# Electrically conducting polymer blends

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A versatile technique for preparing electrically conducting polymer blends is presented which utilizes the soluble precursor approach to conducting polymer synthesis. The water-soluble polymeric sulphonium salt precursor to poly(p-phenylene vinylene) (PPV), a conducting polymer, has been used to prepare blends of PPV with polyacrylamide (PAcr). These phase-separated blends yield flexible and transparent films of good mechanical properties which can be oxidized with strong electron acceptors (e.g. $AsF_5$) and thereby exhibit greatly enhanced electrical conductivity. The ultimate conductivity shows an atypical gradual composition dependence, which lies between that of the pure components. These blends can also be thermally stretched in the manner reported for pure PPV. Stretching of the PPV/PAcr blends results in highly efficient PPV chain orientation and greatly augmented conductivity along the stretch axis.

(Keywords: electrical conductivity; polymer blends; stretching)

## INTRODUCTION

Two major impediments to the further study and utilization of electrically conducting polymers have been poor atmospheric stability and processibility. In addressing the former problem, a variety of composite materials have been prepared in which a second component is added to the conducting polymer to act as a barrier to atmospheric water and oxygen. The polyacetylene/low-density polyethylene (LDPE) blends studied by Wnek[1] and similar systems[2] have shown high conductivity and good stability. However, the insolubility of most conducting polymers has largely limited blend preparation to *in situ* polymerization techniques.

Attempts to improve the processibility of conducting polymers have included copolymerization with monomers that interrupt conjugation and lend mobility to the chain[3]. Most often, the attainment of solubility has required an excessive compromise in conductivity. An alternative approach has been to prepare a suitable precursor polymer which can be processed conventionally and subsequently converted to a fully conjugated structure. The 'Durham route' to polyacetylene is a well known example[4].

In this study, we have applied the soluble precursor polymer concept to the preparation of conducting polymer blends by casting from ternary systems consisting of the two polymeric components in a common solvent. The resulting films can be thermally converted to the conjugated form and 'doped' to yield conducting materials. In this way, a diversity of conducting polymer blend systems can be prepared over the full compositional range, allowing a systematic study of the effect of composition and structure.

Poly(p-phenylene vinylene) (PPV) was used as the conducting component and was prepared from the water-soluble polysulphonium salt intermediate introduced by Wessling[5] and used previously in our laboratory and by others[6–8]. Polyacrylamide (PAcr) was chosen as the second component because the blends thus prepared from aqueous solutions displayed the optical clarity and good mechanical properties suggestive of a compatible (but not necessarily miscible) polymer blend. Thermal conversion of the precursor to PPV was carried out below the polyacrylamide glass transition temperature (178°C), permitting the development of non-equilibrium structures in the final material. The blends that were prepared in this way preserved their mechanical strength and partial clarity through the thermal conversion process, indicating the presence of highly dispersed domains. It was possible to dope or oxidize the blend films with $AsF_5$ vapour, yielding materials whose electrical conductivities varied smoothly over 12 orders of magnitude as a function of composition.

## EXPERIMENTAL

The PPV precursor, poly(xylylidene tetrahydrothiophenium chloride), was prepared according to a previously published procedure[6]. Polyacrylamide (nominal $\bar{M}_w = 5 \times 10^6$) was obtained from Scientific Polymer Products. Blends were prepared by combining weighed amounts of slightly acidified (pH 5–6) aqueous stock solutions of the two polymers. Films were prepared by removing water under dynamic vacuum at room temperature. The films thus obtained were 10–50 $\mu$m thick and were strong, flexible and transparent with a slightly yellow colour, which increased with increasing PPV content. Conversion of the precursor polymer to PPV was achieved by heating the films under vacuum at 150°C for 18 h. This temperature was chosen to maximize PPV conversion while minimizing reaction of the polyacrylamide with the evolving HCl. The films could also be oriented by performing the conversion in a heat zone under tensile stress. This procedure, used for the pure PPV precursor, has been described elsewhere[8].

