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Electrical conductivity of polyblends of poly(1,4-phenylene vinylene) and poly(2,5-dimethoxy-1,4-phenylene vinylene)

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SUMMARY

A series of polyblends of poly(1,4-phenylene vinylene), PPV, and poly(2,5-dimethoxy-1,4-phenylene vinylene), PDMPV, were prepared in film form from precursor polyblends of the respective sulfonium salt polymers, which were separately prepared from the respective bis(sulfonium salt) monomers. The blend films were doped with I_2 at room temperature to obtain a wide range of electrical conductivities (10^{-2} to 10^{2} Scm^{-1}) depending on the blend composition. The higher the content of PDMPV in the blends the higher was the conductivity.

INTRODUCTION

Poly(1,4-phenylene vinylene), PPV, poly(2,5-dimethoxy-1,4-phenylene vinylene), PDMPV, and their copolymers P(DMPV-PV), can be prepared in high molecular weight by a two-step route (1)-(3). In the first step, a water-soluble polyelectrolyte precursor polymer is prepared in aqueous solution from which films can be cast. In the second step, the precursor polymer film is heated at an elevated temperature in vacuum to convert it into the final conjugated polymer.

The PPV films obtained in that manner can be easily "doped" with strong oxidizing agents such as AsF_5 to produce highly conducting materials, but they cannot be effectively doped with I_2. Films of PDMPV and of poly(thienylene vinylene), PVT, and their copolymers (4)-(5), however, can be readily doped with I_2 resulting in conductivities above 10^{2} Scm^{-1}. The high conductivities observed for PDMPV and P(DMPV-PV) copolymers can be attributed to the electron-donating capacity of the methoxy groups on the phenylene group which lowers the oxidation potential of the conjugated polymers with respect to that of PPV (4). Moreover, the conductivity of the I_2-doped films along the polymer chain direction can be greatly enhanced if the precursor films are uniaxially drawn during the second stage, thermal elimination reaction.

Incorporation of readily oxidizable, heterocyclic structures such as the 2,5-thienylene group in place of some of the 1,4-phenylene group in PPV, also greatly increases the electrical conductivities of their films, presumably again by lowering the oxidation potential and improving dopability with I_2 (5). For example, poly(1,4-phenylene vinylene-co-2,5-thienylene vinylene) containing 42 mole % thienylene vinylene units exhibited a conductivity of 20 Scm^{-1} for an oriented film with a draw ratio of 5 on doping with I_2.

It was also reported recently by us that an I_2-doped polyblend film of PPV and PTV displayed remarkably high electroconductivities (6). For instance, a PPV/PTV blend containing only 20 mole % of PTV exhibited a

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conductivity of 0.5 Scm^{-1}, and when the film obtained from the same blend was oriented to a draw ratio of 4, its conductivity was increased to 8 Scm^{-1}.

In this investigation, we prepared a series of blends consisting of PPV and PDMPV. The electrical conductivities of films of these blends were studied after doping with I_2. The two sulfonium salt precursor homopolymers for each were prepared separately and blended in aqueous solution in varying molar ratios and cast into films. The final conjugated polymer, polyblend films were obtained by subjecting the precursor films to thermal elimination at 215°C. Electrical conductivities were measured at room temperature using the four-probe method after doping with I_2.

EXPERIMENTAL

1,4-Bis(chloromethyl)benzene and 1,4-dimethoxybenzene were purchased from Aldrich Chemical and were used as received. 1,4-Bis(chloromethyl)-2,5-dimethoxybenzene was prepared from 1,4-dimethoxybenzene by chloromethylation following a literature method (7).

The bis(sulfonium salt) monomers were synthesized by reacting either 1,4-bis(chloromethyl)benzene or 1,4-bis(chloromethyl)-2,5-dimethoxybenzene with excess tetrahydrothiophene (Aldrich) at 50°C in methanol for 5 hours (2).

The two sulfonium salt monomers, I and II, thus prepared from 1,4-bis(chloromethyl)benzene and 1,4-bis(chloromethyl)-2,5-dimethoxybenzene, respectively, were separately homopolymerized in aqueous NaOH solution under an N_2 atmosphere at 0°C for 1 hour. The polymerization reactions were quenched by neutralization with 1.0 M aq. HCl, and the neutralized solutions were then dialyzed against deionized water for 3 days using a Macro HF dialysis set (Spectrum Co. MW cut-off, 6,000 daltons) (2).

