Morphology, Doping, and Electrical Properties of Poly(*p*-phenylenevinylene)/Poly(ethylene oxide) Blends

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ABSTRACT: Poly(*p*-phenylenevinylene)/poly(ethylene oxide) blends have been prepared under a variety of conditions to yield highly conducting materials (100–300 S/cm) upon either chemical or electrochemical doping. Accelerated doping rates and enhanced conductivities relative to those of pure poly(*p*-phenylenevinylene) were observed for blends over a wide range of compositions. These effects have been attributed to improved dopant transport as a result of blending. The electrical properties of the doped materials have been related to the chemical compositions of the blends and the morphologies observed by using optical microscopy.

Introduction

A number of conducting polymer/insulating polymer composite systems have been previously studied, usually with the aim of improving the atmospheric stability, processibility, or electroactivity of the conducting component.[1,2] The insoluble nature of most fully conjugated polymeric conductors has generally limited blend preparation to two techniques: the in situ polymerization of a conducting macromolecule within an insulating polymer matrix[3] or the dispersion of a conducting polymer powder or colloidal suspension into a second polymer matrix.[4–6] Both techniques have produced materials with improved characteristics. However, despite encouraging results, these techniques are inherently limited to the preparation of materials over a rather narrow range of composition and morphology. In previous work, we have introduced the use of the soluble precursor route to conducting polymer synthesis as part of a more flexible procedure for the preparation of conducting polymer blends, by cocasting polymer blend films from solutions in a common solvent.[7,8] In this way, it is possible to study the full compositional range and exert greater influence over the resultant morphology and electrical properties.[9]

In a previous study, we have blended the poly(sulfonium salt) precursor of poly(*p*-phenylenevinylene) (PPV) with a variety of water-soluble polymers.[7] In the initial study, it was demonstrated that blending PPV with a second polymer possessing high segmental mobility (low T_g) resulted in greatly improved dopant transport for both chemical and electrochemical doping processes. Improved transport resulted in a higher conductivity and greater electrochemical activity. No such improvements were observed in blending PPV with low-mobility (high T_g) polymers. Because the poly(*p*-phenylenevinylene)/poly(ethylene oxide) system exhibited these effects and also permitted the attainment of various and desirable morphologies, a systematic study of this system was undertaken. In this contribution we will discuss the morphology and electrical properties of these blends with respect to blend composition, film casting conditions, precursor conversion conditions, PEO molecular weight, and casting solvent. Both chemical and electrochemical doping results will be discussed.

Experimental Section

The PPV precursor polymer, poly(xylylidene–tetrahydrothiophenium chloride) (PXD), was synthesized according to a published procedure.[10] The material used in this study had an $\bar{M}_w$ of 1.2×10^6 relative to polystyrene standards.[11] Poly(ethylene oxide) (nominal molecular weights of 2×10^5 and 4×10^6) was used as received from Scientific Polymer Products.

Blend solutions with poly(ethylene oxide) were prepared by combining aqueous stock solutions of PPV precursor and PEO. Films, typically 20 μm thick, were cast from aqueous blend solutions by solvent evaporation under dynamic vacuum at room temperature. To examine the effect of casting conditions on blend properties, a second series of films was also cast in a vacuum oven held at 90 °C (i.e., above the PEO melting point). After casting, these films were cooled quickly by immersing the casting dishes in ice–water. All "as cast" PXD/PEO films were converted to PPV/PEO blends by heating under vacuum (~3 °C/min at 10^{-3} Torr) to the desired temperature and maintaining that temperature for a specific time. The optimum conditions of blend conversion were determined by examining a series of conversion temperatures and times.

In another series of experiments, a nonaqueous PPV precursor was prepared by exchanging the chloride ion in the PPV precursor for a tetrafluoroborate ion. This was accomplished by adding a 10-fold excess of 1 M $NaBF_4$ solution to 0.02 M aqueous PPV precursor. With stirring, a white flocculent precipitate formed which was isolated by filtration and washed with cold water. The material was quickly press-dried and redissolved in either DMF or acetonitrile. These solutions were combined with stock solutions of PEO in the same solvent in appropriate quantities to prepare blend solutions. Films of these blends were cast at room temperature by removal of the organic solvent under dynamic vacuum. The films were also converted to PPV/PEO by heating under vacuum.

Films which were to be chemically doped were mounted with Electrodag 502 (colloidal graphite) contacts in a four-probe configuration. Each mounted sample was placed with a second weighed dopant uptake sample into a sealed vessel and evacuated to 10^{-4} Torr. The samples were then exposed to purified AsF_5 dopant vapor at 65 Torr. The electrical resistance of each sample was monitored as a function of time of dopant exposure. When the resistance reached an asymptotic level, the dopant was removed and the vessel was reevacuated. After equilibration (6–8 h), the conductivity was recorded and the sample was transferred to an argon atmosphere drybox where the dopant uptake sample was weighed on a Cahn 31 microbalance. Atmospheric stability studies were performed by removing the mounted sample from the evacuated vessel and monitoring the resistance during exposure to ambient air.

Electrochemical doping of blends was performed in an Ar-filled Vacuum Atmospheres drybox using the doping cell, described previously,[12] that allowed pressed contact of platinum foil to blend films. Potential was controlled with a Princeton Applied Research (PAR) 173 potentiostat and charge was recorded by using a PAR 179 coulometer. The electrolyte used was lithium perchlorate (Aldrich, dried at 180 °C under vacuum) in propylene carbonate (Burdick & Jackson). The counter electrode was lithium ribbon (Alfa Ventron). Typically a sample weighing ca. 2 mg was loaded into the doping cell, immersed in 1 M $LiClO_4$/propylene carbonate electrolyte, and a potential of +4.1 V versus lithium was applied.[7] The time of electrochemical doping varied between 6 and 10 h, depending on the thickness of the film. At the end of the doping

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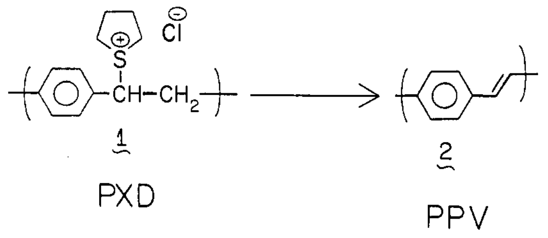
Scheme I



period, samples were removed and dried, and four-probe conductivities were measured using platinum wire contacts.

Infrared spectra of blends were recorded on a Mattson Cygnus 100 FTIR spectrometer. Elemental analyses were obtained at the University of Massachusetts Microanalysis Laboratory. Thermal analyses were performed on a Perkin-Elmer DSC-4 using a scanning rate of 20 °C/min. Morphological investigations were carried out by using a Zeiss Ultraphot II polarizing microscope with a 35-mm camera attachment and a Mettler hot stage. Extraction experiments were performed by immersing the blends in chloroform with mild agitation for 3 days, followed by vacuum drying for 6 h. Weight changes resulting from this extraction procedure were used to calculate the extraction efficiency.

Results and Discussion

(1) Optimization of Elimination Process. An essential element of the conducting polymer precursor process is the conversion of the precursor polymer, PXD, to the fully conjugated product, PPV (Scheme I) by elimination. Previous studies of the PPV precursor have demonstrated the sensitivity of the ultimate conductivity to the conditions of conversion.[13] For a series of alkyl sulfides used to prepare the PPV precursor, the cyclic tetrahydrothiophene (THT) derived sulfonium group has been shown to give complete conversion at the lowest temperatures.[10] For this reason, the THT precursor was used for all blends studied. In the present study of PPV/PEO blends, the optimization of PPV precursor conversion is complicated by the presence of the poly(ethylene oxide) constituent, which is susceptible to thermal degradation under severe elimination conditions. Therefore, an initial study was undertaken to determine the optimum elimination conditions for this system with regard to the electrical conductivity and chemical microstructure of the blends.

