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Synthesis and Electrical Properties of Poly(2-bromo-5-methoxy-1,4-phenylenevinylene) and Copolymers

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ABSTRACT: Poly(2-bromo-5-methoxy-1,4-phenylenevinylene) (PBrMPV) and a series of PPV copolymers containing 2-bromo-5-methoxy-1,4-phenylenevinylene (BrMPV) units were prepared via the water-soluble precursor method. They were obtained in film form and were readily doped with I_2. Doping of undrawn and drawn films of PBrMPV homopolymer with I_2 vapor led to conductivities of 10^{-5}–10^{-3} S cm^{-1}. Conductivities of I_2-doped copolymer films ranged from 10^{-3} to 10^{-1} S cm^{-1}, depending on composition. Films of undrawn copolymers showed a very insensitive composition dependence of electrical conductivity ranging from 1.5×10^{-3} to 8.2×10^{-3} S cm^{-1}. The copolymer containing a very low level (~1 mol %) of BrMPV unit revealed the highest conductivity among the copolymer compositions. The UV–vis spectral characteristics of the copolymers were slightly different from those of the PPV homopolymer, and λ_{max} values were red-shifted to about 435–440 nm, depending on composition.

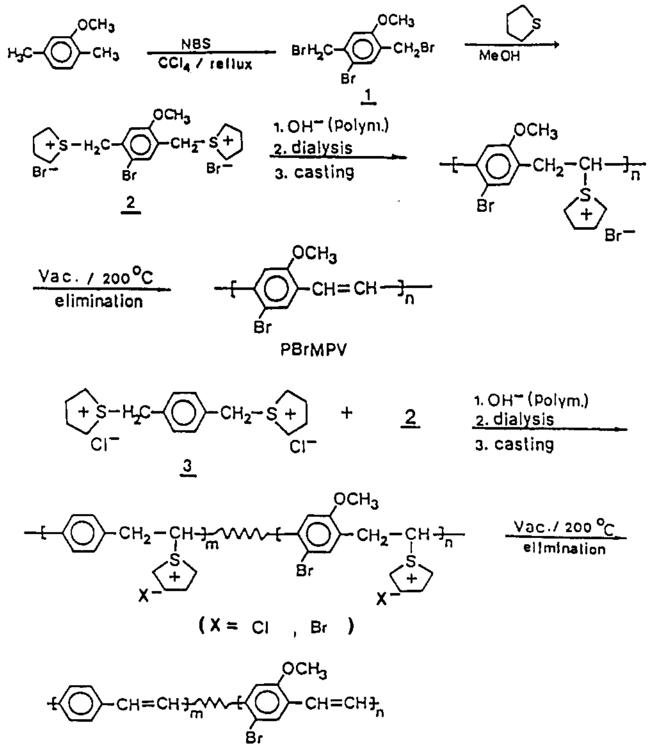
Introduction

The synthesis of high molecular weight poly(1,4-phenylenevinylene) (PPV) and its derivatives and copolymers through the water-soluble precursor route[1–6] is one of the most attractive methods to obtain polymers with extended π-conjugated structures. PPV derivatives are important conductive materials after doping with various dopants, and they also possess good nonlinear optical properties.[7–9] Substitution on the phenylene ring of PPV with different types of electron-donating or electron-withdrawing groups has a significant influence on the electronic structure of the resulting polymer and thus affects the electrochemical properties thereof.

The PPV films can be easily doped with strong oxidizing agents such as AsF_5 to produce highly conductive materials,[10,11] but they cannot be doped with weak oxidants like I_2. Also, the precursor films can easily be stretched before or during the thermal elimination to the final polyconjugated compositions. Such highly stretched films show a significantly enhanced conductivity on doping along the draw direction.[1,2] In contrast, poly(2,5-dimethoxy-1,4-phenylenevinylene)[12,13] (PDMPV) and poly(2-*n*-butoxy-5-methoxy-1,4-phenylenevinylene)[14] (PBMPV) can be doped with weak oxidizing dopants such as I_2 and $FeCl_3$ to give electrical conductivities of 10^2–10^3 S cm^{-1}. These high conductivities can be attributed to the electron-donating capacity of the alkoxy groups on the phenylene ring. The presence of strong electron donors leads to a reduction in the band gap and ionization potential of the polymers, to facilitate oxidation with weak oxidants such as iodine.[15–17]