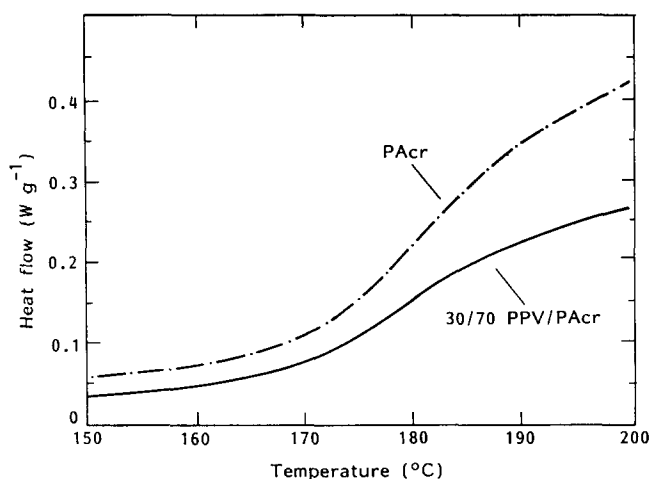Samples were characterized by infra-red spectroscopy using an IBM 30-S *FT*i.r. spectrophotometer. For

**Figure 1** D.s.c. thermograms (20°C min$^{-1}$) of pure polyacrylamide (PAcr) and a 30/70 wt% PPV/PAcr blend. For PAcr, $T_g = 178$°C and $\Delta C_p = 0.30$ J g$^{-1}$ °C$^{-1}$; for 30/70 PPV/PAcr, $T_g = 178$°C and $\Delta C_p = 0.19$ J g$^{-1}$ °C$^{-1}$

oriented samples, i.r. dichroism was examined using the above instrument with a Perkin–Elmer gold wire grid polarizer. Wide-angle X-ray diffraction experiments were carried out using nickel-filtered Cu Kα radiation and a flat-film Statton camera. Densitometry of X-ray diffraction patterns was performed using the gel scan mode of a Beckman DU-7 spectrophotometer at 450 nm wavelength and 50 μm resolution. Chemical doping was performed by exposure of evacuated samples to ~50 torr purified AsF$_5$ vapour (Ozark Mahoning Co.). Conductivity measurements were made using standard four-probe techniques.

## RESULTS AND DISCUSSION

The 'as-cast' films were smooth and transparent; colours were intermediate between those of the two components. This transparency could be preserved through thermal conversion to PPV, if the material were heated very slowly (to prevent internal void formation). Optical microscopy also revealed a smooth, continuous and homogeneous material. This suggests that resultant phase domains are smaller than the wavelength of visible light.

Thermal analysis was used to determine miscibility of the blends. Miscible polymer mixtures exhibit a single glass transition whose value is a weighted average of the $T_g$ values of the two pure components. Where specific interactions occur, a positive deviation from this simple additivity rule is often observed[9]. In immiscible systems, each phase exhibits a separate glass transition.

In the present system the polyacrylamide glass transition of 178°C is observed to be unchanged in the blend, as shown in *Figure 1*. The size of the transition, $\Delta C_p$ (change in heat capacity at $T_g$), corresponds to the amount of PAcr in the blend. Thus, the blends exist as phase-separated materials where both phases exhibit independent thermal responses.

*Figure 2* shows i.r. spectra after thermal elimination. The spectra of the blends correspond very closely to linear combinations of the spectra of the two pure components. For example, it is noted that in the spectrum of the 50/50 wt% blend all major PPV absorbances can be observed with no discernible frequency shifts. The polyacrylamide absorbances in the blend spectrum also

correspond well to pure polyacrylamide with a few exceptions. These are the reduction, in the blend, of the polyacrylamide 1113 cm$^{-1}$ absorbance and the emergence of a peak at 1217 cm$^{-1}$. Also the amide I carbonyl stretch at 1665 cm$^{-1}$ for pure polyacrylamide is broadened slightly in the blend. These effects are ascribed to a minor reaction of the amide group with HCl liberated during the elimination reaction. In a control experiment, pure polyacrylamide cast from hydrochloric acid solution showed the same changes in the i.r. spectrum.