For this optimization study 50/50 wt % PPV/PEO material was used. Samples of this blend were thermally eliminated under vacuum at a series of temperatures and maintained at a selected temperature for a series of times. The samples were then electrochemically doped using the lithium electrolyte and an applied potential of +4.1 V for ca. 9 h. The infrared spectrum of the undoped blend and electrical conductivity after electrochemical doping were obtained for samples subjected to each set of elimination conditions. The conductivities of these samples are shown in Figure 1 where it can be seen that the conductivity is greatly affected by the conditions of elimination. The data indicate that, in terms of obtaining maximum conductivity, there is a compromise between driving the thermal elimination reaction to completion and minimizing thermal degradation. At lower elimination temperatures (150–200 °C), long elimination times (~12 h) are needed to achieve maximum conductivities. At high temperatures (250–300 °C), maximum conductivities are reached at shorter times (1 h). In general, conductivities in excess of 200 S/cm were reproducibly obtained with conversion temperatures between 200 and 250 °C maintained for several hours. Thus, the conditions adopted as standard for subsequent PPV/PEO blend studies were annealing at 225 °C for 4 h.

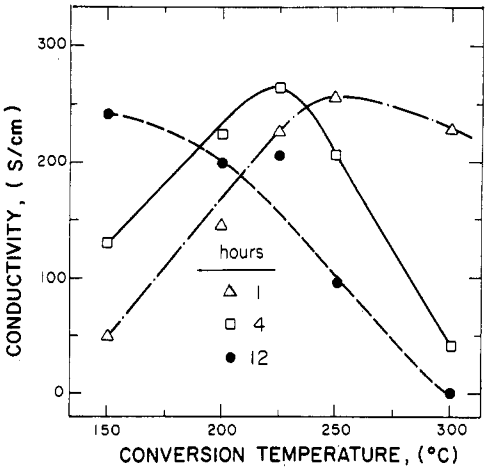


Figure 1. Conductivity of electrochemically doped 50/50 wt % PPV/PEO blends as a function of elimination temperature for a series of holding times: (△) 1 h; (□) 4 h; (●) 12 h.

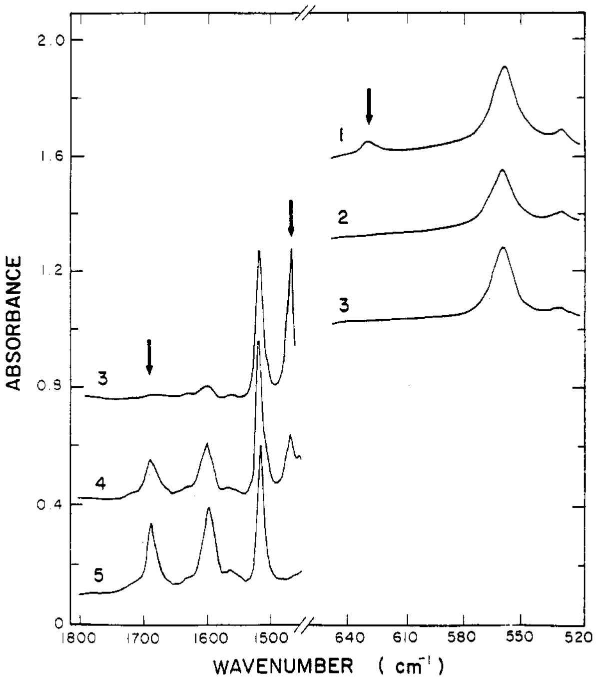


Figure 2. Regions of the infrared spectra of 50/50 wt % PPV/PEO blends eliminated under various conditions: (1) 150 °C, 1 h; (2) 200 °C, 1 h; (3) 225 °C, 4 h; (4) 250 °C, 12 h; (5) 300 °C, 12 h.

The effect of various elimination conditions upon the chemical microstructure of the blends could be observed directly by using infrared spectroscopy. In Figure 2, relevant portions of the IR spectra are displayed for some of the blends whose conductivities are shown in Figure 1. It may be noted that the absorption at 631 cm^{-1}, indicative of uneliminated units,[14] is still present for material annealed at 150 °C for 1 h. However, it disappears when the temperature is raised (200 °C, 1 h) or the time extended (150 °C, 12 h). At the other extreme of thermal treatment, spectroscopic evidence for thermal degradation (the emergence of a carbonyl absorbance at 1687 cm^{-1} and disappearance of the PEO 1463-cm^{-1} absorbance) begins to occur for elimination temperatures of 250 °C and becomes severe at 300 °C. Also linked to thermal degradation is intensification of the absorbance at 1595 cm^{-1}, attributed to an aromatic ring breathing mode. The intensity of this band is greatly enhanced when the *p*-phenylene ring becomes asymmetrically substituted as a result of oxidation of the vinylene linkages. However, because this absorption

Table I
Elemental Analyses of PPV/PEO Blends

composition, wt/wt %	exptl			theoretical		
PPV/PEO	C	H	O	C	H	O
0/100	53.30	8.87	36.80	54.55	9.09	36.36
10/90	55.83	8.72	32.79	58.71	8.77	32.72
16/84	57.80	8.59	30.84	60.88	8.58	30.54
21/79	61.33	8.57	29.00	62.86	8.42	28.72
42/58	71.03	7.43	21.48	71.17	7.74	21.09
58/42	77.29	6.78	15.63	77.50	7.23	15.27
82/18	86.30	6.43	6.58	87.00	6.46	6.54
87/13	87.25	5.98	4.70	88.97	6.30	4.73
100/0	93.67	5.96	0.58	94.12	5.88	0

corresponds to a normal mode for all para-substituted aromatics, it exhibits weak absorption for chemically pure PPV as seen in the IR spectrum of optimized material. The IR spectrum of optimized material (225 °C, 4 h) shows no evidence for the presence of either uneliminated (631 cm^{-1}) units or of thermal degradation (1687 cm^{-1}).

(2) Chemical Microstructure. Using optimized conversion conditions for this system, we studied the chemical microstructure of the converted material, particularly with respect to the electroinactive component. A previous study of PPV/poly(acrylamide) blends showed evidence of some modification of the poly(acrylamide) component by HCl during the conversion reaction.[8] Similarly in this system, PEO could affect or be affected by the PPV precursor elimination reaction.

Elemental analyses for a series of PPV/PEO blends are listed in Table I. The oxygen content has been used to evaluate the blend composition, which is also shown. The agreement between experimentally determined and calculated results supports a clean elimination process without observable chemical modification of PEO in these blends. Additional support for this conclusion is gained from the IR spectra. The spectra of various PPV/PEO blends were compared with the calculated spectra obtained by addition of the spectra of the two pure components. The equivalence of these spectra strongly indicates that the eliminated materials can be viewed as physical mixtures of pure poly(*p*-phenylenevinylene) and poly(ethylene oxide), without significant side reactions.

(3) Thermal Properties. In terms of morphological characterization, the most fundamental problem is to identify the state of dispersion of the phases. To accomplish this, differential scanning calorimetry (DSC) has proven to be a simple and reliable technique.[15] Previous studies of polymer blends in which one polymer can crystallize have invariably shown that the crystallizable component segregates as a pure crystalline phase. The remaining amorphous fraction may or may not exhibit miscibility with the second component. Miscibility is, however, exceptional in polymer blend systems.