Recently, we prepared poly(1,4-phenylenevinylene-*co*-2-nitro-1,4-phenylenevinylene)[18] (poly(PV-*co*-NPV)) via water-soluble precursor polymers using varying mole ratios of the two respective sulfonium salt monomers. Unexpectedly, the copolymer films could be readily doped with I_2, contrary to the fact that, as mentioned above, PPV films are hardly doped with the same dopant. The copolymer film containing 2 mol % of the NO_2–PV unit, when doped with I_2, showed a maximum conductivity of 3.4×10^{-2} S cm^{-1}. On the other hand, as the content of the NO_2–PV unit in the copolymer increased further, the electrical conductivity steadily decreased. It was originally expected that the presence of the electron-withdrawing property of the nitro group would raise the oxidation potential of the polymer chain, resulting in reduced dopability. The unexpected result obtained appears to be due to the interplay between the morphological changes and the electronic effects caused by the presence of NO_2 substituents on the phenylene ring.

In this investigation, we prepared poly(2-bromo-5-methoxy-1,4-phenylenevinylene) (PBrMPV) and its PPV copolymers by the water-soluble precursor method. These polyconjugated polymers contain an electron-donating methoxy group(OCH_3) together with an electron-attracting bromine atom (Br) on each phenylene ring. It was our purpose to learn more about the effect of substituents on the electrical properties of PPV derivatives and their copolymers. The synthetic route and the structures of PBrMPV and the copolymers prepared and characterized in this study are shown below:



The properties of the polymers were studied by spectroscopy and also by electrical conductivity measurements before and after doping with I$_2$.

Experimental Section

Monomer Synthesis. 4-Bromo-2,5-bis(bromomethyl)anisole (1) was prepared by reacting 2,5-dimethylanisole with *N*-bromosuccinimide (NBS) in CCl$_4$. NBS (26.8 g, 0.15 mol) and 1.0 g of benzoyl peroxide were dissolved in 150 mL of CCl$_4$. This suspension solution was mixed with 2,5-dimethylanisole (5.0 g, 0.037 mol). The mixture was stirred with a mechanical stirrer for 7 h at 70 °C. The solution was poured into petroleum ether, and the precipitate was filtered. Pure 4-bromo-2,5-bis(bromomethyl)anisole was obtained by recrystallizing the crude product from ethanol. The yield was 8.6 g (62%): mp 115–116 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.3 (s, 1 H), 6.9 (s, 1 H), 4.5 (s, 2 H), 4.4 (s, 2 H), 3.9 (s, 3 H) (see Figure 1a).

Compound 1 (12.0 g, 0.032 mol) and tetrahydrothiophene (8.30 g, 0.094 mol) were reacted for 21 h at 55 °C in 100 mL of methanol.[19] The product **2**, 2-bromo-5-methoxy-1,4-phenylenedimethylenebis(tetrahydrothiophenium bromide), was obtained by concentration of the reaction solution, precipitation in cold acetone, filtration, and vacuum drying. The product yield was 69%, and the product was very hygroscopic. ^{1}H NMR (D$_2$O) δ 7.9 (s, 1 H), 7.3 (s, 1 H), 4.8 (s, 2 H; buried in the water peak), 4.6 (s, 2 H), 4.0 (s, 3 H) 3.4–3.8 (m, 8 H), 2.2–2.6 (m, 8 H) (Figure 1b).

Compound **3** was prepared similarly from 1,4-bis(chloromethyl)benzene and tetrahydrothiophene following the literature method.[11,19,20]

Polymerization. Synthetic methods for the homopolymer and copolymers were the same as reported by us[3,14] and others.[1,6,19] The monomer sulfonium salt solution (0.4 M) was polymerized in an NaOH solution (1 M) under a nitrogen atmosphere at 0 °C. A homogeneous viscous solution was obtained. For the copolymers, the total moles of the two monomers, **2** and **3**, were kept constant (0.4 M), but their mole ratio was varied. The reaction was quenched by neutralization with 1.0 N aqueous HCl, and the neutralized polyelectrolyte precursor solutions were dialyzed against deionized water for 3 days using a dialysis tube (Sigma) with a molecular weight cutoff at 12 000. The films cast from these aqueous precursor polymer solutions were subjected to thermal elimination in vacuo (10^{-2} Torr) at 200 °C for 8 h to transform them into the final polyconjugated polymer films (thickness 10–20 μm). If desired, the precursor polymer films were uniaxially drawn in the temperature range 110–120 °C using a zone-heating apparatus.