Exposure of PPV/PAcr blends to AsF$_5$ vapour resulted in conductivity increases that depended upon the blend composition. The kinetics of the doping reaction were found to be independent of composition, indicating that the diffusion rates of AsF$_5$ through the two components were similar. All compositions absorbed approximately equal quantities of AsF$_5$ during doping (up to 25 wt%), indicating that both components reacted with the dopant. The reaction products of polyacrylamide with AsF$_5$ are not known; however, the conductivity of pure polyacrylamide did not increase under prolonged AsF$_5$
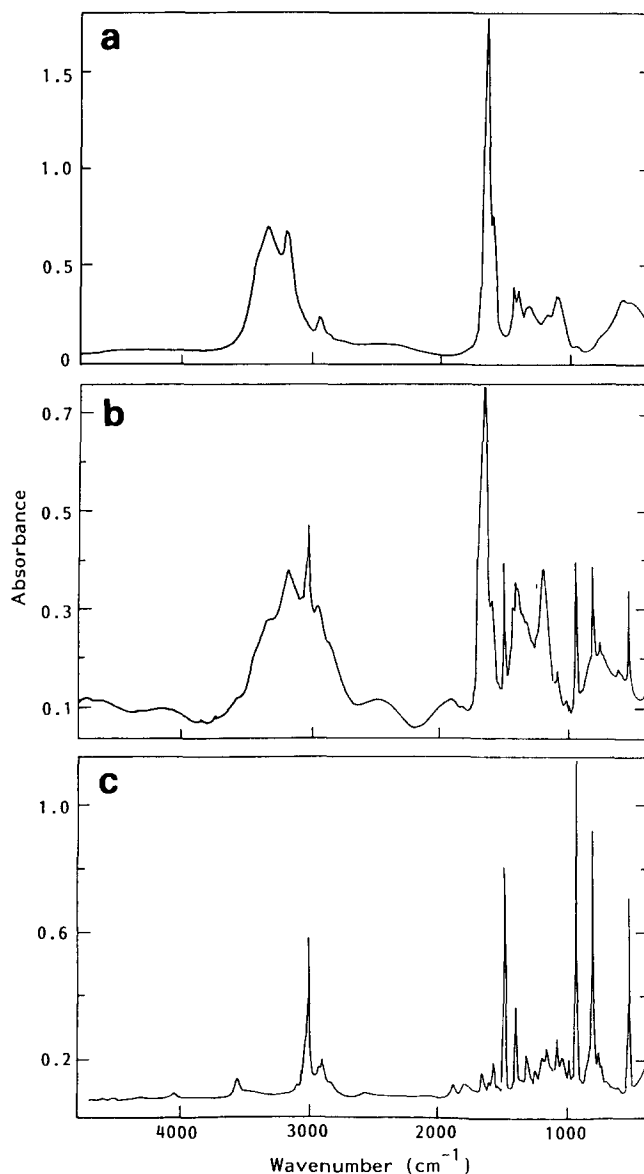


**Figure 2** FTi.r. spectra of films after thermal elimination: (a) polyacrylamide; (b) 50/50 wt% PPV/PAcr; (c) poly(phenylene vinylene)
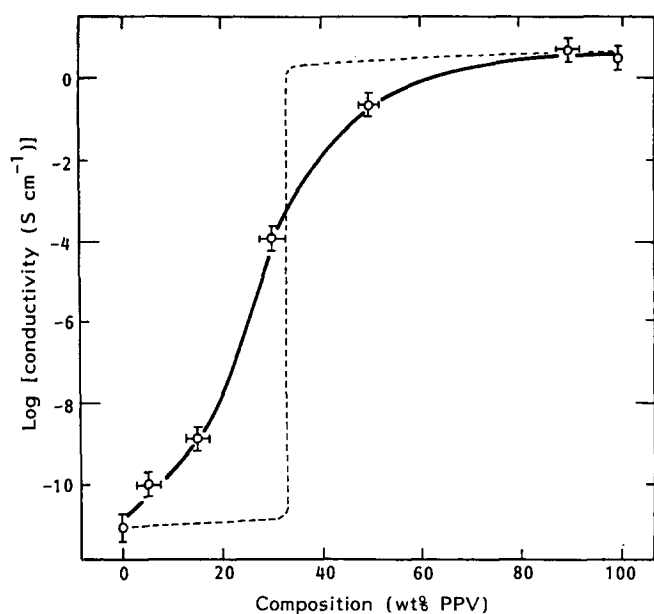
**Figure 3** Conductivity of AsF$_5$-doped blends as a function of composition (———), and the theoretical prediction of the effective medium model (———)

exposure, while that of pure PPV, prepared under the conditions of blend preparation, increased by over 10 orders of magnitude to about 5 S cm$^{-1}$. The conductivities of intermediate compositions are shown in *Figure 3*. Although the conductivity–composition relationship shows an inflection point at around 25 wt% PPV, the transition is much broader and more gradual than is commonly observed[10], or theoretically predicted[11] for a two-phase mixture of a conductor and an insulator. *Figure 3* also shows the theoretical prediction for the system according to the 'effective medium' model of Landauer[12], which has been applied to random two-phase mixtures. When the two pure components possess greatly differing conductivities, this model predicts a discontinuous change in conductivity, because of percolation effects, at a volume fraction of one-third. This clearly is not observed in the present case.