For the present case, we have previously demonstrated that PPV and PEO are immiscible both in the precursor and fully eliminated forms.[7] Immiscibility in this system is manifested by a constant glass transition temperature (−55 °C) independent of blend composition, implying the continuing presence of a pure amorphous PEO phase.

The PEO crystalline phase is readily identified in the blends by a melting endotherm in the region of 60 °C. Pure PEO, prepared with similar solvent/thermal history, has a T_m of 66 °C, and thus a significant melting point depression is observed in the blends. Figure 3 displays T_m as a function of composition for fully annealed PPV/PEO blends. Although large melting point depressions are usually characteristic of miscible systems, this behavior has also been observed in a number of immiscible crystalline polymer blends and is attributed to a reduction in the average crystalline size as a result of blending.[16,17]

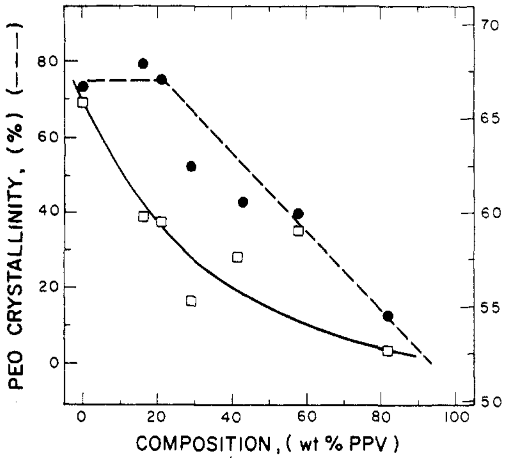


Figure 3. Melting point (●) and degree of crystallinity (□) of the PEO component as a function of the blend composition in PPV/PEO blends (heating rate 20 °C/min).

The measured enthalpy of melting, ΔH, for each of the blends has been related to the degree of crystallinity of the PEO component by using the relation

$$\Delta H = X_c X_{\mathrm{PEO}} \Delta H_0$$

where X_c represents the PEO degree of crystallinity, X_{PEO} is the weight fraction of PEO in the blends, determined by oxygen analysis, and ΔH_0 is the enthalpy of melting of pure PEO crystals, reported to be 45 cal/g.[18] In Figure 3, X_c is plotted against blend composition. It may be noted that the degree of crystallinity of PEO remains rather constant up to about 30 wt % PPV content, at which point crystallinity decreases markedly with increasing PPV content. The suppression of PEO crystallinity at higher PPV contents affects the resulting blend morphology and the subsequent doping behavior, as will be discussed in sections 4 and 6 below. Similar reductions in crystallinity have been reported for a number of blend systems including PEO/PMMA[19] and polyacetylene composites.[2,3]

(4) Morphology. The morphology of the "as cast" PXD/PEO system is composition dependent. Blends rich in PEO (≳40 wt %) crystallized into spherulites when cast from solution at room temperature. The spherulites were large (100–500-μm diameter), birefringent, and volume filling (see Figure 4). The resulting samples are mechanically rather fragile. For blends rich in the PPV precursor, PXD (≳60 wt %), spherulites do not form. These films are transparent, flexible, and tough. They are featureless in the optical microscope, indicating highly dispersed phases, consistent with the observed melting point depressions shown in Figure 3.

Figure 4 demonstrates that the total birefringence of the spherulites decreases with increasing PXD content, concomitant with the reduction in crystallinity measured by calorimetry (Figure 3). Thus, the absence of spherulites at still higher PXD contents may be attributed to the reduction of crystallinity below a threshold level required for spherulitic growth.

The morphology of blends containing crystalline polymers has been well studied experimentally and theoretically, and several reviews are available.[20,21] For systems in which one component crystallizes, three types of spherulite formation have been observed. The noncrystalline component may be excluded from the interlamellar regions of growing crystallites, forming amorphous domains with dimensions on the order of the lamellar thickness (~10 nm), or the noncrystalline component may be ex-

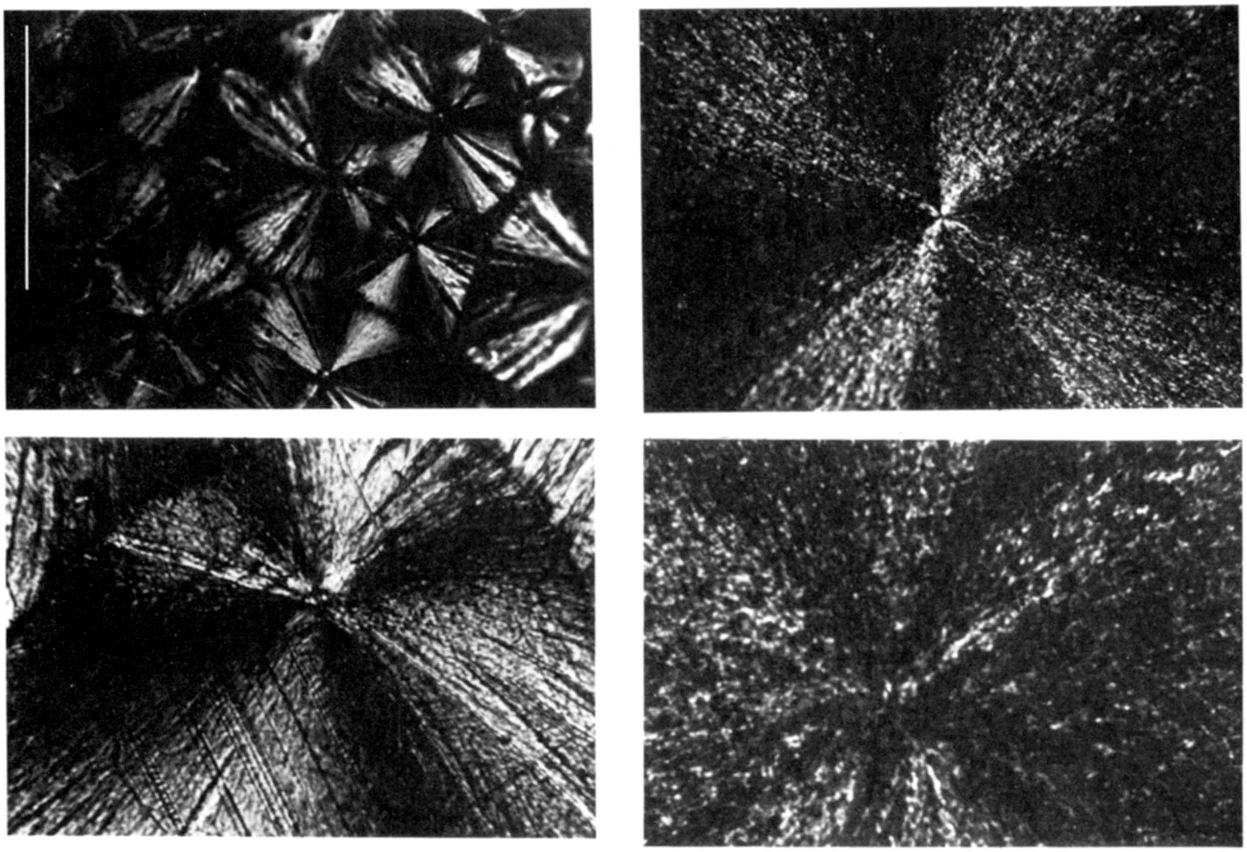


Figure 4. Optical micrographs of spherulites in "as cast" PXD/PEO blends showing decreasing birefringence with increasing PXD content: (a, top left) pure PEO; (b, top right) 10/90 wt % PXD/PEO; (c, bottom left) 21/79 wt % PXD/PEO; (d, bottom right) 42/58 wt % PXD/PEO. Scale marker is 100 μm. Magnification is constant.

cluded from regions between growing crystalline fibrils, forming domains with dimensions of the order of fibrillar width ($\sim$1 μm). A third possibility is that the noncrystalline component may be excluded completely from the growing spherulite, forming inter-spherulitic domains of the order of 100 μm.