Characterization. Melting points were determined with a Fisher-Johns melting point apparatus. Elemental analyses were performed by the Microanalytical Laboratory of the University of Massachusetts. ^{1}H NMR spectra were recorded on a Bruker AM 300 spectrometer. IR spectra were obtained on a Mattson Alpha Centauri FT-IR, and the UV–vis spectra of the polymer films were recorded on a Hewlett-Packard 8452A spectrometer. Thermogravimetry (TGA) was performed on a Mettler 3000 thermal analyzer, and differential scanning calorimetric (DSC) thermograms were recorded on a DuPont DSC 910 instrument. Scanning electron microscopy (SEM) was performed on a JEOL JSM-T330A microscope. Electrical conductivities were measured by the four-in-line probe method by evacuating the doping chamber to a pressure of 10^{-3} Torr and then opening the system to the I$_2$ source at room temperature. Carbon paste was used for sample–electrode contact.

Results and Discussion

Recently, Karasz and co-workers[21] prepared 2,5-bis(bromomethyl)anisole by reacting 2,5-dimethylanisole with NBS. In the present investigation, we employed a large excess of NBS to obtain compound 1, which is nothing but a brominated product of 2,5-bis(bromomethyl)anisole. Excess NBS certainly supplies enough Br$_2$ in the reaction mixture to bring about bromination of the benzene ring in addition to the normal benzylic bromination. The ^{1}H NMR spectrum shown in Figure 1 agrees with the anticipated spectrum of compound 1.

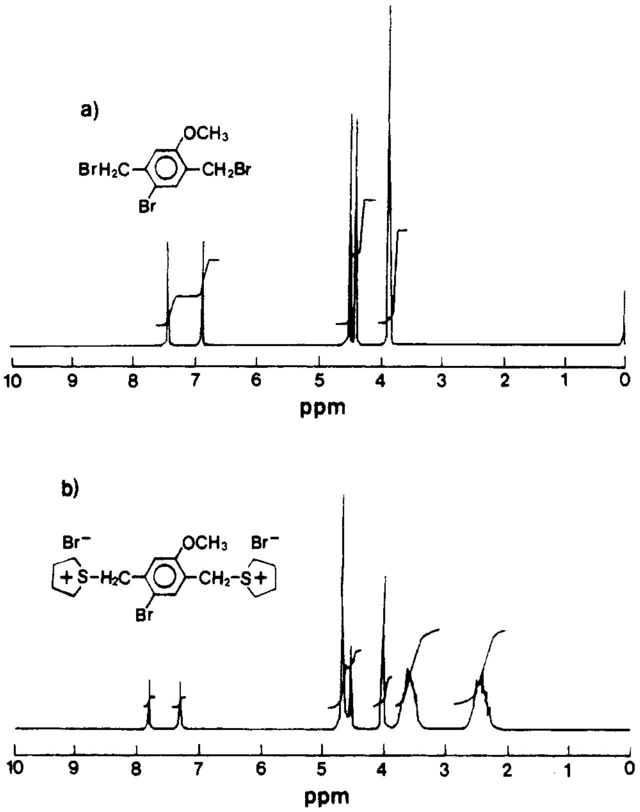


Figure 1. NMR spectrum of (a) 4-bromo-2,5-bis(bromomethyl)anisole and (b) 2-bromo-5-methoxy-1,4-phenylenedimethylenebis(tetrahydrothiophenium bromide).

Table I
Monomer Conversions and Polymer Yields

polymn system	feed molar ratio 3:2	monomer conv, %	polymer yield,[a] wt %
PBrMPV	100:0	73	20
poly(PV-*co*-BrMPV)	80:20	71	25
	67:33	71	22
	50:50	70	19
	33:67	72	19
	20:80	75	17

[a] The values were estimated from the weight of polyconjugated polymers obtained after the final thermal elimination.