A sharp percolation threshold has been observed in many composite systems; *Figure 4* shows some examples. Curves B and D represent two poly(methyl methacrylate) (PMMA)/graphite composite systems in which the matrix differs in molecular weight. Both exhibit a sharp percolation threshold, which is shifted to higher graphite loadings with increasing matrix viscosity. This shift has been attributed to non-equilibrium structures in the composite and is discussed in ref. 13. Curve A represents polyacetylene/LDPE blends[1], which exhibit a threshold at extremely low loadings ($\sim 1\%$). This has been associated with the fact that polyacetylene is incorporated only into the amorphous regions of the LDPE matrix. Curve E shows a phthalocyanine/Kevlar composite system[14], which exhibits a broadened percolation at high loadings. Curve C refers to the present system; this shows no obvious discontinuity in conductivity.

Attempts to model the percolation threshold for a two-phase system have been made on the basis of several assumptions. Scher and Zallen proposed a 'universal' volume fraction of 0.15 for percolation based upon empirical results and calculations for spheres in ordered three-dimensional lattices[15]. Seager and Pike have

pointed out that the calculation is straightforward only when either or both components have well defined shapes (spheres, discs, needles) and that in the general case specific structural information is required[16]. In the present case, the lack of abrupt percolation behaviour may be attributed to non-equilibrium morphology generated as a result of conversion to PPV within a glassy matrix.

The stability of AsF$_5$-doped PPV/PAcr blends upon exposure to air under ambient conditions is displayed in *Figure 5*. Polyacrylamide did not stabilize the doped material, as has been reported for some systems[1]. This is probably a result of the ability of polyacrylamide to absorb atmospheric water. It is noted that the blends that contain large fractions of polyacrylamide achieved a final ambient conductivity of 10$^{-5}$ S cm$^{-1}$. This conductivity was ionic in nature, which is attributed to absorbed water.

## ORIENTED MATERIALS

PPV/PAcr blends can be thermally stretched in a manner analogous to that reported for pure PPV. It is believed that the same mechanism is responsible, namely, plasticization of the polymers by the diffusing volatile products of elimination resulting in a local and temporary reduction in modulus. Thermal elimination under tensile stress permits the achievement of molecular orientation[8]. In the case of PPV, orientation is totally irreversible, owing to the rigidity of the conjugated product. For the more flexible polyacrylamide component, relaxation is possible. The attainable draw ratio increases with
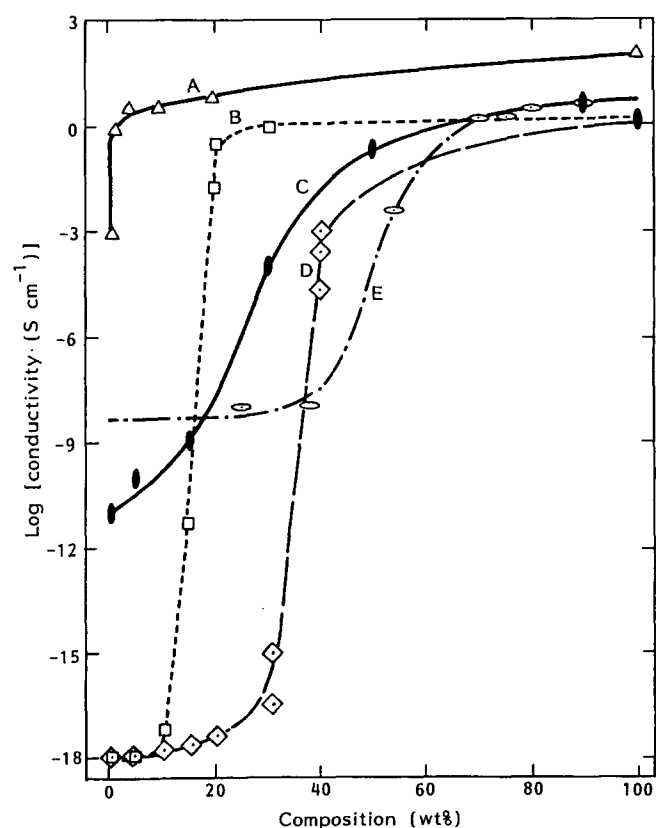


