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# Synthesis and Characterization of Poly(2-methoxy-5-nitro-1,4-phenylenevinylene) and Poly(1,4-phenylenevinylene-*co*-2-methoxy-5-nitro-1,4-phenylenevinylene)s

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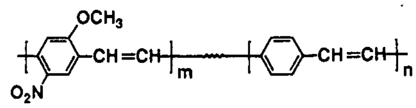
ABSTRACT: The preparation of poly(2-methoxy-5-nitro-1,4-phenylenevinylene) (PMNPV) and a series of poly(1,4-phenylenevinylene-*co*-2-methoxy-5-nitro-1,4-phenylenevinylene)s (poly(PV-*co*-MNPV)s) is described. All the polymers could be synthesized via the water-soluble polyelectrolyte precursor route. The precursor copolymers revealed diminished solution viscosity values with increasing content of the MNPV unit. The UV–vis spectra of the copolymers were blue-shifted when compared with that of the parent PPV, which implies an increased band-gap. This can be ascribed to the strong electron-withdrawing nature of the $NO_2$ group, which overwhelms the electron-donating power of the $OCH_3$ group. In spite of such spectroscopic characteristics, the copolymers containing a low level of MNPV units exhibit improved dopability toward $I_2$ and $FeCl_3$. Electrical conductivity of the doped copolymers depends strongly on their composition; it reaches a maximum value at about 5 mol % of MNPV units and then drops rapidly with further increase in the content of the comonomer unit. For this maximum composition, conductivity values are $5.2 \times 10^{-3}$ and $2.2 \times 10$ S cm$^{-1}$, respectively, for the two dopants. Uniaxially stretched samples, in general, showed much higher conductivities along the drawing direction.

## Introduction

Poly(1,4-phenylenevinylene) (PPV) and its derivatives have been attracting considerable interest in recent years because of their electrical properties[1–10] after being doped with oxidants such as $AsF_5$, $I_2$, $FeCl_3$, etc. and also their nonlinear optical (NLO) properties.[11–16] These polyconjugated polymers can be synthesized via the water-soluble polyelectrolyte precursor route originally reported by Wessling and Zimmerman[17] and later studied more in detail by Murase et al.[4] and Gagnon et al.[3] Recently, we[18] reported the synthesis of poly(2-bromo-5-methoxy-1,4-phenylenevinylene) (PBrMPV) and its copolymers containing PV units. The bromo group is an electron-withdrawing substituent whereas the methoxy group is of electron-donating nature. Therefore, PBrMPV and its copolymers are expected to exhibit high second-order NLO activity if one can find a way to align the dipoles in such a way that all or the majority of the bromo groups take positions on one side of the polymer chain and the methoxy groups on the other side.

One of the unsatisfactory structural features of PBrMPV and its copolymers resides in the fact that the electron-withdrawing power of the bromo group is not sufficiently high. This consideration prompted us to make an attempt to prepare the present poly(2-methoxy-5-nitro-1,4-phenylenevinylene) (PMNPV) and poly(1,4-phenylenevinylene-*co*-2-methoxy-5-nitro-1,4-phenylenevinylene)s. It is well known[19] that the nitro group is a much stronger electron acceptor than the bromo group. Moreover, it was previously demonstrated by us[20] that PPV copolymers containing comonomer units having a nitro substituent on the phenylene ring could be synthesized by a slightly modified synthetic method. We observed that the nitro substituent not only decreases the reactivity of the bis-sulfonium salt monomer but also reduces the molecular weight of the copolymers.

The structure of the polymers to be reported in this article is given below:



The values of *m* and *n* describe only the overall composition of the copolymers, not the block lengths. For example, the copolymer containing *m* mol % of the 2-methoxy-5-nitro-1,4-phenylenevinylene (MNPV) unit is designated *m*-poly(PV-*co*-MNPV). In this report, we describe synthetic details and characterization of the polymers. Electrical conductivity of the polymers after being doped with $I_2$ and $FeCl_3$ is also described.