Table I summarizes the data for monomer conversions to precursor polymers and polymer yields. Data for conversions were obtained by titration of the precursor polymer solution with 1.0 N HCl. Polymer yields were estimated gravimetrically from the weight of cast films. The degrees of monomer conversions (70–75%) to precursor polymers are comparable to or slightly higher than those reported for other similar polymerization systems,[3,15,22] but the polymer yields (17–25%) after dialysis are not high. However, it is our belief that the molecular weights of these polymers are reasonably high since they were obtained after dialysis using a dialysis tube whose molecular weight cutoff was 12 000. All of the precursor polymer films cast from aqueous solutions after dialysis appeared homogeneous and transparent. They could be oriented by drawing before or during the final elimination process.

The results of elemental analyses and the compositions of the final copolymers as calculated from bromine contents are shown in Table II. The content of Br-containing units incorporated in the copolymers was significantly lower than that in the monomer mixture, suggesting that the

Table II
Results of Elemental Analyses of Final Polymers

polymer	molar ratio feed	PV:BrMPV actual	elemental content,[a] wt % C	H	Br
1-poly(PV-*co*-BrMPV)	80:20	98.7:1.30	90.0	6.13	1.00
			(90.9)	(5.92)	(1.00)
8-poly(PV-*co*-BrMPV)	67:33	91.9:8.10	85.7	5.61	5.43
			(87.6)	(5.50)	(5.43)
9-poly(PV-*co*-BrMPV)	50:50	90.9:9.10	87.5	5.89	5.50
			(86.8)	(5.44)	(5.50)
16-poly(PV-*co*-BrMPV)	33:67	84.1:15.9	82.6	5.29	10.9
			(82.0)	(5.13)	(10.9)
45-poly(PV-*co*-BrMPV)	20:80	55.1:44.9	67.5	5.10	14.8
			(67.2)	(4.27)	(14.8)

[a] Values in parentheses are calculated ones based on the actual composition estimated from the experimentally found bromine content.

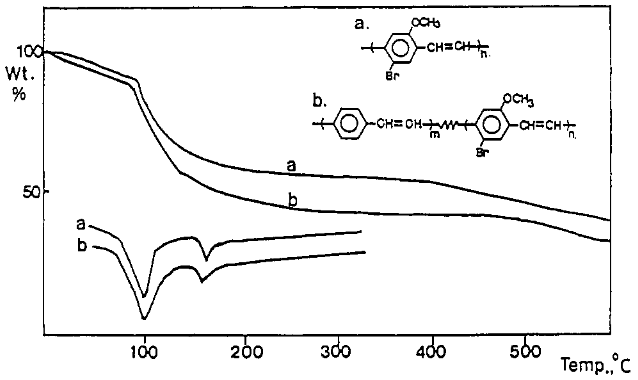


Figure 2. TGA and DSC thermograms of the precursor polymers: (a) homopolymer; (b) 9-poly(PV-*co*-BrMPV) copolymer.

reactivity of the PV monomer, **3**, is greater than that of the Br-containing monomer, **2**.

Thermal analyses of the elimination reaction of the precursor polymers by TGA and DSC with a heating rate of 10 °C/min indicate that major weight losses occurred from about 100 to 200 °C as shown in Figure 2. DSC thermograms exhibit two major endothermic processes at about 100 and 160 °C. The low-temperature endotherms correspond to the loss of water and the higher temperature ones to the elimination of tetrahydrothiophene and HCl.[20]

The FT-IR spectrum of PBrMPV film is compared with that of the precursor polymer film in Figure 3. The precursor polymer film exhibits a broad absorption at 3100–3600 cm^{-1} due to absorbed water, which disappears in the spectrum of the final polyconjugated film. A strong absorption peak appears at 960 cm^{-1} after elimination, which corresponds to the out-of-plane bending mode of the *trans*-vinylene =CH group.[1,23] The IR spectrum of the precursor polymer also shows a small, but sharp absorption peak at the same position. This results from a premature elimination reaction which occurred during film casting.