**Figure 4** Conductivity as a function of composition for several composite systems: A, polyacetylene/LDPE (I$_2$-doped)[1]; B, graphite/PMMA (4 × 10$^4$ poise)[13]; C, PPV/PAcr (AsF$_5$-doped), as *Figure 3*; D, graphite/PMMA (1.4 × 10$^5$ poise)[13]; E, Ni(Pc)/Kevlar (I$_2$-doped)[14]
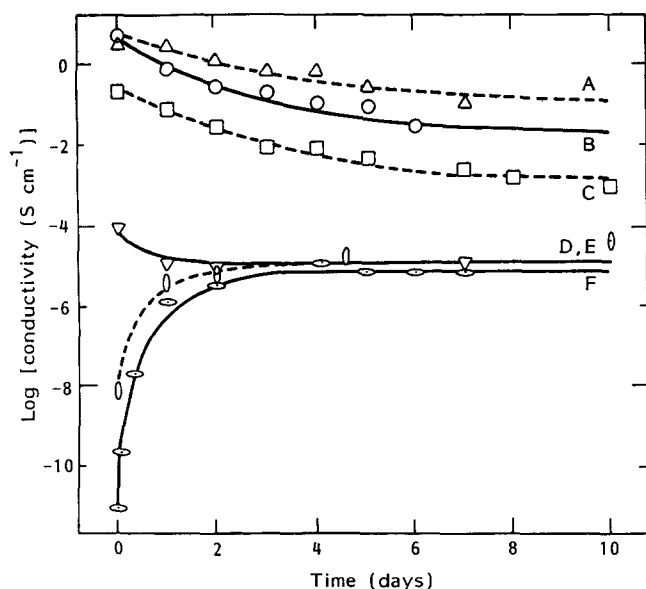
**Figure 5** Conductivity of PPV/PAcr blends as a function of time upon ambient air exposure: A, 100/0 wt% PPV/PAcr; B, 90/10 wt%; C, 50/50 wt%; D, 30/70 wt%; E, 15/85 wt%; F, 0/100 wt%

**Table 1** Conductivity of oriented blends

| Sample | Composition (PPV/PAcr) | Draw ratio | $\sigma$ (S cm$^{-1}$) | $f_{\mathrm{ir}}$ |
|--------|------------------------|------------|------------------------|------|
| SB-01 | 50/50 | 6.7 | 28 ($\parallel$) | 0.96 |
| SB-04 | 30/70 | 3.4 | 0.33 ($\parallel$) | 0.87 |
| | | | $9.3 \times 10^{-3}$ ($\perp$) | |

increasing PPV content because of a greater evolution of volatiles.

Stretching was found to increase conductivity substantially in the draw direction. *Table 1* lists the results for the AsF$_5$ doping of oriented blends. For a 50/50 wt% blend, stretching to a draw ratio of 6.7 resulted in an increase in conductivity of two orders of magnitude in the draw direction. For a 30/70 wt% PPV/PAcr blend stretched to a draw ratio of 3.4, the relative increase was even greater in the draw direction ($> 10^3$), and notably there was an increase in conductivity perpendicular to the draw direction relative to the unstretched material. This suggests that there is an increase in the connectivity of the PPV phase upon stretching. This would be expected if the PPV domains are elongated during the orientation process, because the percolation threshold for prolate ellipsoids decreases with increasing aspect ratio at constant composition[17].

*Figure 6* shows the wide-angle X-ray diffraction (WAXD) patterns for the above stretched sample and for pure stretched PPV annealed under the same conditions. The two patterns are very similar, with equatorial reflections corresponding to $d$-spacings of 4.3 and 3.2 Å and two orders of layer lines corresponding to spacing of 6.6 Å. (The circular reflections originate from the NaCl used to calibrate the instrument.) The sharpness of the equatorial reflections in the azimuthal direction and the lack of *hkl* reflections indicate a very highly oriented but axially disordered (nematic) structure[18].