## Experimental Section

**Synthesis of Bis-sulfonium Salt Monomers.** The synthetic method of 1,4-bis(tetrahydrothiopheniumylmethyl)benzene dichloride (**7**) was reported earlier by others.[3] Therefore, only the preparation method of 1,4-bis(tetrahydrothiopheniumylmethyl)-2-methoxy-5-nitrobenzene dichloride (**6**) is described. 2,5-Dimethylanisole was nitrated to 4-nitro-2,5-dimethylanisole (**1**), which then was oxidized to 2-methoxy-5-nitroterephthalic acid (**2**). Dicarboxylic acid **2** was converted to the corresponding diacid dichloride (**3**) followed by reduction to 2,5-bis(hydroxymethyl)-4-nitroanisole (**4**). Dihydroxy compound **4** was reacted with $SOCl_2$ to make 2,5-bis(chloromethyl)-4-nitroanisole (**5**).[21] Compound **5** was then converted to the bis-sulfonium salt.

**4-Nitro-2,5-dimethylanisole (1).** Sodium nitrite (45.0 g, 0.65 mol) was dissolved in 500 mL of ice-cold 60% nitric acid. To this solution was added dropwise 30.0 g (0.22 mol) of 2,5-dimethylanisole. The whole mixture was stirred vigorously for 5 h in an ice/water bath. At the end of the reaction, the mixture was poured into 1.5 L of distilled water, precipitating the crude product. The precipitates was collected on a filter and washed thoroughly with distilled water. The crude product was purified by recrystallization from a mixture of ethanol/water = 7/1 (v/v). The product

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yield was 29.0 g (73%), mp 78–79 °C. $^1$H-NMR (acetone-$d_6$) δ 7.76 (s, 1 H, aromatic H ortho to NO$_2$), 6.86 (s, 1 H, aromatic H ortho to OCH$_3$), 3.92 (s, 3 H, OCH$_3$), 2.54 (s, 3 H, CH$_3$ ortho to NO$_2$), 2.71 (s, 3 H, CH$_3$ ortho to OCH$_3$); IR (KBr) 2950 (aliphatic C–H stretch), 1620 and 1475 (aromatic C=C stretch), 1517 and 1336 (N–O stretch), 862 cm$^{-1}$ (aromatic C–H out-of-plane bending). Anal. Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.12; N, 7.73. Found: C, 59.73; H, 6.23; N, 7.47.

**2-Methoxy-5-nitroterephthalic Acid (2).** A mixture of compound 1 (20.0 g, 0.11 mol) and 150 g of KMnO$_4$ in 1.6 L of distilled water was refluxed for 5 h. The mixture was filtered through a filter paper, and the filtrate was concentrated to 500 mL using a rotary evaporator. The solution was acidified to pH 1 with concentrated HCl. The precipitate formed was thoroughly washed with cold water and then dried. The product yield was 16.5 g (62%), mp 256–257 °C. $^1$H-NMR (DMSO-$d_6$) δ 8.07 (s, 1 H, aromatic H ortho to NO$_2$), 7.17 (s, 1 H, aromatic H ortho to OCH$_3$), 3.78 (s, 3 H, OCH$_3$); IR (KBr) 2600–3400 (COOH), 1708 (C=O stretch), 1500 and 1343 (N–O stretch), 862 cm$^{-1}$ (aromatic C–H out-of-plane bending). Anal. Calcd for $C_9H_7NO_7$: C, 44.83; H, 2.93; N, 5.81. Found: C, 45.02; H, 2.94; N, 5.85.

**2,5-Bis(hydroxymethyl)-4-nitroanisole (4).** Compound 2 (15.0 g, 6.12 × 10$^{-2}$ mol) was dissolved in 70 mL of purified thionyl chloride,[22] and the mixture was refluxed for 5 h. Excess thionyl chloride was distilled out. Dry petroleum ether (20 mL) was added to the residue, 3, and the mixture was vigorously stirred. Then petroleum ether was again removed under reduced pressure. Sodium borohydride (6.95 g, 0.184 mol) dissolved in 70 mL of dry tetrahydrofuran was added to the acid chloride 3. The solution was then refluxed for 3 h, after which it was cooled in an ice/water bath. To the cold solution was added dropwise cold distilled water. The precipitate was collected on a filter and washed thoroughly with distilled water. The product, 4, thus obtained was utilized in the next step without any further purification. The product yield was 8.35 g (63%), mp 184–185 °C. $^1$H-NMR (DMSO-$d_6$) δ 8.07 (s, 1 H, aromatic H ortho to NO$_2$), 7.30 (s, 1 H, aromatic H ortho to OCH$_3$), 5.40 (broad, 2 H, OH), 4.84 (s, 2 H, benzylic CH$_2$ ortho to NO$_2$), 4.48 (s, 2 H, benzylic CH$_2$ ortho to OCH$_3$), 3.90 (s, 3 H, OCH$_3$); IR (KBr) 3400 (OH stretch), 1513 and 1329 cm$^{-1}$ (N–O stretch). Anal. Calcd for $C_9H_{11}NO_5$: C, 50.71; H, 5.20; N, 6.57. Found: C, 50.83; H, 4.99; N, 6.24.

