Electrically conducting derivative of poly(p-phenylene vinylene)

## Gary E. Wnek, James C. W. Chien, Frank E. Karasz and C. Peter Lillya

Department of Polymer Science and Engineering and Department of Chemistry, Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003, USA
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It has been well established[1-5] that polyacetylene, $(CH)_x$, undergoes a large increase in electrical conductivity upon doping with any of a wide range of electron donating or accepting moieties, for example I_2, AsF_5 or Na. Many aspects of this phenomenon are now understood in considerable detail, although the basic conduction mechanisms and the fine structure of the characteristic fibrillar morphology are still under debate. The heavily doped polyacetylene in many respects manifests metallic properties while less heavily doped materials can be more correctly represented in terms of a classical semiconducting material[1-5].

More recently, somewhat similar behaviour has been reported[6] with poly(p-phenylene) in the sense that the latter material, an electrical insulator in its pure state, becomes increasingly conducting upon doping with AsF_5 and eventually again assumes properties of a metal at sufficiently high doping levels. In contradistinction to polyacetylene, however, the range of dopants effective in inducing a semiconducting to metallic transition is limited; I_2 is apparently insufficiently electron attracting, whereas AsF_5 is able to produce materials whose room temperature conductivities are in the 500 $(\Omega\ cm)^{-1}$ range, i.e., within an order of magnitude of the highest doped $(CH)_x$ conductivities.

To obtain further insight into the chemistry of macromolecular structures which can be doped to yield metallic states we have examined the properties of pure and doped poly(phenylene vinylene), PPV, which may be regarded as a regular alternating copolymer of acetylene and p-phenylene, with the structure:
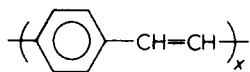
Our work was further motivated by the prospect of a more versatile substituent chemistry of PPV, yielding ultimately a soluble macromolecular system, in contrast, therefore, to the relatively intractable insoluble polyacetylene and polyphenylene. However, the materials described herein are not soluble, precluding any direct molecular weight determinations.

Synthesis and properties of PPV and analogous and derivative materials have been reported on in the literature in considerable detail[7,8]. Although there are some variations in electrical conductivity as a function of chemical structure, the conductivities of these nominally pure materials all fall completely in the range of insulators, i.e. with conductivities less than 10^{-9} $(\Omega\ cm)^{-1}$. This Communication demonstrates that the selected doping of PPV can, however, increase these conductivities by eight or nine orders of magnitude and yield, ultimately, materials whose properties can again be described as metallic.

EXPERIMENTAL

Poly(p-phenylene vinylene) was synthesized via a Wittig reaction as described by McDonald and Campbell[7], and was washed in a Soxhlet extractor in benzene for 2 days. Infrared spectra were obtained with a Perkin–Elmer model 283 spectrometer on pressed Teflon film (~10 mils thickness), indicating also the presence of aromatic aldehydic end-groups ($\nu_{C=0}$ = 1694 cm^{-1}), as expected from the synthesis. The number of repeat units, x, was determined to be ~3 and ~8 in two separate syntheses from elemental analysis (see *Table 1*). In the case of sample A, the deviation of elemental analysis (C, H, O) from the theoretical are (3.3×10^{-4}, 1.4×10^{-2}, 9.8×10^{-2}), (3.8×10^{-3}, 1.05×10^{-2}, 8.9×10^{-2}), (7.1×10^{-3}, 7.0×10^{-3}, 1.18×10^{-1}), respectively, for degrees of polymerization of 7, 8 and 9. It appears that the material has a DP of 8 ± 1 due to distribution in molecular weight. The DP of sample B is ~3 but agreement with any given DP is poor, as expected from the effect of distribution on very low molecular weight materials.

The oligomer as synthesized contains both *cis-* and *trans*-vinylenes but it can be isomerized to the all-*trans* structure by refluxing in toluene with a catalytic amount of iodine[9]. Samples used in this study have been treated to contain predominantly *trans*-vinylene units.