The primary differences between the WAXD patterns of blended and pure PPV can be observed in *Figure 7*, which shows an equatorial profile of the X-ray patterns discussed above. The intense innermost reflection corresponds to a $d$-spacing of 4.3 Å and has been assigned
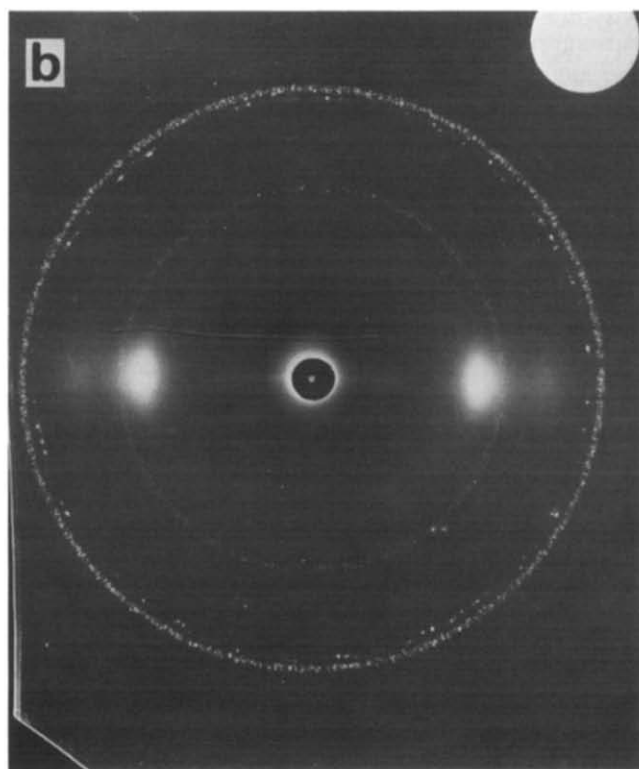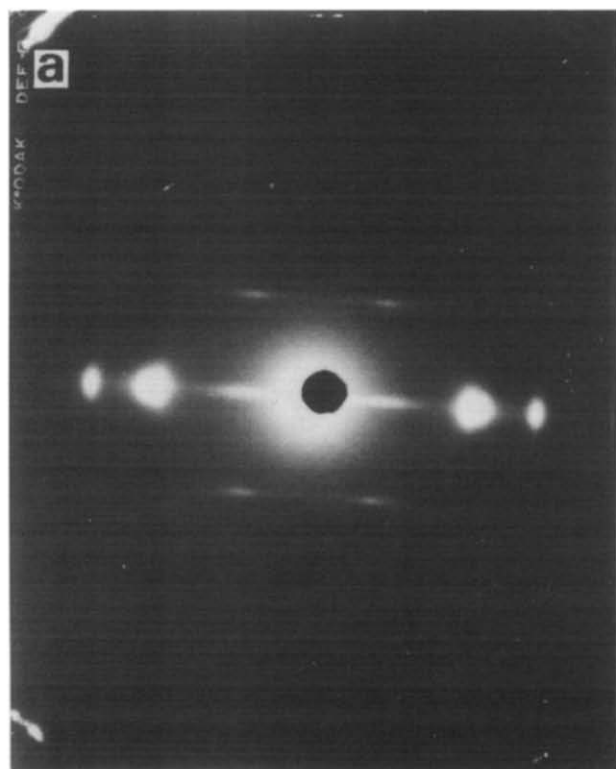


**Figure 6** Wide-angle X-ray diffraction pattern of oriented films: (a) PPV, $l/l_0 = 9.7$; (b) 50/50 wt% PPV/PAcr, $l/l_0 = 6.7$
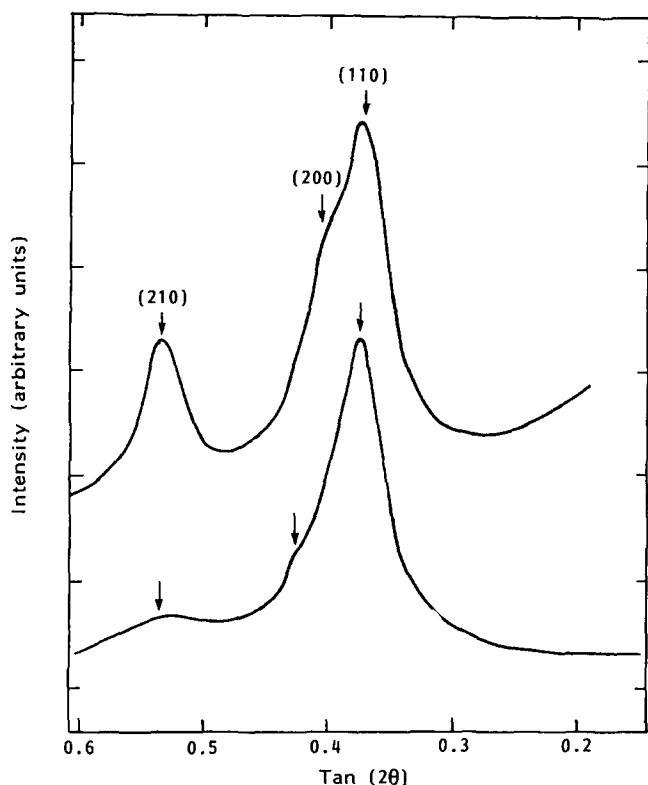
**Figure 7** Equatorial densitometry scan of WAXD patterns of *Figures 6a* (upper curve) and *b* (lower curve)

to the (1 1 0) PPV crystal plane. It has a shoulder with a *d*-spacing of about 3.9 Å, which is assigned to the (2 0 0) plane. The outer reflection at a *d*-spacing of 3.2 Å has been assigned to the (2 1 0) plane. Oriented PPV has been described as having a paracrystalline sheet-like structure with partial axial registry in the *b* crystallographic direction but almost complete axial disorder in the *a* direction; *c* is the direction of the chain axis[18]. Thus, intermolecular interaction is a minimum in the *a* direction normal to the 'sheets'.