Interlamellar segregation has been verified in the poly(ϵ-caprolactone)/PVC and PEO/PMMA systems by using SAXS techniques.[22,23] Interfibrillar segregation has been observed in a number of systems, for example, blends of *trans*- and *cis*-polyisoprene.[24] Interspherulitic segregation is commonly encountered upon crystallizing from heterogeneous melts, for example, in PEO/PS and PP/LDPE immiscible blends.[19,25]

In the present system, segregation on the interfibrillar scale can be directly observed by using hot-stage microscopy. The spherulites are completely volume filling, even up to a PXD content of 50 wt %. The boundaries between impinged spherulites are sharp and well defined. Therefore, the PPV precursor domains must be included within the spherulite structure. The implication is that, during film casting, the spherulitic linear growth rate surpasses the diffusion rate of excluded material so that PXD domains are entrapped within the spherulite.

Evidence for interfibrillar segregation is presented in Figure 5. An as cast 30/70 PXD/PEO film at room temperature is shown in Figure 5a. This sample was heated to 60 °C, at which point the melting of PEO crystallites was manifested by a sudden reduction in birefringence. However, the spherulitic texture remained otherwise intact. Of course, pure PEO when melted suffers complete extinction of light between crossed polars because no optically anisotropic species remain. However, the weak birefringent pattern which persists in the blends is attributable to "form" birefringence associated with the anisotropy of shape of the dispersed domains.[26] The sample in Figure 5a was further heated to temperatures where the conversion of PPV precursor to PPV proceeds. Figure 5b shows the sample held at 150 °C. In this micrograph, one can discern the meandering domains of PPV in the molten PEO matrix. These domains appear to be fibrils which extend radially with an average width of a few microns. This radiating fibrillar structure is even more evident in Figure 5c, which shows a 50/50 wt % PPV/PEO blend also held above the PEO melting point. From these micrographs, the conclusion may be drawn that the morphology obtained during the casting of PXD/PEO films from solution is largely maintained throughout the PXD elimination to PPV at elevated temperatures. This is a result of the infusibility of the PXD and PPV domains. It is expected that the observed bicontinuous interfibrillar spherulitic morphology is a desirable one for conducting polymers because it results in a highly connected (and hence conductive) electroactive phase which is still relatively "open", allowing the rapid diffusion of dopant into the material (cf. "Shirakawa" polyacetylene).[27]

Additional hot-stage microscopy studies showed that the persistence of spherulitic texture after PEO melting was observed at PXD contents as low as 10 wt %. In Figure 6a, a micrograph of a 10/90 PXD/PEO as cast blend shows the strongly birefringent (highly crystalline) extinction pattern. In Figure 6b, the same spherulite is held at 150 °C (90 °C above T_m). The birefringence is, of course, greatly diminished; however, the texture of radiating fibrils persists, strongly suggesting a continuous PPV phase even at this loading. Upon cooling again to room temperature, the PEO melt phase crystallizes over the surface of the material; the advancing crystallization front is shown in Figure 6c. The result is a layer of pure PEO coating the fully converted blend. The presence of this layer has ra-

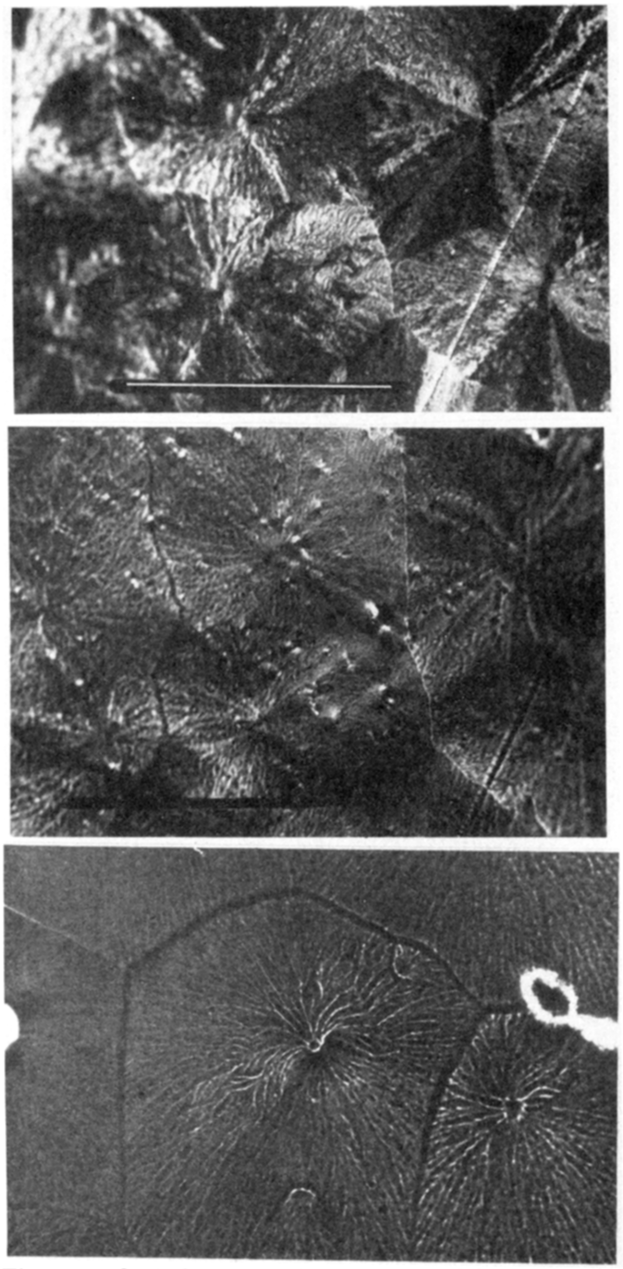


Figure 5. Optical micrographs of PXD/PEO blends showing separate PXD/PEO domains upon melting: (a, top) 30/70 wt % (scale marker is 100 μm) PXD/PEO blend "as cast" at room temperature; (b, middle) the same sample held at 150 °C; (c, bottom) 50/50 wt % PXD/PEO blend held at 150 °C (showing radiating fibrillar domains). Scale marker is 100 μm. Magnification is constant.

mifications during subsequent chemical doping (producing an induction period) which will be discussed in section 6 below.