Figure 4 shows UV–vis spectra of thin films of PBrMPV and copolymers. For comparison purposes, spectra of PPV and poly(2,5-dimethoxy-1,4-phenylenevinylene) (PDMPV) films prepared by us separately are included in the figure. The maximum absorption positions of PBrMPV and its copolymers have moved slightly to longer wavelength when compared with the λ_{max} of PPV. However, the degree of the bathochromic shift in PBrMPV and its copolymers is much less than in PDMPV. This can be explained on the basis of the much weaker bathochromic effect of the bromine substituent than the methoxy group.[24] In fact, according to a recent report,[25] the λ_{max} of poly(2-methoxy-1,4-phenylenevinylene) is 435 nm. In addition, it should be pointed out that the degree of conjugation defect that occurred during the synthetic process also is expected to exert a very strong influence on the absorption characteristics.

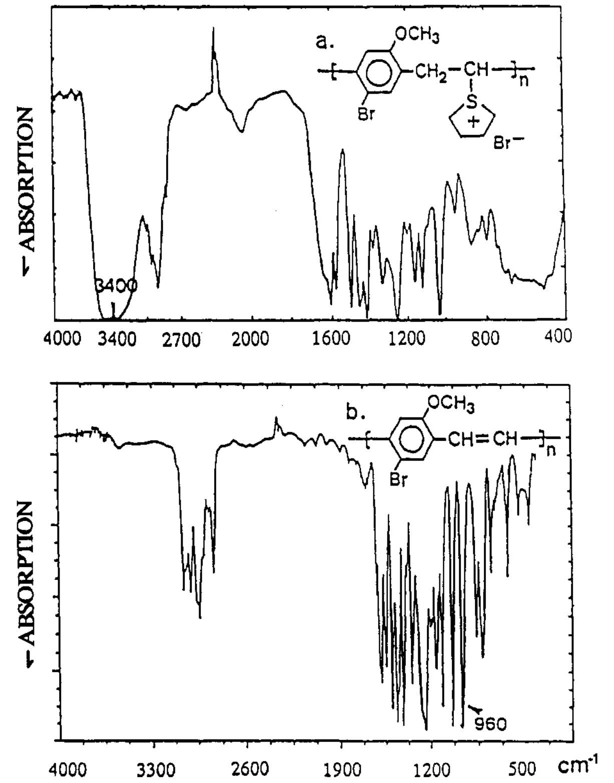


Figure 3. IR spectra of (a) precursor polymer and (b) final homopolymer.

Electrical conductivities of the polymers were measured using a standard four-probe technique. Table III shows draw ratios, degrees of doping, and the maximum conductivity values obtained for the oriented and unoriented polymer films. PBrMPV is readily doped with I_2 vapor, but the maximum conductivity is far lower than that of PDMPV. For unstretched films, I_2-doped PDMPV was reported to have an electrical conductivity of about 200 S cm^{-1},[13,26] whereas the corresponding value for PBrMPV is only 7.4×10^{-5} S cm^{-1}. Even the stretched film of PBrMPV with a draw ratio of 6 after doping with I_2 to saturation had an electrical conductivity of only 2.0×10^{-3} S cm^{-1}. PBrMPV has two different types of substituents: one is the electron-donating methoxy group and the other is the electron-withdrawing bromine atom. The effect of the electron-withdrawing bromine atoms appears to counterbalance the opposite effect by the methoxy groups. This coincides well with the fact that the absorption maxima for PBrMPV in the UV–vis spectrum is very close to that of PPV. In addition, copolymers containing both PV and