Mixtures of solutions of the two dialyzed sulfonium salt precursor polymers, III and IV, in varying ratios were cast into films at room temperature under a reduced pressure. Some of the films were uniaxially drawn at 110-150°C during the elimination reactions using a zone heating apparatus as described earlier (2). All of the polymer blend films were transformed into the final conjugated polymer blend films by thermolysis under vacuum at 215°C for 21 hours.

The polyblend films (2.0x20 mm) so obtained were mounted onto four platinum electrodes with Electrotag. Doping with I_2 was carried out at room temperature at 10^{-4} Torr pressure until a steady, minimum electrical resistance was obtained. Conductivities were measured by the four-probe method using an Autoranging Microvolt DMM digital multimeter.

Differential scanning calorimetry, DSC (du Pont 910 or Perkin Elmer DSC-II) and thermogravimetry, TGA (Rigaku 8150 or Perkin Elmer TGA-2) of the precursor blends were conducted at a heating rate of 10°C/min under an N_2 atmosphere.

RESULTS AND DISCUSSION

In this investigation the two sulfonium salt precursor polymers, III and IV, were separately prepared from their bis-sulfonium salt monomers, I and II, and mixed in varying ratios in aqueous solution (8). The mixed solutions were cast into films, which were then heated for conversion into the final polyblend films (2), as shown at the top of the following page. All of the polyblend films studied, as listed in Table 1, which were obtained from the precursor polymers, were clear and appeared homogeneous in composition.

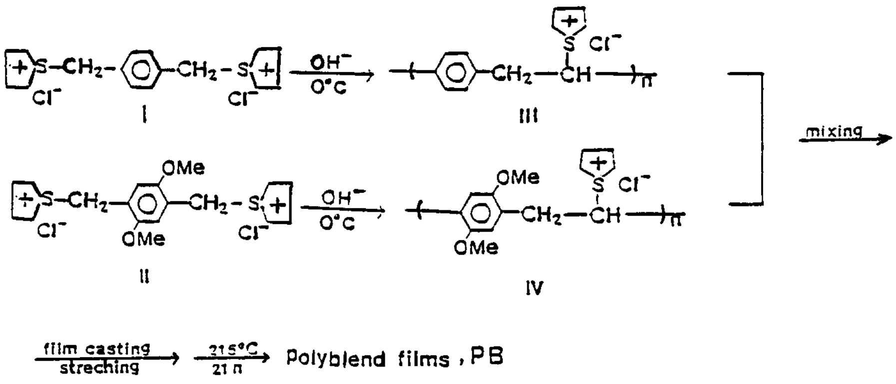

Table 1. Conductivities of blend films of PPV, III, and PDMPV, IV, doped with I_2.

Blend Film[a]	Blend Molar Ratio, III:IV	Draw Ratio,[b] L/L_0	Film Color	Maximum Conductivity, Scm^{-1} [c,d]
PB-100	0:100	1	dark red	51
PB-80	20:80	1	red	35
		1.5		91
PB-50	50:50	1	reddish	16
		1.5	brown	24
PB-20	80:20	1	brown	12
		2.0		21
PB-14	85:14	1	brown	5.2
PB-9.1	89.9:9.1	1	brownish	3.0
		4.0	yellow	8.0
PB-4.8	95.2:4.8	1	yellow	0.02

a. Numbers designate the molar contents of PDMPV in the blends.

b. L_0 and L are the lengths of the film before and after orientation.

c. Maximum conductivity achieved after repeating doping with I_2.

d. The equivalent conductivities of undrawn films of P(PV-DMPV) copolymers were 28, 18 and 27 Scm^{-1} for III:IV ratios of 47:53, 81:19, and 87:13, respectively; orientation by drawing during elimination increased these values to 304, 298, and 428 Scm^{-1}, respectively (4).

Figure 1 contains both DSC and TGA thermograms for the polyblend films of the two precursor polymers, PB-14 of Table 1. The DSC thermogram of this film, shown in Figure 1a, contained a strong endothermic peak at 105°C and a broad, weaker second endotherm at 120-240°C. The first peak corresponds to the loss of water present in the cast film, and the second to the thermolysis of the precursor polymers with the loss of hydrogen chloride and tetrahydrothiophene. According to the TGA thermogram of the same blend, which is shown in Figure 1b, an initial fast weight loss began at about 93°C, followed by a gradual weight loss from about 115°C to 250°C, with the total weight loss of about 35%. Polymer chain degradation apparently begins near 400°C. The DSC and TGA results agree closely.