**2,5-Bis(chloromethyl)-4-nitroanisole (5).**[21] Compound 4 (3.0 g, 1.4 × 10$^{-2}$ mol) was dissolved in 18 mL of dry *N*,*N*-dimethylformamide, to which was slowly added 6.52 g (5.48 × 10$^{-2}$ mol) of purified thionyl chloride. The mixture was stirred at room temperature for 15 h. The reaction mixture was then slowly added to 100 mL of 0.05 M HCl. The precipitate was collected on a filter and washed with distilled water. The product obtained was purified by recrystallization from *n*-hexane. The product yield was 2.1 g (60%), mp 62–63 °C. $^1$H-NMR (CDCl$_3$) δ 8.11 (s, 1 H, aromatic H ortho to NO$_2$), 7.18 (s, 1 H, aromatic H ortho to OCH$_3$), 4.96 (s, 2 H, benzylic CH$_2$ ortho to NO$_2$), 4.55 (s, 2 H, benzylic CH$_2$ ortho to OCH$_3$), 3.95 (s, 3 H, OCH$_3$); IR (KBr) 1527 and 1348 (N–O stretch), 1277 (CH$_2$Cl bending), 1064 (C–O stretch), 719 cm$^{-1}$ (C–Cl stretch). Anal. Calcd for $C_9H_9NO_3$: C, 43.23; H, 3.63; N, 5.60. Found: C, 43.86; H, 3.74; N, 5.85.

**1,4-Bis(tetrahydrothiopheniumylmethyl)-2-methoxy-5-nitrobenzene Dichloride (6).** Compound 5 (2.0 g, 8.0 mmol) was dissolved in 20 mL of dry methanol and 2.8 g (3.2 × 10$^{-2}$ mol) of tetrahydrothiophene. The mixture was stirred for 24 h at 50 °C. The solvent and excess tetrahydrothiophene were removed under reduced pressure using a rotatory evaporator. The solid residue was dispersed in cold and dry acetone, and the precipitate was collected on a filter followed by washing with cold acetone. The product was dried in a vacuum oven. The product yield was 2.1 g (61%). $^1$H-NMR (D$_2$O) δ 8.55 (s, 1 H, aromatic H ortho to NO$_2$), 7.40 (s, 1 H, aromatic H ortho to OCH$_3$), 4.80 (s, 2 H, benzylic CH$_2$ ortho to NO$_2$ superposed on the D$_2$O peak), 4.63 (s, 2 H, benzylic CH$_2$ ortho to OCH$_3$), 4.14 (s, 3 H, OCH$_3$), 3.68–3.50 (m, 8 H, CH$_2$S$^+$CH$_2$)), 2.55–2.35 (m, 8 H, CH$_2$CH$_2$$^+$SCH$_2$-CH$_2$); IR (KBr) 1528 and 1343 (N–O stretch), 1069 cm$^{-1}$ (C–O stretch).

**Procedure for Polymerization and Thermal Elimination of Precursor Polymers to the Final Polyconjugated Polymers.** The general procedure of polymerization can be found in the literature.[3,4] As a representative example, the synthetic procedure of 55-poly(PV-*co*-MNPV) is described. Monomer 6 (0.606 g 1.42 mmol) and monomer 7 (0.500 g, 1.42 mmol) were dissolved in 4 mL of ice-cold distilled water. To this solution was added 0.711 mL (2.82 mmol) of 4 M tetramethylammonium hydroxide, and then the whole solution was allowed to warm to room temperature and stirred for 24 h. The reaction mixture was titrated against 1.0 M HCl. Conversion of monomers to precursor polymer was estimated to be 96%. The neutralized precursor polymer was dialyzed for 3 days using a dialysis tube (Sigma) with a molecular weight cutoff at 12 000 to remove low molecular weight species. Films (ca. 7–15 μm thick) cast from aqueous precursor solutions were clamped between Teflon sheets in a glass tube and subjected to thermal elimination in vacuo (10$^{-2}$ Torr) at 230 °C for 5 h. When necessary, precursor polymer films (ca. 1 cm × 5 cm strips) were stretched manually along one direction at 120–140 °C over a zone-heating apparatus made of Pyrex glass.