*Figure 7* shows that, upon blending PPV, the (2 1 0) and (2 0 0) reflections are reduced in intensity and broadened relative to the (1 1 0) reflection. The lowest-order non-overlapping equatorial reflection is the (2 1 0) reflection at 3.2 Å. For this reflection the full width at half-maximum (FWHM) reflection width in the $2\theta$ direction increases from 0.027 to 0.073 rad upon blending. The broadening can be interpreted either as a decrease in crystalline perfection within the crystallites in the blend, or as a decrease in the average crystallite dimensions perpendicular to the chain[19]. The latter explanation is preferred because it seems unlikely that the presence of separate polyacrylamide phases would adversely affect the very local relaxations that improve crystalline perfection. However, the net dilution of PPV in the blend could impede the aggregation of PPV chains, resulting in smaller crystallites. The loss of intensity upon blending of the (2 1 0) and (2 0 0) reflections relative to the (1 1 0) reflection is consistent with the view of PPV as a sheet-like structure with minimum interaction between adjacent sheets in the *bc* plane. Thus the disruption of crystalline growth due to blending should occur preferentially for planes that are nearly perpendicular to the nematic *a* direction, in which interaction is minimum.

To measure the extent of orientation for PPV and polyacrylamide chains independently, i.r. dichroism was

used. *Figure 8* displays the spectra obtained for the stretched 50/50 wt% PPV/PAcr sample ($l/l_0 = 6.7$), with incident radiation polarized perpendicular and parallel to the stretch axis.

The relationship between the dichroic ratio ($A_\perp/A_\parallel$) for an i.r. mode and molecular orientation has been discussed previously[20]. The analysis is unambiguous only if the angle $\theta$ between the chain axis and the transition moment and the shape of the orientation distribution function are known. In the present analysis, we used values of $\theta$ and peak assignments for oriented PPV obtained by Bradley and Friend[21] in agreement with other data[22]. Net orientation is described using the two-phase convention. That is, a volume fraction, *f*, of the material is assumed perfectly axially oriented (but with rotational symmetry), while the remainder, $(1-f)$, has a completely random orientation. The parameter *f* is comparable to the Hermans orientation function obtained in X-ray diffraction experiments. Bands that are appropriate for quantitative analysis are listed in *Table 2*, along with peak assignments, dichroic ratios, values of $\theta$ and orientation functions.

For all PPV modes considered, the calculated orientation function, *f*, was $0.96 \pm 0.02$ for the above sample where $l/l_0 = 6.7$. In *Figure 9*, the 964 cm$^{-1}$ *trans*-vinylene C–H bending mode is shown with both polarizations. This band is the most useful for quantitative analysis because of its absorption strength, sharpness and isolation from other bands. This band showed the highest dichroic ratio observed. Assuming $\theta$ equal to 90° for this band assigns a minimum value of orientation, *f*, of 0.96. It is seen that the PPV chains in the
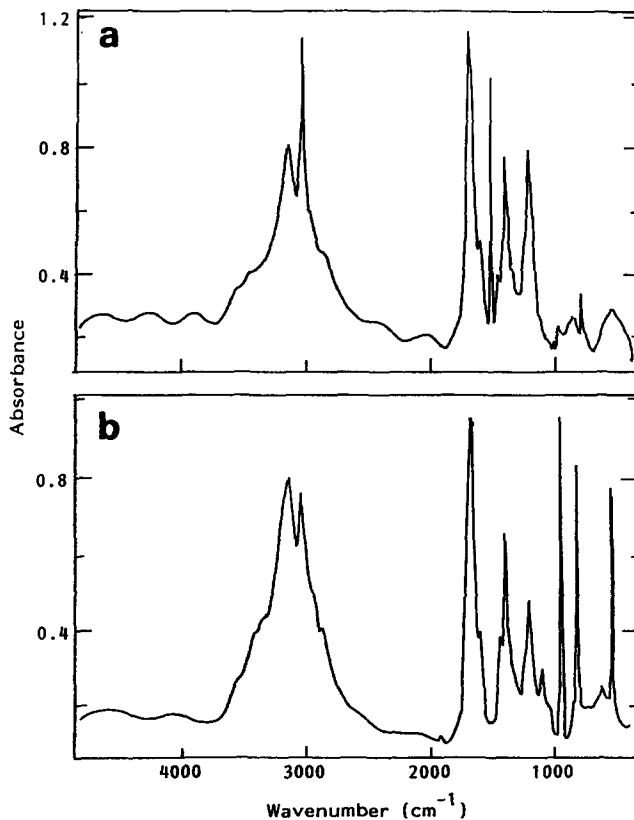