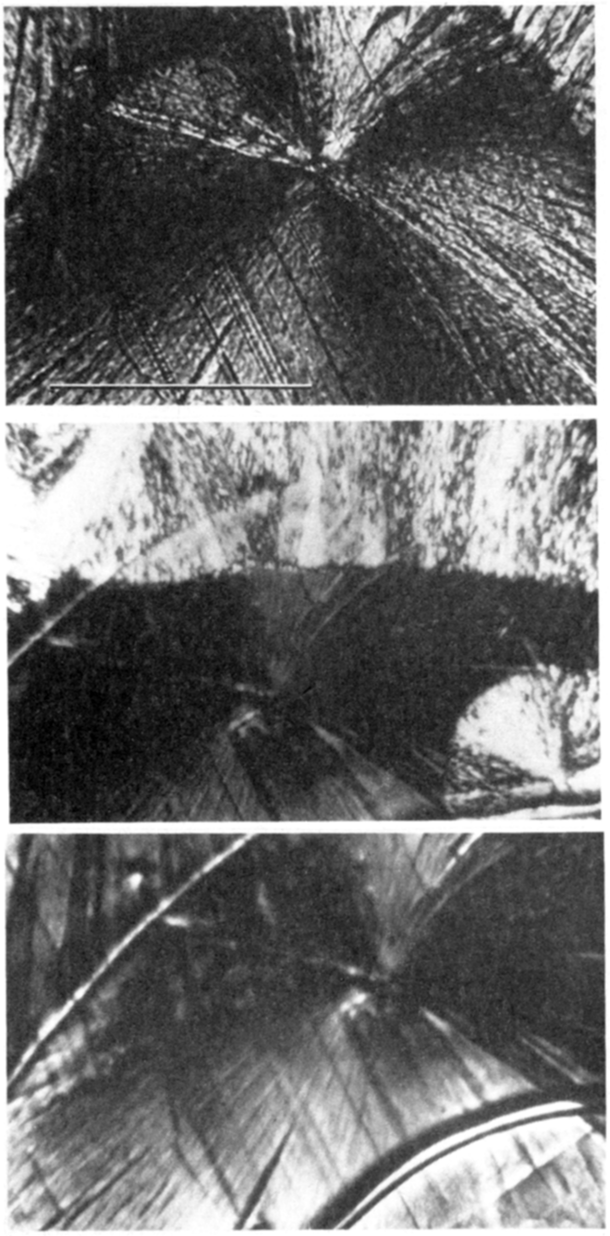


Figure 6. Optical micrographs of a 10/90 wt % PPV/PEO blend at various temperatures: (a, top) "as cast" at room temperature; (b, middle) held at 150 °C; (c, bottom) upon cooling to room temperature (showing crystallization front). Scale marker is 100 μm. Magnification is constant.

Spherulitic morphologies, similar to those already discussed, were also observed for PEO-rich blends cast from DMF and acetonitrile, as well as for blends prepared with high molecular weight PEO. However, unusual nonspherulitic textures could be prepared if films were cast by removing the solvent at a temperature above the PEO melting point. Thus, a series of films were cast from aqueous solutions at 90 °C to dryness and were cooled rapidly to room temperature. In this procedure PEO crystallization does not occur during the film casting process. Instead liquid–liquid phase separation occurs followed by vitrification of the amorphous PPV precursor phase. When the film is cooled, PEO crystallizes out of droplets of pure melt. The resulting morphology, shown in Figure 7, is a grainy microcrystalline structure with irregular domains on the order of several microns in size. The materials prepared in this way were tougher and stronger than films cast at room temperature (particularly for PEO-rich formulations) and showed differing doping characteristics to be discussed in section 6, below.

(5) Extraction. Experiments were performed to determine the extent to which the PEO component could be extracted from the blends by a good solvent. This study was stimulated by results on electrochemical doping, discussed in section 7 below, where the blend is exposed to electrolyte solution and introduction of dopant and extraction of PEO occur simultaneously. Chloroform was used because of its high volatility and strong solvating power for PEO. Figure 8 shows the extraction efficiency or amount of material extracted compared to the composition of PEO in the blend. (Previous work has shown that fully eliminated PPV is insoluble in all common solvents.[28])

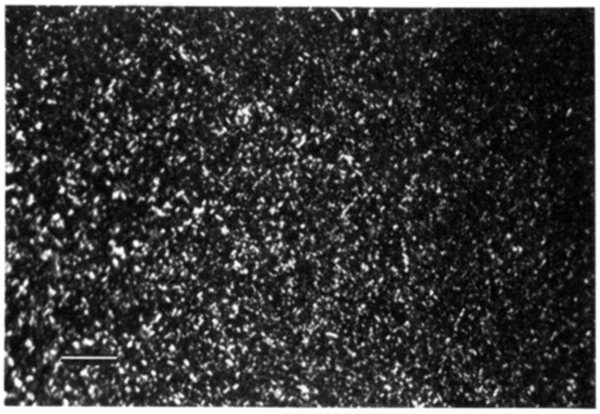


Figure 7. Optical micrograph of 30/70 wt % PPV/PEO blend cast under vacuum at 90 °C and quenched to room temperature showing grainy (non-spherulitic) morphology. Scale marker is 100 μm.

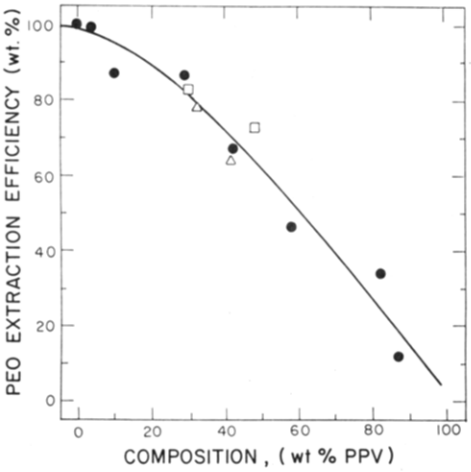


Figure 8. Weight fraction of PEO extractable with chloroform for PPV/PEO blends as a function of blend composition: (●) PEO, 2×10^5, cast at room temperature; (□) PEO, MW 4×10^6, cast at room temperature; (△) PEO, MW 2×10^5, cast at 90 °C.

It may be noted in Figure 8 that for PEO-rich (spherulitic) blends nearly all (80–90%) of the PEO is extractable. As the PPV content increases, progressively less of the PEO can be extracted, presumably because PEO becomes the dispersed (and thus less solvent accessible) phase. This effect has relevance for electrochemical doping because electroactivity is achieved as a result of infiltration of electrolyte into the material through interaction with the PEO phase. To obtain facile and complete charge storage, channels for such infiltration must be present throughout the material.

At extremely low PPV contents (2 and 4 wt % PPV), extraction resulted in complete disruption of the film, leaving micron size particles of PPV. However, a 10/90 wt % PPV/PEO blend could be fully extracted, leaving a continuous, although fragile, film, implying a continuous PPV phase at this loading. Optical microscopy revealed that extracted films retained their spherulitic texture, with the expected greatly weakened birefringence. Chemical and electrochemical doping of extracted films was performed and will be discussed in sections 6 and 7, respectively.

(6) Chemical Doping. Chemical doping of the blends, using AsF_5 vapor, resulted in highly conductive materials. Previous work has shown that blending PPV can in fact result in increased conductivity relative to the pure material.[7] This observation was confirmed in the present study. Conductivities of greater than 100 S/cm were obtained over a very wide compositional range. The rates of chemical doping were also greatly enhanced.

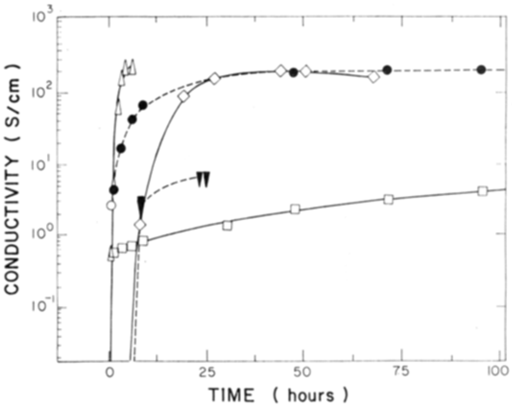


Figure 9. Electrical conductivity as a function of time of exposure of 65 Torr AsF_5 (dopant) to a variety of PPV/PEO blends: (□) pure PPV; (●) 90/10 wt % PPV/PEO; (◇) 42/58 wt % PPV/PEO; (▼) 10/90 wt % PPV/PEO; (△) 48/52 wt % PPV/PEO (cast at 90 °C).