**Doping and Electrical Conductivity Measurement of Polymer Films.** I$_2$ doping of thin (ca. 10 μm thick) strip samples attached to a four-in-line probe was conducted at room temperature in a vacuum line at a pressure of 1.0 × 10$^{-3}$ Torr. Carbon paste was used for sample–Pt electrode contact. For FeCl$_3$ doping, the polymer films were soaked at room temperature in a FeCl$_3$-saturated nitromethane solution. The doped films were washed with fresh nitromethane before drying at a pressure of 1.0 × 10$^{-3}$ Torr. The degree of doping was calculated from the weight uptake in both cases. Electrical conductivities were measured by the well-known four-in-line probe method[23] at the doping-chamber's pressure of 10$^{-3}$ Torr.

**Characterization of Precursor and Final Polyconjugated Polymers.** Elemental analysis was performed by the Analytical Department of the Korea Research Institute of Chemical Technology. Inherent viscosities of the dialyzed precursor polymers were measured at 30 °C for aqueous solutions containing 0.012 M sodium sulfate. IR spectra were obtained on a Mattson Alpha Centauri FT-IR spectrometer. UV-vis spectra were recorded on a Hewlett-Packard 8452A spectrometer. Thermograms were recorded on a Rigaku 8150 instrument. $^1$H-NMR spectra of intermediates and monomers were recorded on a Bruker AM300 spectrometer, and the resonance positions are reported relative to the TMS standard on the δ scale in ppm.