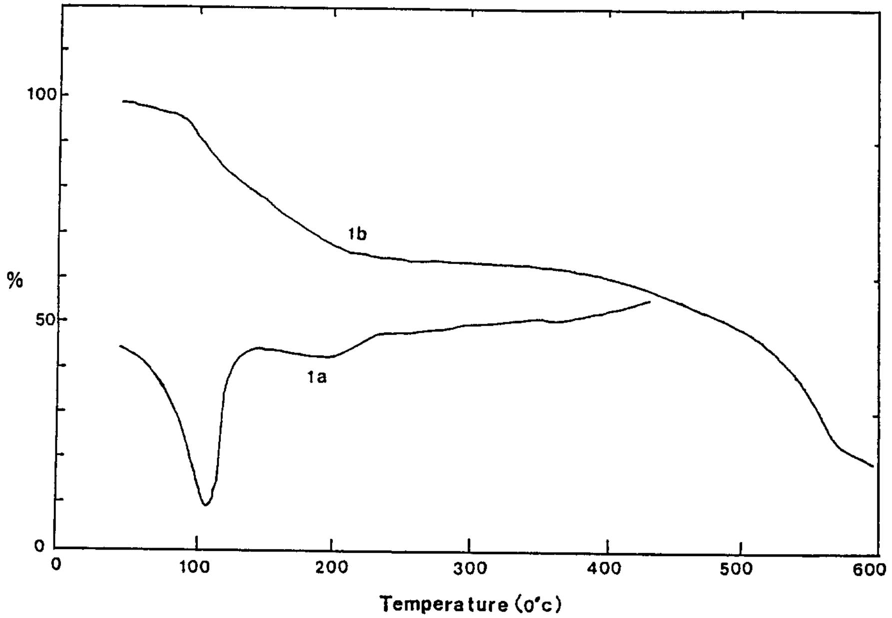

Figure 1 (a) DSC and (b) TGA thermograms of a film of PB-14 of Table 1 before elimination at a heating rate of 10°C/min under an N_2 atmosphere.

Considering the fact that the precursor polyblend film contained a significant amount of water (about 15% according to Figure 1b), the weight loss of about 35% observed at 250°C is much lower than the theoretically expected value of 52.8%. This result most likely can be attributed to premature elimination reactions which occurred during film casting. This suggestion is supported by the observation that the as-cast blend films were yellow to reddish yellow in color with increasing PDMPV content. Furthermore, their IR spectra contained a sharp absorption at 960 cm^{-1}, which corresponds to the presence of a trans vinylene C-H out-of-plane vibration mode.

Table 1 lists the blend ratios of the two homopolymers and the maximum conductivities of their I_2-doped films, as well as the dependence of conductivity after orientation of the polymer films by uniaxial drawing. For comparison, data for the two homopolymers, and for copolymers whose overall compositions are comparable to the blends (4), are included in the table.

The polyblend films showed reduced electrical conductivities as the content of PDMPV decreased. For example, the electrical conductivities of PB-50, containing 50 mole % of PDMPV, and PB-14, containing 14 mole % of PDMPV, were 16 and 5.2 Scm^{-1}, respectively, when the films were doped with I_2 in an undrawn state. It is rather remarkable that the undrawn, I_2-doped film containing only 9.1% of PDMPV, PB-9.1, had a conductivity as high as 3.0 Scm^{-1}, which is at least 5 orders of magnitude greater than the conductivity of I_2-doped PPV. A similar trend was previously reported by us for the conductivities of I_2-doped, polyblend films of PPV and PTV (6). These observations suggest that interchain conductivity is as important as intrachain conductivity for polyblends consisting of two different polymers having vastly different conductivities.

Although both the precursor polymer blend films and the final conjugated polymer blend films appeared very uniform and homogeneous, their homogeneity at the molecular level should be determined. All of the final blend films were transparent, which can be taken as an indication of compatibility, but no detailed study was made of this property. The oriented films displayed considerably higher conductivities along the draw direction than did the unoriented films, as shown in Table 1, as is generally observed with other systems (2),(3),(5),(6), but a comparison of the conductivities of the polyblend films with those of related copolymers reveals that the former were, in general, lower than the latter. The difference becomes larger as the PDMPV content in the blend becomes very low. This result suggests that intrachain conduction is more efficient than interchain conduction in the blends, as would be expected, but it was found that compositions having a wide range of conductivity can be prepared by blending a highly conductive polymer with a polymer of very low conductivity for a given dopant.

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