**Figure 8** Polarized *FT*i.r. spectra of oriented ($l/l_0 = 6.7$) 50/50 wt% PPV/PAcr film: (a) polarization parallel to draw direction; (b) polarization perpendicular to draw direction

**Table 2** I.r. dichroism results of oriented blend (50/50 wt% PPV/PAcr; $l/l_0 = 6.7$)

| $v$ (cm$^{-1}$) | Assignment | $R$ ($A_\perp/A_\parallel$) | $\theta$ (deg) | $f$ |
|---|---|---|---|---|
| 558 | PPV: phenylene out-of-plane ring bend | 30.8 | 90 | 0.952 |
| 838 | PPV: phenylene C–H out-of-plane bend | 18.0 | 83 | 0.962 |
| 964 | PPV: *trans*-vinylene C–H out-of-plane bend | 39.3 | 84 | 0.995 |
| 1518 | PPV: C–C ring stretch | 0.0234 | 9 | 0.968 |
| 1670 | Polyacrylamide C=O stretch | 0.998 | – | ∼0 |



**Figure 9** Dichroism of 964 cm$^{-1}$ PPV band from spectra of *Figure 8*: A, parallel polarization; B, perpendicular polarization

sample are extremely highly oriented. As has been shown for pure PPV[21], the orientation process is considerably more efficient than predicted by the Kratky model[23,24], which assumes a pseudo-affine deformation of structural elements. This model does not include relaxation effects and is usually considered as an upper limit for orientation in drawing processes. Presumably this high orientation efficiency is intimately connected with the irreversible formation of rigid units during stretching.

Although no quantitative dichroic ratio could be obtained for the 3025 cm$^{-1}$ vinylene C–H stretch mode, owing to overlap with polyacrylamide absorptions, a qualitative inspection confirms the findings of Bradley and Friend that the mode has parallel polarization ($\theta \approx 30°$)[21]. This is in contrast to the expectation that the transition moment lies along the bond direction for a stretching mode. The observed parallel polarization for the C–H stretch mode, which has also been observed for *trans*-polyacetylene, has been interpreted in terms of a vibration-induced charge flux along the chain[25].

The characteristic polyacrylamide bands do not show any significant dichroism. The only band that possesses sufficient strength and lack of overlap for quantitative treatment is the carbonyl stretch at 1670 cm$^{-1}$. The dichroic ratio of 0.998 indicates either that there is no molecular orientation or that $\theta$ is very close to 55°. Observation of the polyacrylamide methylene stretching modes at 2950 and 2870 cm$^{-1}$ and the N–H stretching mode at 3180 cm$^{-1}$ also suggests ratios close to unity and hence the absence of molecular orientation.

## CONCLUSIONS

The soluble precursor route to conducting polymers is presented as a versatile method of preparing conducting polymer blends. In this study, poly(phenylene vinylene)/polyacrylamide blends have been prepared over a wide compositional range. Conductivity (after AsF$_5$ doping) shows an atypical gradual composition dependence, which is attributed to the *in situ* method of PPV conversion and the resulting non-equilibrium morphologies.

The blends could be thermally stretched, improving conduction in the draw direction (by $> 10^2$). Polarized i.r. measurements of the stretched material demonstrated exceptionally high orientation for the PPV chains ($f = 0.96$) and negligible orientation for polyacrylamide chains. WAXD patterns indicated a highly oriented paracrystalline ordering of the PPV chains with reduced crystallite size upon blending.
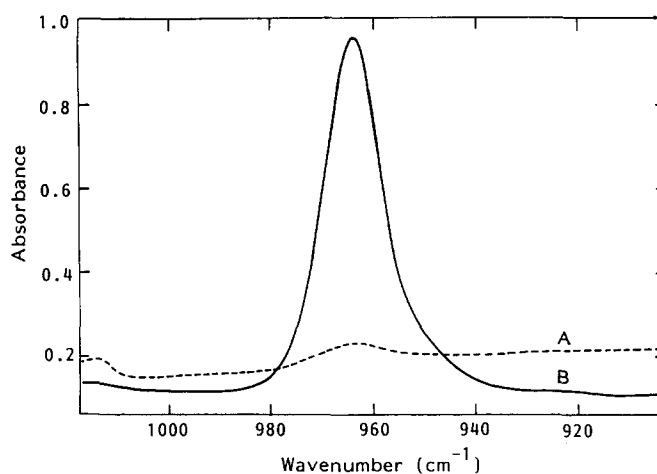
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