Rectangular wafers of PPV were made by pressing the lemon yellow powder between Teflon film at ~300 p.s.i. and cutting with a razor blade into the desired sample shape. Electrical conductivity measurements were performed using the standard 4-probe d.c. technique; contacts were made with Electrodag. Arsenic pentafluoride (Ozark Mahoning Co.) was maintained at -98°C (methanol slush) during the doping experiments to freeze-out traces of HF present in the AsF_5 (vapour pressure of AsF_5 ~30 torr at -98°C). Electron paramagnetic resonance (e.p.r.) spectra were recorded with a Varian E-9 spectrometer operating at the X-band frequency.

Results

The room temperature conductivity of a PPV wafer is ~10^{-10} $(\Omega\ cm)^{-1}$, somewhat higher than the value of ~10^{-14} $(\Omega\ cm)^{-1}$ reported by Manecke *et al.*[9]. The effect of doping PPV with the electron acceptor, AsF_5, is qualita-

Table 1 Analysis of PPV samples*

Sample number	Elemental analysis* (%)				Calculated for			
	C	H	O	Structure	X	C	H	O
A	90.6	5.74	3.40	$C_{72}H_{54}O_2$	8	90.95	5.70	3.04
B	87.71	6.07	6.22	$C_{32}H_{24}O_2$	3	87.27	5.45	7.27

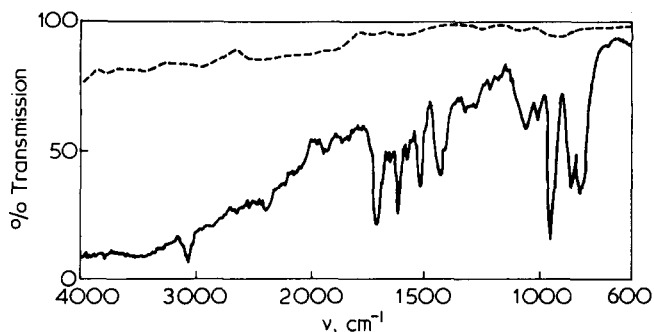* Galbraith Laboratories Inc, Knoxville, Tennessee, USA

Figure 1 Infra-red spectra of undoped PPV (full curve) and AsF$_5$-doped PPV (broken curve)

Table 2 Room temperature conductivity of AsF$_5$ doped PPV

σ $(\Omega$ cm$)^{-1}$	AsF$_5$ (wt %)
4.3×10^{-5}	5.6
1.3×10^{-3}	8.9
6.2×10^{-2}	16.4
~3	57.0

Final molar composition $[C_8H_6(AsF_5)_{0.92}]_x$

tively analogous to that observed with polyacetylene and polyphenylene. Exposure of PPV to ~30 torr AsF$_5$ results in a conductivity increase of ten orders of magnitude to ~3(Ω-cm)$^{-1}$ in 2–3 h. The yellow sample develops an olive greenish hue and eventually assumes a dark brown colour with a slight brassy lustre. The dependence of conductivity on the amount of AsF$_5$ incorporated into the sample as determined by weight uptake of a reference PPV wafer is given in *Table 2* (sample A). A significant and surprising observation is that there was found to be essentially no difference in conductivity between the doped higher and lower molecular weight PPV samples. This suggests that very high molecular weight of conjugated polymers is not a prerequisite for attainment of metal-like properties. However, we are uncertain of possible interaction between chain ends through the mediation of the dopant, thus increasing the effective chain lengths.

It should be noted that exposure of PPV to either I$_2$ or NH$_3$ vapour for several hours produced no dramatic change in electrical conductivity, in analogy with studies concerning polyphenylene. Apparently these molecules do not interact strongly via a charge transfer mechanism with the polyaromatic substances. The AsF$_5$ doped samples are somewhat unstable to oxygen and/or water and rapidly lose conductivity upon room temperature exposure to air. However, the conductivity is reduced by less than 25% when kept in a vacuum of about 10^{-5} torr for 18 h. The conductivity of AsF$_5$-doped PPV is electronic; passage of 0.5 mA through the sample for 14 h caused almost no change in resistance.