Figure 9 shows the increase in conductivity as a function of time upon exposure to dopant vapor for samples of differing composition. Pure PPV shows a very rapid initial increase in conductivity, associated with surface doping, followed by a slow rate of further increase. Asymptotic values may take as long as 4–5 weeks to be attained under the conditions employed. This response is associated with the slow diffusion of dopant molecules through the PPV film. Slow dopant transport is commonly observed in conducting polymers possessing dense morphologies, such as "Durham" polyacetylene,[29] and is sufficient to completely prevent doping in highly ordered single crystals of poly(diacetylenes).[30]

In the present case, blending PPV with PEO in the manner described results in greatly enhanced doping rates. It may be noted, for example, in Figure 9 that a 40/60 wt % PPV/PEO blend, doped under the same conditions as pure PPV, attained a maximum conductivity in only 2 days of exposure and achieved an appreciably higher conductivity than the pure material. In fact, even blends containing modest amounts of PEO (e.g., 90/10 wt % PPV/PEO) exhibited complete doping within 2 days and achieved a final conductivity greater than 200 S/cm. These PPV-rich formulations may prove to be the most useful in applications because they retain the rapid doping and enhanced conductivity of the blends without compromising the mechanical strength and unique processing characteristics of pure PPV.[31]

PEO-rich formulations could also be doped to high conductivities. However, these materials exhibited a composition-dependent induction period before high conductivity was attained. For compositions containing ≤40 wt % PPV, this period lasted approximately 6 h. We attribute this effect to the presence of a PEO-rich surface, i.e., an electrically inactive skin, which coats the blend during the recrystallization of the PEO phase following the thermal conversion process. The direct observation of this phenomenon using hot-stage microscopy was discussed in section 4, above.

The doping rates were quite similar for blends using PEO of different molecular weights (2×10^5 and 4×10^6) or for blends cast from different solvents (H_2O, DMF, acetonitrile). Blend films which were cast at elevated temperatures exhibited the maximum doping rates. In Figure 9, a 48/52 wt % PPV/PEO cast from aqueous solution at 90 °C is shown to have reached a maximum conductivity of 250 S/cm within 5 h of doping. This

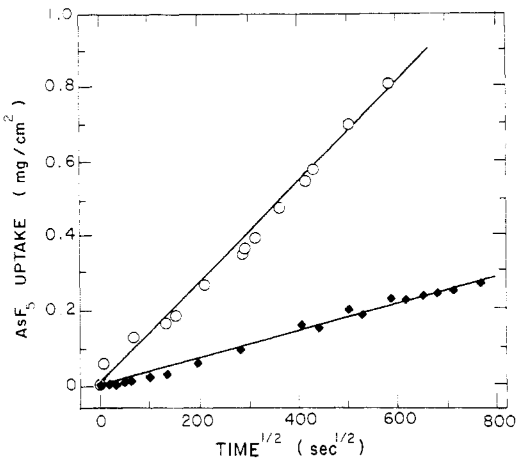


Figure 10. Weight uptake of dopant (AsF_5) normalized to sample surface area as a function of $(time)^{1/2}$ upon exposing PPV to dopant vapor: (◆) 65 Torr; (○) 300 Torr.

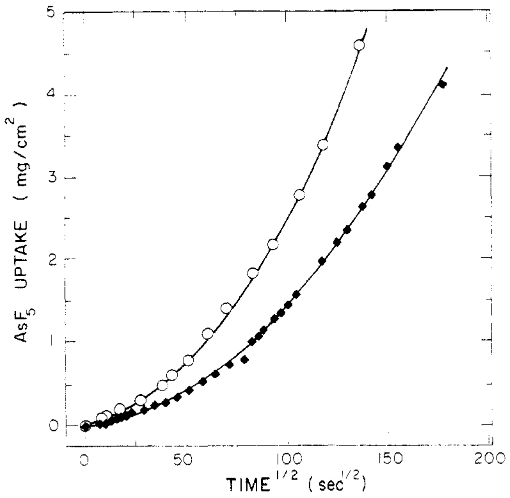


Figure 11. Weight uptake of dopant (AsF_5; 65 Torr) as a function of $(time)^{1/2}$ of exposure to dopant for (○) pure PEO and (◆) 50/50 wt % PPV/PEO.

represents a 2 orders of magnitude reduction in required doping time compared to pure PPV, demonstrating the important role that morphology can play in controlling dopant transport.

In Figures 10 and 11, a quantitative treatment of AsF_5 diffusion into PPV, PEO, and a 50/50 wt % PPV/PEO blend is presented. Dopant uptake of sample films was monitored as a function of time by using a quartz spring. Figure 10 shows the weight uptake of dopant, normalized to the film surface area, of unblended PPV doped with two vapor pressures of AsF_5. The data were analyzed according to a Fickian model of planar semiinfinite diffusion:

$$Q/A = 2D^{1/2}t^{1/2}C_o/\pi^{1/2}$$

where Q/A is the normalized weight uptake (mg/cm^2), D is the diffusion coefficient, and C_o is the surface concentration of dopant. C_o was obtained from the limiting concentration of dopant found after long doping times (1 AsF_5 per 4 PPV repeat units for the lower pressure and 1 AsF_5 per PPV repeat unit for the higher pressure[31]). Values of D calculated for the higher and lower pressures were 3×10^{-13} and 4×10^{-13} $cm^2\ s^{-1}$, respectively, which compare well with the diffusion coefficients obtained from doping of polyacetylene with AsF_5.[29,32] These values for the diffusion coefficients should be regarded as apparent coefficients for the pseudo-Fickian diffusion process, relevant only to the conditions used here, since the process involves simultaneous chemical reaction of AsF_5 with undoped PPV. However, it may be that the rate-limiting process is diffusion of AsF_5 through the layer of PPV already doped with AsF_5 (as suggested for polyacetylene doped with AsF_5[29]), a possibility supported by the finding that the measured diffusion coefficients have similar values for two different pressures of AsF_5.

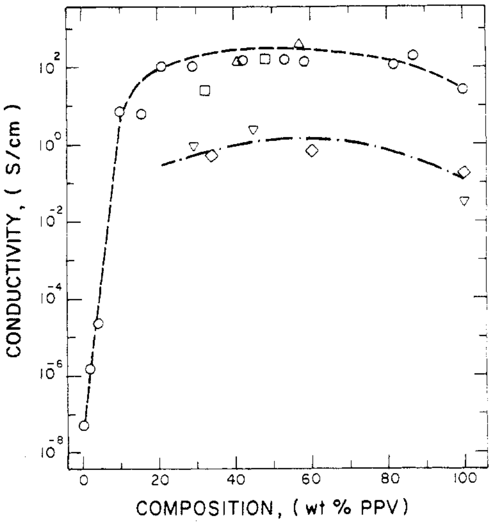


Figure 12. Final conductivity (after AsF_5 doping) as a function of composition for PPV/PEO blends prepared under various conditions: (□) cast from aqueous solution at room temperature; (○) cast from aqueous solution at 90 °C; (△) PEO, MW 4×10^6; (◇) cast from DMF solution; (▽) cast from acetonitrile.

The rate of dopant uptake is much faster for PPV/PEO blends and PEO, as shown in Figure 11. Doping kinetics are considerably more complicated for the PEO-containing systems, since PEO itself reacts extensively with AsF_5 and forms a viscous liquid product.