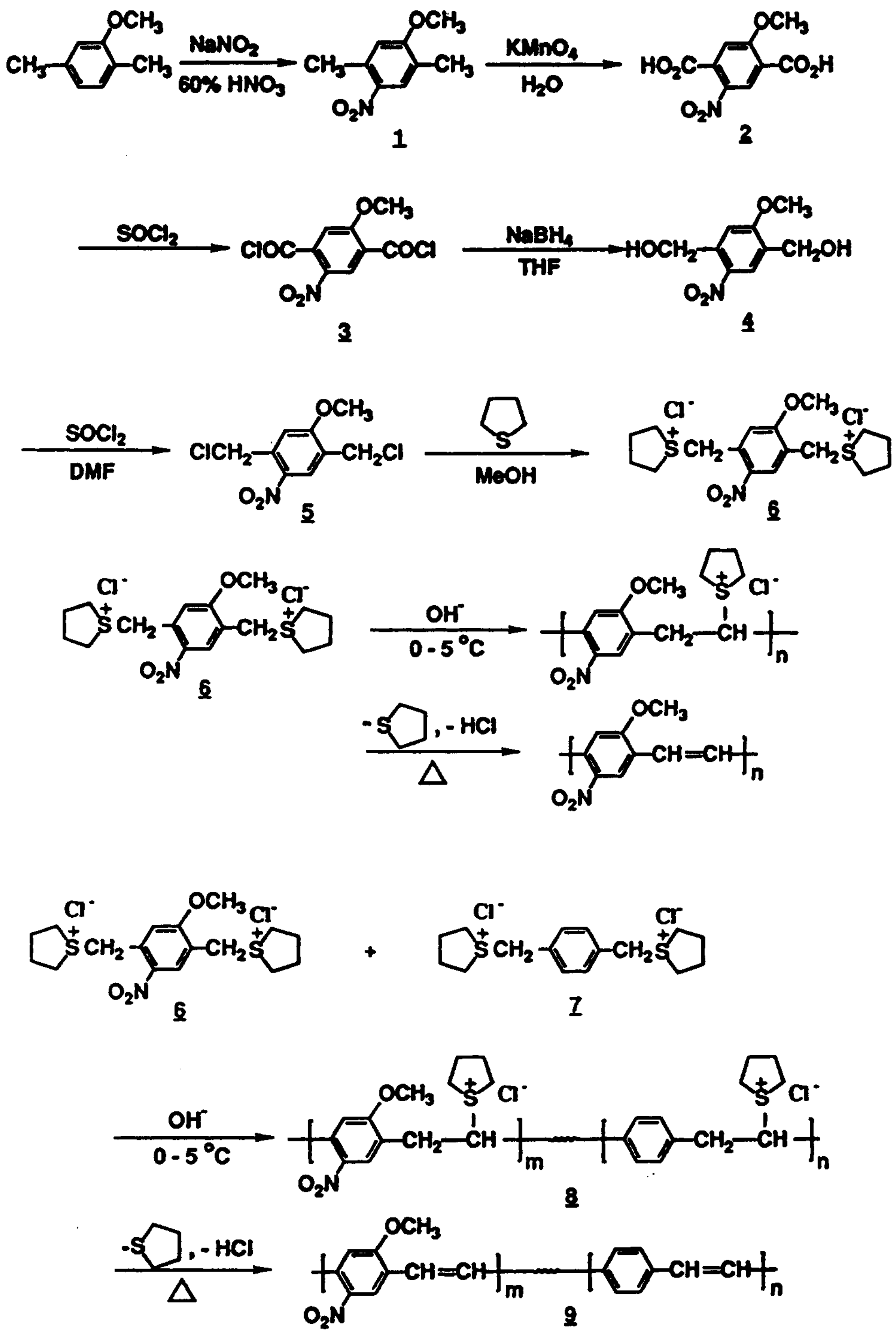
## Results and Discussion

**Synthesis of Poly(2-methoxy-5-nitro-1,4-phenylenevinylene) (PMNPV) and Poly(PV-*co*-MNPV) Copolymers.** High molecular weight PPV and other related polymers and copolymers can be prepared from water-soluble polyelectrolyte precursors obtained from base-catalyzed polymerization of a *bis*-sulfonium salt or a mixture of bis-sulfonium salts.[3,4,17] Scheme I shows the synthetic route utilized for our syntheses of PMNPV and poly(PV-*co*-MNPV)s.

Nitration of commercially available 2,5-dimethylanisole to compound 1 was performed by a standard method. The compound could be easily converted to 2 by simple oxidation with potassium permanganate. Reduction of 2 to the corresponding alcohol 4 was carried out via diacid dichloride 3. Transformation of 4 to bis-chloromethyl compound 5 could be conducted following a conventional method using thionyl chloride. Finally, compound 5 was converted to bis-sulfonium salt 6 by treatment with excess tetrahydrothiophene.[24] The salt was purified by repeated precipitation from dry acetone. Comonomer 7 is a known compound, and its preparation method can be found elsewhere.[5]

Polymerization of 6 or 7 or a mixture of 6 and 7 was conducted at room temperature under a N$_2$ atmosphere in aqueous solution. Tetramethylammonium hydroxide was used as a catalyst. For the preparation of copolymers, the molar ratio of 6:7 was varied from 100:0 to 0:100 as shown in Table I. At the end of the polymerization, the

Scheme I



| | | |
|---|---|---|
| m = 100 | n = 0 | PMNPV |
| m = 3.9 | n = 96.1 | 4-poly(PV-co-MNPV) |
| m = 8.4 | n = 91.6 | 8-poly(PV-co-MNPV) |
| m = 35.4 | n = 64.6 | 35-poly(PV-co-MNPV) |
| m = 55.2 | n = 44.8 | 55-poly(PV-co-MNPV) |
| m = 0 | n = 100 | PPV |

solution was neutralized to pH 7 by addition of dilute hydrochloric acid.[3] Aqueous solutions of precursor polymers 8 thus obtained were dialyzed against distilled water using a dialysis tube with a molecular weight cutoff at 12 000. Therefore, only relatively high molecular weight polymers were collected in the tube. Aqueous solutions of precursor polymers then were cast into thin films (ca. 7–15 μm thick) by slow evaporation under reduced pressure. Polyconjugated polymers 9 were finally obtained by thermal elimination of the precursor polymers.

Table I summarizes the data for conversion of monomers, inherent viscosities of precursor polymers, yields after dialysis, and polymer compositions. Conversions were estimated by titration of the final polymerization mixture with standard HCl solution. The conversion of monomers to precursor polymers is very high, ranging from 89 to 93%, with the only exception for PPV precursor. To obtain high conversions polymerization reactions were inten-

