, thus explaining the similar temperature dependence but greatly differing magnitudes of the orthogonal conductivities.

## IV. CONCLUSIONS

The dc conductivity of $AsF_5$-doped PPV films prepared by a polymer precursor technique has been studied over the temperature range $4<T<300$ K. The data for the as-doped samples are well represented by a power law of the form $a_0+bT^{1/2}$, with $a_0$ generally decreasing with decreasing $\sigma(300\text{ K})$, and becoming negative for $\sigma(300\text{ K})\approx 300\ (\Omega\,\text{cm})^{-1}$. For samples which have been aged by exposure to air, the conductivity data obtained parallel to the stretch direction are in good agreement with the temperature dependence $\sigma(T)\sim\sigma_0\exp[-(T_0/T)^\alpha]$, $\frac{1}{4}\le\alpha\le\frac{1}{2}$, if $\sigma(300\text{ K})<100\ (\Omega\,\text{cm})^{-1}$. We interpret these results as indicative of a metal-insulator transition as observed in a number of other systems. Further, measurements made perpendicular to the stretch direction suggest that the perpendicular conduction mechanism is the same as for the parallel direction, but that the magnitude of the conductivity is significantly reduced compared to an unstretched sample.

## ACKNOWLEDGMENTS

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