Of particular interest in the chemical doping study was the composition dependence of ultimate conductivity for this system. Shown in Figure 12 are the final values of conductivity achieved as a function of the blend composition. Most notably, there is a wide range of compositions over which conductivity is rather insensitive to composition. Between 25 and 90 wt % PPV content, the ultimate conductivities of the materials fall between 100 and 200 S/cm, whereas pure PPV reached only 25 S/cm under these conditions. Thus, a highly connected yet very dopant accessible morphology is postulated over this range of composition.

We attribute the unexpectedly high conductivity of the blends compared to the pure material to more complete doping of the PPV domains in the blends as a result of the accelerated dopant diffusion discussed earlier. Thus, blending results in greatly enhanced conductivity of the electroactive phase. A minimum conductivity for this phase can be estimated by normalizing the macroscopic conductivity of the sample by the volume fraction (we must substitute the weight fraction with PPV) of electroactive component. This assumption is equivalent to treating the two phases as parallel resistors and is admittedly inappropriate at low PPV loadings. However, in view of the highly connected morphologies discussed earlier, we will apply the formalism:

$$\sigma_{PPV} \geq \sigma_{Blend}/w_{PPV}$$

Thus, for the 21/79 wt % PPV/PEO formulation which attained a conductivity of 109 S/cm, the minimum local conductivity of the PPV phase is 520 S/cm. This result strongly implies improved doping of PPV domains in the blends.

Table II
Conductivity and Dopant Uptake of Chemically Doped PPV/PEO Blends

composition, wt/wt % PPV/PEO	ultimate conductivity, S/cm	dopant uptake, wt %
0/100	5.1×10^{-8}	644
2/98	1.5×10^{-6}	159
4/96	2.4×10^{-3}	78
10/90	6.94	
16/84	5.69	288
21/79	109	106
29/71	112	149
42/58	166	265
53/47	148	
58/42	136	299
82/18	131	105
87/13	210	36
100/0	25.9	11
41/59[a]	165	242
57/43[a]	464	208
42/58[b]	103	262
32/68[c]	28	122
48/52[c]	162	188
48/52[c]	250	
34/66[d]	0.554	146
60/40[d]	0.699	293
100/0[d]	0.175	48
29/71[e]	0.810	153
45/55[e]	2.19	287
100/0[e]	0.0324	18

[a] Blends were prepared with high molecular weight PEO (4×10^6). [b] Blend was extracted with chloroform before doping. [c] Blends were cast at 90 °C under vacuum. [d] Blends were prepared with ion-exchanged precursor and cast from DMF solutions. [e] Blends were prepared with ion-exchanged precursor and cast from acetonitrile solutions.

At very low contents of PPV, the behavior is also of some interest. High conductivities are reached at very modest levels of PPV. Of course, pure PEO does not become conductive even under prolonged exposure to dopant. However, upon adding 2 and 4 wt % PPV, significant increases in conductivity were observed (see Figure 12). At 10 wt % PPV, conductivity rose abruptly, reaching a value of 6 S/cm. Thus, percolation of the conducting phase is observed between 4 and 10 wt % PPV. This observation is consistent with the extraction and microscopy results, which indicated the onset of a continuous PPV phase at or below 10 wt %. The well-connected nature of the electroactive phase in the 10/90 wt % PPV/PEO blend is verified by the current carrying capacity. The chemically doped 10/90 wt % PPV/PEO blend was able to sustain a dc current density of 80 A/cm^2 before ohmic heating caused appreciable degradation of the doped blend, whereas very heavily doped pure PPV can sustain a maximum current density of 1400 A/cm^2.[33] Normalizing to composition, this result indicates that at 10% loading the current-carrying capacity of the blend is already 60% of its maximum value, which would be observed if the two phases were connected in parallel.

Blends containing high molecular weight PEO, also shown in Figure 12, attained conductivities which were comparable to their lower molecular weight counterparts. This was expected since the blend morphology did not change with the inclusion of higher molecular weight PEO. Also, extraction with chloroform (to remove PEO) did not seriously affect the attainable conductivity of a 50/50 wt % blend (see Table II). However somewhat different behavior was observed for blends cast at elevated temperatures. Under these conditions, the 50/50 wt % blend attained a conductivity of about 200 S/cm after doping, which was very close to that of the room-temperature cast blend of the same composition. However, the 30/70 wt % PPV/PEO blend cast at high temperature attained a conductivity of only 28 S/cm, considerably less than the corresponding blend cast at room temperature which reached more than 100 S/cm. Thus, the high-temperature cast blends exhibit conductivities that are composition sensitive in this regime, which reflects the more random morphology observed for these materials.

The behavior of PPV/PEO blends which were cast from DMF and acetonitrile warrants some discussion. The goal of these experiments was to determine the effect of the casting solvent on the properties of the blends because many previous studies have shown significant solvent dependence of morphology for a number of solvent cast blend systems.[34,35] In the present case, in order to obtain an additional common solvent for the PPV precursor and PEO, an ion-exchange step had to be performed on the PPV precursor (PXD) to replace the chlorine anion in the polyelectrolyte with a tetrafluoroborate ion. The ion-exchanged precursor, $PXD^+BF_4^-$, whose preparation is described in the Experimental Section, exhibits excellent solubility in DMF and acetonitrile, which are also both good solvents for PEO.

Surprisingly, pure PPV, prepared by casting the modified precursor from either DMF or acetonitrile solutions followed by thermal conversion and doping under standard conditions, resulted in materials with much lower conductivities than that of PPV prepared from the aqueous precursor. Doped PPV derived from the aqueous precursor, PXD^+Cl^-, rose to a conductivity of 25 S/cm in this study as stated earlier; however, PPV prepared from the organic precursor solution, $PXD^+BF_4^-$, only reached conductivities in the vicinity of 0.1 S/cm, a very substantial decrease. We attribute this difference to a cleaner and more complete elimination reaction for the chloride precursor relative to the tetrafluoroborate precursor, resulting in a more highly conjugated product for the former. Both products exhibit the characteristic IR absorbances of PPV with no obvious absorbances due to impurities. However, the PPV arising from the chloride precursor exhibits the expected elemental analysis results (see Table I) for pure PPV, with very little residual chlorine (<0.5 wt %). PPV obtained from the tetrafluoroborate precursor retained as much as 5 wt % residual fluorine after thermal treatment, indicating incomplete conversion. The attainable conductivity of PPV has been shown to depend significantly on the nature of the sulfide moiety in the precursor polymer;[10] however, the effect was not quite as large as that observed in this case for a change in the anion.

In spite of the lower conductivity found for the organic precursor system, blends with PEO were prepared. These blends showed the same synergistic behavior as those prepared from the aqueous system. That is, the PPV/PEO blends had conductivities which were about an order of magnitude larger than the corresponding unblended PPV, as shown in Figure 12. Thus, PPV/PEO blends cast from DMF or acetonitrile solutions exhibited conductivities after AsF_5 doping in the vicinity of 1 S/cm. Blends cast from DMF and acetonitrile did not differ appreciably from each other. Both exhibited thermal behavior and spherulitic morphologies similar to those described for the aqueous systems. Thus, although casting solvent and precursor counterion affected the properties of the electroactive phase, they did not greatly affect the overall blending behavior with PEO.