Table I
Polymerization Conditions, Monomer Conversion, Yield, and Inherent Viscosity of Polymers

| polymer | feed ratio *m*:*n* | actual ratio[a] *m*:*n* | reacn time | conv, % | yield, % | $\eta_{inh}$, dL/g |
|---|---|---|---|---|---|---|
| PMNPV | 100:0 | 100:0 | 18 day | 91.6 | 80.4 | 0.15 |
| 55-poly(PV-*co*-MNPV) | 50:50 | 55.2:44.8 | 24 h | 90.0 | 60.7 | 0.13 |
| 35-poly(PV-*co*-MNPV) | 33:67 | 35.4:64.6 | 24 h | 92.9 | 57.0 | 0.21 |
| 8-poly(PV-*co*-MNPV) | 25:75 | 8.4:91.6 | 24 h | 92.9 | 55.8 | 0.38 |
| 4-poly(PV-*co*-MNPV) | 10:90 | 3.9:96.1 | 24 h | 89.4 | 57.8 | 2.13 |
| PPV | 0:100 | 0:100 | 20 min | 38.9 | 19.5 | 2.10 |

[a] Refer to Table II.

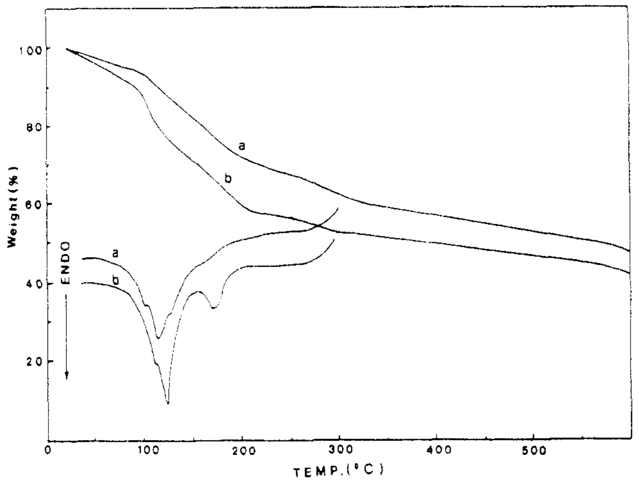


**Figure 1.** TGA and DSC thermograms of precursor polymers of (a) 55-poly(PV-*co*-MNPV) and (b) 35-poly(PV-*co*-MNPV) (heating rate: 10 °C/min in $N_2$).

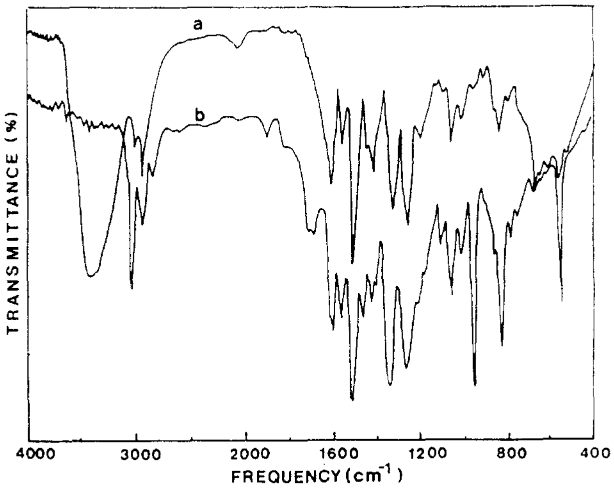


**Figure 2.** FT-IR spectra (a) precursor polymer of 35-poly(PV-*co*-MNPV) and (b) 35-poly(PV-*co*-MNPV) after elimination.

tionally run for a prolonged period of time as shown in Table I.

Polymerization was allowed to continue for 18 days for the preparation of the precursor polymer of PMNPV. In contrast, the reaction for PPV precursor was stopped after 20 min. Solution viscosities of the dialyzed polymers were measured in the presence of $Na_2SO_4$ to avoid the possible complication caused by the conformational changes of polyelectrolyte precursors to the extended chains in dilute solutions.[25] The viscosity decreases rather rapidly with increasing content of MNPV units in the precursor, suggesting that monomer **6** retards the chain propagation or facilitates chain termination or both. The value for the PPV precursor was 2.10, whereas that of the PMNPV precursor was only 0.15. We[10,20] earlier observed a similar phenomenon in the copolymerization of monomer **7** with 1,4-bis(tetrahydrothiopheniumylmethyl)-2-nitrobenzene dichloride, which also carries the electron-withdrawing nitro ($NO_2$) substituent.

The yields of the polymerization reactions, as calculated from the weight of the remaining precursor polymers after removing low molecular weight species and evaporating water range from about 56 to 80%. Here again, the value for the PPV precursor is the lowest (39%) due to shorter reaction time. Comparison of the values of yield with those of conversion indicates that a substantial amount of precursor polymers formed was removed during dialysis.