It has been shown that chemical compensation of donor and acceptor species readily occurs in polyacetylene and polyphenylene[4,6]. This compensation effect can also be observed in PPV. Thus, exposure of AsF$_5$-doped PPV [σ = 3(Ω cm)$^{-1}$ to ~100 torr of the electron donor, NH$_3$, results in a rapid decrease in conductivity, the light brown sample assuming insulator-like properties after several minutes.

Infra-red spectroscopy was used to obtain evidence of metal-like properties in doped PPV. The i.r. spectrum of pure PPV pressed on Teflon film (with Teflon film in the reference beam of the spectrophotometer) is shown in *Figure 1*

(full curve). Exposure of this sample to AsF$_5$ at 30 torr for ~3 h renders the spectrum featureless (broken curve), the high transmission being due to passage of i.r. radiation through the Teflon as a result of incomplete coverage of sample on the Teflon film. The featureless spectrum is consistent with metallic behaviour. Details of the onset of a semiconductor—metal transition in the context of i.r. spectral changes are not yet available.

Finally, electron paramagnetic resonance (e.p.r.) spectroscopy has been used to study the effect of doping and the nature of free spins in PPV. Although undoped PPV possesses no unpaired electrons, exposure to ~1 torr AsF$_5$ for 1 min results in a narrow (width, 0.5 G) e.p.r. signal (*Figure 2a*), presumably the result of charge transfer between AsF$_5$ and PPV. Heavily doped PPV exhibits a broadened signal (width, 1.8 G) which is asymmetric (*Figure 2b*). This Dysonian[10] lineshape, which has also been observed for AsF$_5$-doped polyacetylene[11], is consistent with metallic behaviour in AsF$_5$-doped PPV.

Conclusion

The central observation that we wish to report here is that doping of PPV with AsF$_5$ yields new materials of greatly enhanced electrical conductivities, with values of the latter parameter in the lower part of the range associated with classical metals. Additional i.r. and e.p.r. evidence substantiates the contention that heavily doped PPV assumes a metallic-like state. In several respects, the phenomena already investigated are qualitatively analogous to those observed in polyacetylene and to a lesser extent, in poly(*p*-phenylene).
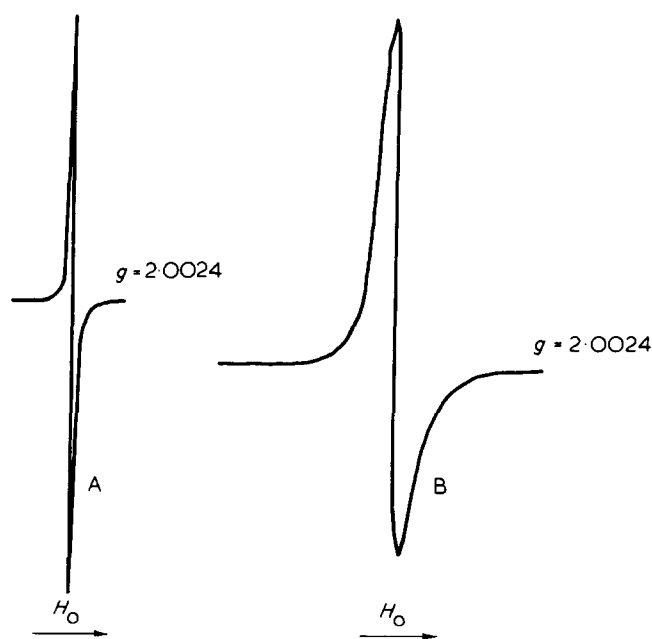
Figure 2 E.p.r. spectra of AsF$_5$-doped PPV. (a) lightly doped; (b) heavily doped

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Characterization of densified polystyrene using SANS and thermal measurements