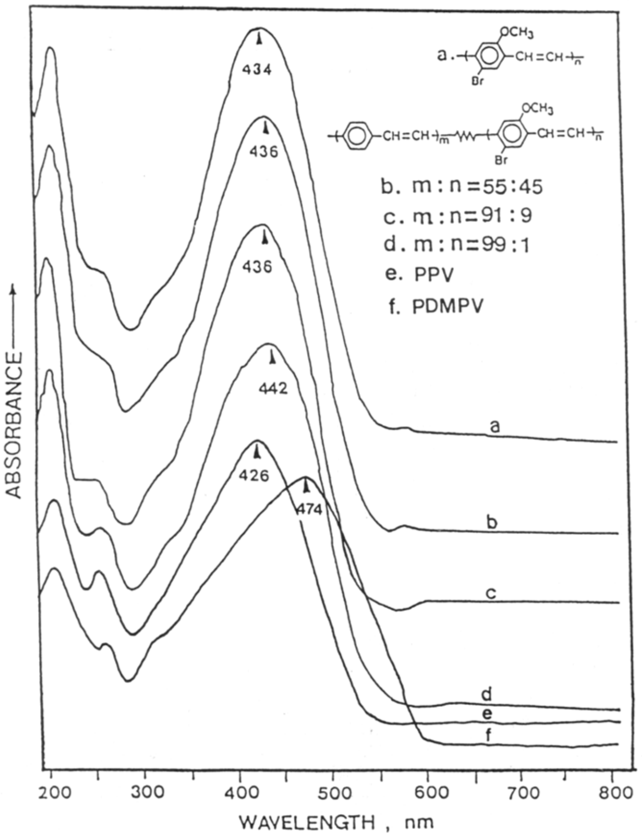


Figure 4. UV–vis spectra of homopolymer and copolymers.

Table III
Maximum Conductivities of I_2-Doped Polymers

polymer	draw ratio L/L_0	conductivity, S cm^{-1}	deg of doping, I atoms/RU[a]
1-poly(PV-*co*-BrMPV)	1	8.2×10^{-3}	0.59
	6	9.7×10^{-1}	0.66
8-poly(PV-*co*-BrMPV)	1	6.1×10^{-3}	0.57
	6	8.0×10^{-1}	0.64
9-poly(PV-*co*-BrMPV)	1	6.1×10^{-3}	0.59
	6	8.4×10^{-1}	0.65
16-poly(PV-*co*-BrMPV)	1	5.0×10^{-3}	0.58
	6	9.4×10^{-2}	0.60
45-poly(PV-*co*-BrMPV)	1	1.5×10^{-3}	0.58
	6	5.7×10^{-2}	0.61
PBrMPV	1	7.4×10^{-5}	0.51
	6	2.0×10^{-3}	0.55

[a] RU stands for average repeating unit.

BrMPV units showed a very insensitive composition dependence of electrical conductivity, ranging from 1.5×10^{-3} to 8.2×10^{-3} S cm^{-1} (Table III).

Interestingly enough, the copolymer film containing only 1 mol % of BrMPV unit, 1-poly(PV-*co*-BrMPV), not only could be readily doped with I_2 but also showed the highest conductivity among the polymers with a value of 8.2×10^{-3} S cm^{-1}, which is about 10^2 times the value of the PBrMPV homopolymer. As described in the Introduction, the poly(PV-*co*-NPV)s[18] revealed the same trend; the PPV copolymer containing a very low level (ca. 2 mol %) of NO_2–PV unit exhibited the highest conductivity when doped with I_2. We observed a similar phenomenon in the electrical conductivity of I_2-doped poly(1,4-phenylenevinylene-*co*-2,3,5,6-tetramethyl-1,4-phenylenevinylene)s.[27] In fact, even in the poly(1,4-phenylenevinylene-*co*-2,5-dimethoxy-1,4-phenylenevinylene) series,[13] the electrical conductivity steeply increases with the amount of DMPV units up to 10 mol % and thereafter the increase is very much reduced.

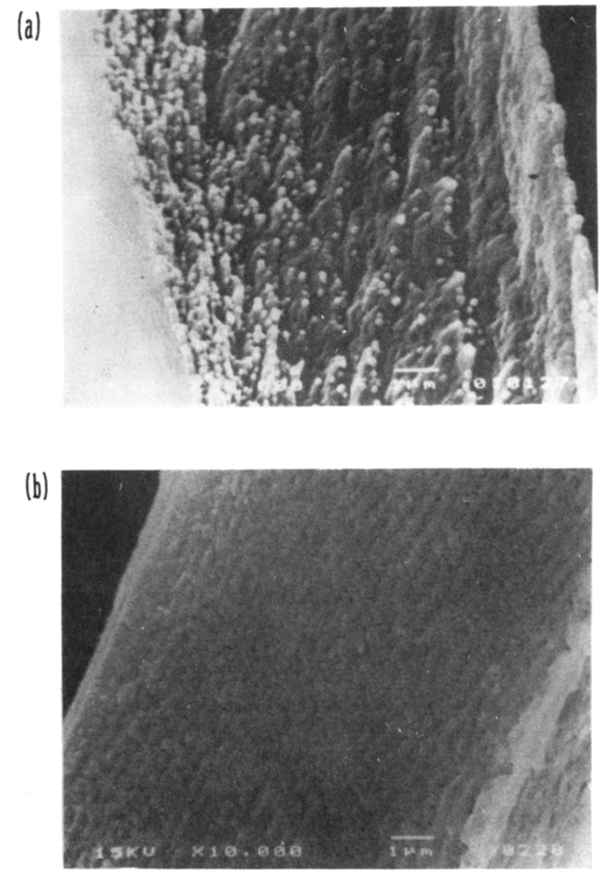


Figure 5. Scanning electron micrographs of 9-poly(PV-*co*-BrMPV) copolymer: (a) undrawn; (b) drawn (L/L_0 = 6).