Thermal analyses of the elimination reaction of the precursor polymers by TGA (Figure 1) and DSC (Figure 1) with a heating rate of 10 °C/min indicate that two major weight losses occur from about 80 to 140 °C and again from about 150 to 200 °C. The low-temperature endotherm on the DSC thermogram corresponds to the loss of absorbed water, and the higher-temperature endotherm corresponds to the elimination of tetrahydrothiophene and hydrogen chloride. To ensure as much complete elimination as possible, we conducted the elimination reaction at 230 °C for 5 h at the pressure of $10^{-2}$ Torr. Preliminary tests suggested to us that the elimination reaction at higher temperature may lead to considerable side reactions, resulting in lower electrical conductivity after doping. Too servere thermal treatment of precursor polymer films at a higher temperature can lead to adverse side reactions of vinylene groups, resulting in disappearance of vinylene C=C bonds.[20]

The results of elemental analyses of the eliminated polymers and actual compositions calculated from the contents of nitrogen are included in Table I. Since the polymerization were stopped at high conversions, actual polymer compositions are not far from those of the feed. Therefore, it is difficult to compare the reactivities of monomers **6** and **7**. We,[10,20] however, earlier observed that the presence of the electron-withdrawing nitro ($NO_2$) group not only reduces the reactivity of the bis-sulfonium salt monomer, but also causes a significant decrease in the molecular weight of the obtained copolymers. In light of the fact that copolymerization with monomer **6** decreases drastically solution viscosities of precursor copolymers as described above, it is our conjecture that the reactivity of monomer **6** is substantially lower than that of unsubstituted monomer **7**.

**Characteristics of Polymers.** The FT-IR spectrum of a copolymer containing 35 mol % of MNPV units, 35-poly(PV-*co*-MNPV), is compared with that of the corresponding precursor film in Figure 2. The precursor polymer film exhibits a very broad and strong absorption at 3100–3700 cm$^{-1}$ due to the presence of absorbed water, which disappears in the spectrum of the eliminated film. A strong and sharp absorption peak appears at 960 cm$^{-1}$ after elimination, indicating that the vinylene C=C bonds formed have the trans configuration.[8] This absorption is known to be characteristic of the *trans*-vinylene C–H out-of-plane bending mode. The IR spectrum of the precursor

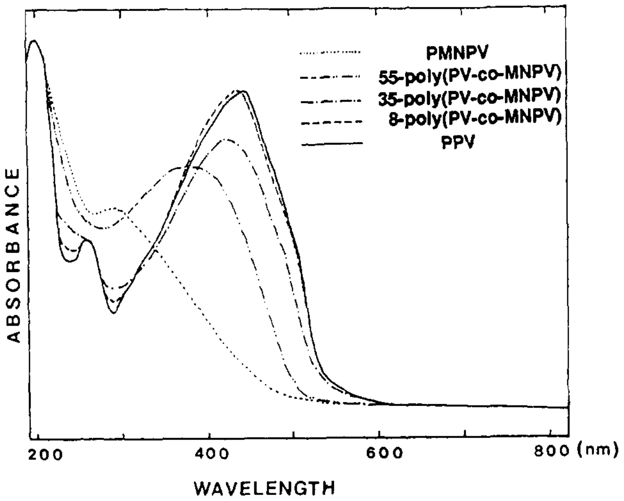


**Figure 3.** UV–vis spectra of PMNPV, poly(PV-*co*-MNPV)s, and PPV.

films shows a small absorption at the same position, which can be ascribed to premature partial elimination of tetrahydrothiophene and hydrogen chloride during film casting. Both the precursor and eliminated polymer films exhibit two strong absorption peaks at 1510 and 1340 cm$^{-1}$ characteristics of the $NO_2$ group.