D. G. H. Ballard, A. Cunningham, G. W. Longman and A. Nevin

Imperial Chemical Industries Limited, Corporate Laboratory, The Heath, Runcorn, Cheshire, WA7 4QE, UK

and J. Schelten

Institut für Festkörperforschung der Kernforschungsanlage Julich GmbH, 517 Julich 1, Postfach 1913, West Germany
(Received 28 August 1979)

Previous work by ourselves[1,2] and others has shown that atactic polystyrene is a random coil in the glassy state and that no significant change in the radius of gyration occurs on heating above the glass transition. More recently this study has been extended and the radius of gyration measurements carried out on polymers with molecular weights as low as 2300. The latter samples were also heated above T_g and subjected to a pressure of 6 Kbars, then cooled to 23°C; measurements were carried out at atmospheric pressure. The volume changes associated with this treatment are shown in *Figure 1*. The curve CBA is the volume—temperature behaviour at atmospheric pressure[3]. The volume changes to which the samples are subjected is shown by the path CBAEFG and the percentage volume changes are listed in *Table 1*. The
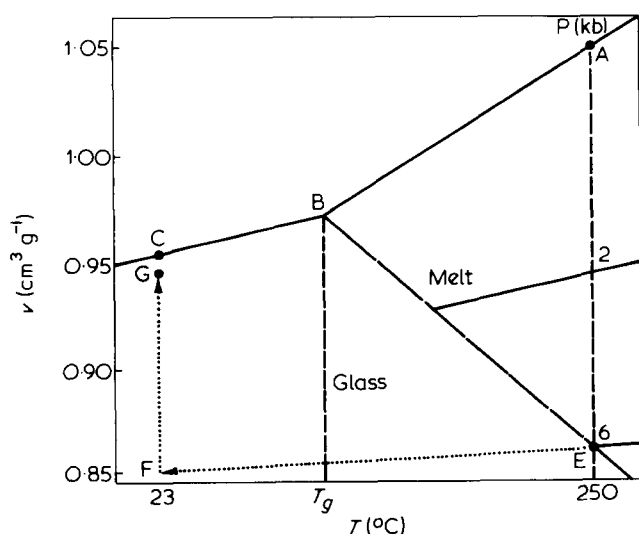
radius of gyration obeys the $M_w^{1/2}$ law precisely, and the following relationships were determined:

$$R_w = (0.27 \pm 0.017)M_w^{1/2} \text{ cooled below } T_g \text{ at 1 bar} \quad (1)$$

$$R_w = (0.22 \pm 0.015)M_w^{1/2} \text{ cooled below } T_g \text{ at 6 kbars} \quad (2)$$

The contraction of the coil is more than 30 times larger than the overall volume change in the bulk material as determined from the density measurements; the data is summarized in *Table 1*. However, it is only twice as large as the volume change produced in the melt on compression at 6 kbars. It would appear, therefore, that the polymer in the glassy state can expand (represented by the volume change from F to G in *Figure 1*) without the coil expanding. Expansion of the coil is achieved by heating the samples to a temperature below the glass temperature at which calorimetry measurements (d.s.c.) show that a small but significant heat absorption occurs. The results are summarized in *Table 2* and the effect is most noticeable at the highest molecular weight. The plaque, which is in the condition described by the point G in *Figure 1*, on heating to 80°C absorbs 0.49 cal g^{-1} of heat and this is accompanied by an expansion of the coil to the equilibrium value at atmospheric pressure. Further heating above T_g produces no addition expansion. Similar changes are observed at the lower molecular weights.

Figure 1 Volume—temperature diagram of atactic polystyrene and densification cycle

Table 1

Volume contraction of coil on compression. Calculated from equations (1) and (2)	46%
Volume contraction on compression of melt at 250°C at 6 kbars (at point E, *Figure 1*, ref 3)	23%
Overall volume contraction on compression of melt at 250°C at 6 kbars, cooled to 23°C measurements at atmospheric pressure (point G, *Figure 1*, ref 3)	1.4%