The weight uptake of dopant (together with the ultimate conductivities) for each of the blends is listed in Table II. As these data show, all the blends absorbed a considerable

Table III

composition, wt/wt% PPV/PEO	charging rate after 5 min, mA/g PPV	ultimate conductivity, S/cm	conductivity ratio, $\sigma_{\text{inner}}/\sigma_{\text{outer}}$
92/8	7	0.2	0.5
85/15	6	6.7	0.5
73/27	16	3.0	1.4
67/33	95	33	1.3
59/41	80	55	1.2
48/52	150	34	1.3
46/54	145	20	1.1
30/70	315	6.1	1.3
25/75[a]	315	5	

[a] Doped films with <20 wt % PPV were too fragile to handle.

quantity of dopant. Typical samples absorbed greater than 200% of their original weight when doped to a maximum conductivity. By comparison, pure PPV absorbed only 11 wt % dopant under the same conditions. As is known, AsF_5 is a strong oxidizing agent of rather low selectivity.[36] Thus, it reacts with both the PPV phase, forming a conducting complex, and with the PEO phase, resulting in a nonconducting adduct. From inspection of Table II, it is evident that PEO-rich blends tended to absorb more dopant than PPV-rich compositions. In fact, we attribute the strong affinity of the dopant for PEO to the rapid absorption of dopant molecules by the blends giving rise to more complete doping of the PPV domains and unexpectedly high conductivities for these materials.

None of the blends in this study showed improvements in atmospheric stability compared to pure doped PPV. It is, of course, conceivable that the PEO degradation products adversely affected long-term environmental stability. For typical doped samples of various compositions, conductivity decreased by over an order of magnitude within 1 h of exposure and by 4 orders of magnitude within 1 day of exposure. It is likely, however, that blending with hydrophobic polymers would lead to improved stability, as has been suggested by Galvin and Wnek.[2] Such work is currently under way.

(7) Electrochemical Doping. Electrochemical doping has proved to be a valuable method for the accurate and homogeneous doping of conducting polymers.[37] A requirement for electrochemical doping is the diffusion of "dopant" ions, supplied by the electrolyte, into the doped material to preserve charge neutrality. Such ionic transport processes generally prove to be the rate-determining step in the electrochemical doping of conducting polymers. It has been demonstrated that the slow ionic transport of nascent PPV can be greatly accelerated by blending the precursor with a nonelectroactive polymer such as PEO.[7] In the present work, the rate of electrochemical doping of PPV/PEO blends was studied as a function of blend composition in order to define the optimum composition range for applications of PPV that require electrochemical activity, such as rechargeable battery electrodes.[38,39]

A series of blends was thus prepared over the range 100/0 to 20/80 wt % PPV/PEO. Films 50 μm thick were cast and subjected to the elimination reaction. Two similar samples of each composition were then cut and sandwiched together in the doping cell. A doping potential of +4.1 versus Li^+ was applied for 410 min, and charge was recorded as a function of time. At the end of the doping period, samples were removed and peeled apart, and their four-probe conductivities measured. The purpose of using this novel sandwich configuration was to arrive at an estimate of the homogeneity of the doping process. Thus, in Table III, the ratio of the conductivity of the film closest to the electrode (σ_{inner}) to that of the film facing the electrolyte (σ_{outer}) is given, together with the final conductivity of the film that had the highest conductivity. Doping appears to be relatively homogeneous, with the trend toward slightly higher conductivities for regions of the sample that are closer to the platinum electrode. It should be noted that the maximum conductivity value in Table III at around 60 wt % PPV probably represents a compromise between faster doping due to higher PEO content and greater ultimate conductivity due to higher PPV content. In other words, the compositions containing more than 60% PPV have probably not reached their limiting value in the time allowed for doping.

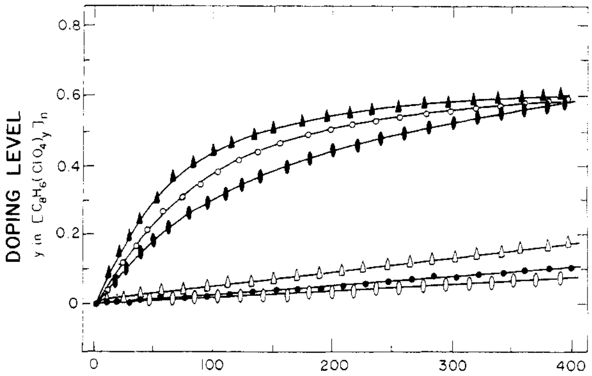


Figure 13. Doping level (measured coulometrically) as a function of time at constant potential (+4.1 V versus Li) during electrochemical doping of PPV/PEO blends of various compositions: (▲) 25/75 wt % PPV/PEO; (○) 46/54 wt % PPV/PEO; (⬮) 59/41 wt % PPV/PEO; (△) 73/27 wt % PPV/PEO; (●) 85/15 wt % PPV/PEO; (0) 90/10 wt % PPV/PEO.

Also listed in Table III is the current density for each sample after 5 min of charging. It is evident that a PEO content above 30 wt % allows PPV to be charged considerably faster. For example, upon changing the composition from 70/30 wt % PPV/PEO to 30/70 wt % PPV/PEO the initial rate of doping increases by a factor of 20. Figure 13, in which the doping level, determined coulometrically, is plotted as a function of doping time, also demonstrates the enhancement of doping rates on increasing the PEO content. It may be noted in Figure 13 that the marked transition from complete to incomplete doping during the time allowed occurs at a composition of about 60 wt % PPV, which coincides with the transition from spherulitic to non-spherulitic morphology. Thus, incomplete doping for samples of lower PEO concentration is attributed to the dispersed nature of PEO domains in this regime.

The blends richer in PEO have all reached the same doping level at the end of the doping period (0.6 electronic charge per PPV repeat unit). It should be noted that the current passed during oxidation includes a background component due to oxidation of electrolyte. Previous studies have shown charging in this electrolyte at +4.1 V to be 73% efficient;[7] i.e., 27% of the charge passed is consumed in the oxidation of electrolyte. Thus, the final doping level is probably closer to 0.4 than 0.6. We have shown previously[7] that, in propylene carbonate electrolytes, the PEO promotes dopant ion transport by acting as a solvent-extractable phase rather than as a solid electrolyte. We ascribe the marked increase in dopant ion transport, as indicated by higher charging rates and higher doping levels, to the formation of a continuous PEO phase above 40 wt % PEO, as observed in the morphological studies, which is then extracted on exposure to electrolyte. Extraction and swelling of PEO by electrolyte does not lead to a collapse of the remaining interconnected PPV network since upon doping films increased in volume by 5–20%

over the whole composition range studied.

Conclusions

Polymer blends made up of electroactive PPV and electroinactive PEO can be prepared by casting from common solvents for PEO and the PPV poly(sulfonium salt) precursor. The phase-separated morphology of the blends may consist of large spherulitic structures, micron-size disordered phases, or submicron dispersed phases, depending on the blend composition and casting conditions.

In light of the results obtained in this investigation, we can divide the morphological and electrical behavior of the PPV/PEO system into three distinct composition regimes. At extremely low PPV content (less than 10 wt %), a spherulitic morphology is formed which resembles pure PEO; the PPV constituent in this regime does not form a continuous phase; and although it may be effectively doped, the macroscopic conductivity remains insulating or at best lightly semiconducting (up to 10^{-3} S/cm). The second regime extends from 10 to 60 wt % PPV and is characterized by a spherulitic morphology in which the PPV domains are excluded into interfibrillar regions forming a highly connected network. Materials in this range can be doped very quickly to high conductivity (>100 S/cm). The third regime consists of materials containing greater than 60 wt % PPV. Materials in this region are flexible and tough, containing highly dispersed PEO domains in a PPV matrix. In this region, the PEO constituent is still effective in accelerating chemical doping; however it is less effective in accelerating electrochemical doping. Electrical conductivities in this regime reach a maximum (>200 S/cm).

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Registry No. PPV, 96638-49-2; PEO, 25322-68-3; AsF_5, 7784-36-3.

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