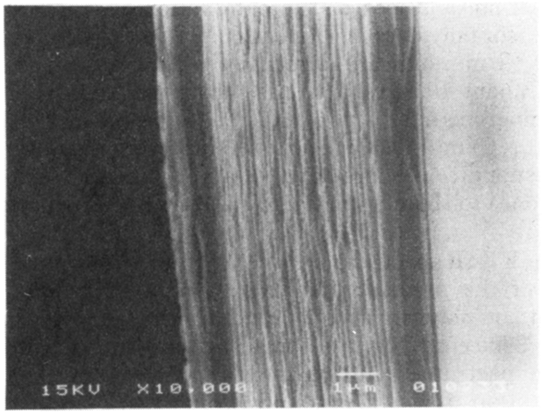


Figure 6. Scanning electron micrograph of drawn (L/L_0 = 6) 45-poly(PV-*co*-BrMPV) film along the stretching direction.

All these observations lead to the generalization that the inclusion of a relatively small amount of a comonomer unit having bulky substituents, regardless of their nature, into PPV enhances dopability and, thus, electrical conductivity. Although the initial sharp increase in electrical conductivity by copolymerization of PPV with a comonomer having bulky groups appears to be universal, it certainly is premature to draw a definite conclusion on the effect of the comonomer units or substituents. However, it is our present conjecture that inclusion of a low level of a comonomer unit having bulky groups will loosen the chain structure locally, allowing I_2 to gain easier access to the polymer chains than in the PPV homopolymer. At high levels of comonomer units, the electronic as well as the steric effect of the substituents must play more important roles in controlling the electrical conductivity of doped polymers. It is also expected that the overall morphological changes will become a more important factor when the amount of comonomer units included increases. Nevertheless, it is our belief that more experimental data are required before we can draw firm conclusions on these points. All of the stretched films displayed higher conductivities along the stretch direction than did the unstretched films (see Table III). The same phenomenon has been observed repeatedly by us and others.[1,3,14,20]

Figure 5 shows scanning electron micrographs (SEM) for the cross-cut surfaces of 9-poly(PV-*co*-BrMPV) films. Figure 5a reveals an unoriented, sparse fibrillar morphology for the original film, whereas oriented, denser fibrillar structures can be clearly seen in Figure 5b for the drawn film. Orientation of polymer chains by stretching the films certainly improves interchain contact, which, in turn, would increase conductivity as we observed in the present and earlier works. Figure 6 reveals an aligned fibrillar morphology for the stretched film for 45-poly(PV-*co*-BrMPV). This micrograph was obtained for the cut surface along the stretching direction.

Conclusion

The following conclusions are drawn from the results of the present investigation:

(1) A new series of PPV copolymers having a methoxy group and a bromine atom on the same phenylene rings can be readily prepared via water-soluble precursor polyelectrolytes.

(2) PBrMPV and its copolymers can be doped with I_2 at room temperature, and their electrical conductivities are rather insensitive to their composition. This can be ascribed to the opposite substituent's effect by the electron-donating methoxy group and the electron-attracting bromine atom.

(3) The UV–vis spectral profile of all of the polymers including λ_{max} is almost the same.

(4) Doping of PPV derivatives with I_2 can be facilitated by increasing interchain distance through putting bulky substituents on the phenylene rings. Drawn films reveal denser, better oriented fibrillar morphology than undrawn films and, therefore, higher conductivities upon doping.

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Registry No. 1, 135588-90-8; 2, 135517-32-7; 2 (homopolymer), 139101-61-4; (2)(3) (copolymer), 139101-62-5; PBrMPV (SRU), 139101-63-6; I_2, 7553-56-2; 2,5-dimethylanisole, 1706-11-2; tetrahydrothiophene, 110-01-0.