Figure 3 shows the UV–vis spectra of the copolymer films. The spectrum of PPV film prepared under the same conditions is included for the sake of comparison. Although it is not included, the uneliminated precursor film of 35-poly(PV-*co*-MNPV) displays a weak absorption band at about 325 nm, which shifts to a $\lambda_{max}$ of about 435 nm and whose intensity grows after elimination. The positions of $\lambda_{max}$ and $\lambda_{edge}$ shown in Figure 3 clearly demonstrate that the presence of nitro ($NO_2$) and methoxy ($OCH_3$) substituents on the phenylene rings causes a hypsochromic shift. As the content of MNPV units in the copolymers increases, the position of maximum absorption ($\lambda_{max}$) gradually shifts from 442 nm for PPV to the shorter wavelength of 292 nm for PMNPV. This spectroscopic change must be arising from a combination of electronic and steric effects of the two substituents. The strong electron-withdrawing power of the nitro group may overwhelm the electron-donating power of the methoxy group. It also appears highly probably according to a molecular model that the two bulky substituents, i.e., the nitro and methoxy groups, present in the phenylene rings hinder the polymer chains from attaining a perfectly coplanar $\pi$-conformation. Disturbance of coplanarity in the $\pi$-system should cause a blue shift. At the same time, the band onset, i.e., the $\lambda_{edge}$ position, also decreases from 525 nm of PPV to 468 nm of PMNPV, which indicates a steady increase in band-gap with increasing content of MNPV units. This point will be discussed further in the following section.

**Electrical Conductivity.** As alluded to in the Introduction, we tried to synthesize the present PPV derivatives containing electron-donating as well as electron-withdrawing groups on the phenylene rings to investigate their NLO properties, which are presently under investigation. We, however, became interested in the electrical conductivities of the polymers and examined their dependence on the nature of the substituents and also on the copolymer composition. We[8-10,18,20] observed earlier that, surprisingly enough, PPV copolymers containing a low level of ring-substituted PPV units, regardless of whether the substituent is an electron donor or an electron acceptor, show much increased dopability toward a dopant such as $I_2$ and/or $FeCl_3$ and exhibit markedly elevated conductivity. For example, poly(1,4-phenylenevinylene-*co*-2-nitro-1,4-phenylenevinylene)[10,20] containing 2 mol % of the $NO_2$-PV comonomer unit, when doped with $I_2$ or $FeCl_3$, showed maximum values of conductivity of $3.4 \times 10^{-2}$ and $3.1 \times 10^{-1}$ S cm$^{-1}$, respectively. In contrast, PPV and poly(2-nitro-1,4-phenylenevinylene) themselves, however, are hardly doped with $I_2$ or $FeCl_3$. Moreover, we[16] recently observed that the copolymer containing 1–2 mol % of the $NO_2$-PV unit exhibits a much higher value of the third-order NLO susceptibility than those containing higher levels of the $NO_2$-PV unit.

Electrical conductivities of the present copolymers were measured using a standard four-in-line probe method.[23] All of the undoped polymer films had conductivities less than $10^{-7}$ S cm$^{-1}$. The maximum conductivity values and degrees of doping are listed in Table II. In general, the copolymer films reveal significantly higher electrical conductivities when doped with $FeCl_3$ than when doped with $I_2$. According to the data given in Table II, the conductivity of the copolymers increases rapidly with increasing content of MNPV unit, reaching the maximum value of 30 S cm$^{-1}$ for $FeCl_3$-doped 8-poly(PV-*co*-MNPV). Further increase in the content of MNPV unit brings about a gradual decrease in conductivity, finally reaching that ($1.2 \times 10^{-5}$ S cm$^{-1}$) of PMNPV. Although the conductivity values are much lower, the $I_2$-doped polymers also exhibit a similar dependence of their conductivity on composition. This observation presents a striking contrast to the UV–vis absorption behavior of the copolymers. As described above, $\lambda_{max}$ and $\lambda_{edge}$ values (Figure 3) of the copolymers gradually shift to shorter wavelength relative to the unsubstituted PPV as the content of comonomer unit increases, which suggests that increasing content of MNPV unit increases the band-gap, $E_g$. Therefore, one would expect that inclusion of MNPV units in the PPV structure generates compositions that would be more difficult to be doped by so-called p-dopants. Such a spectroscopic and physical picture does not parallel what we observe in the dopability and conductivity of $I_2$- or $FeCl_3$-doped copolymers. Presently, we can only make a couple of reasonable conjectures to explain this antinomy: The morphological changes brought about by the low level of MNPV unit in the copolymers make it easier for the doping species to approach and oxidize the polymer chain. At higher content of MNPV unit in the copolymer, however, the electronic and steric effects of the substituents predominate and, thus, the dopability as well as conductivity of doped film diminishes. The rather marked blue shift of PMNPV relative to the unsubstituted PPV strongly suggests that destruction of the coplanarity of the $\pi$-system by the two bulky substituents occurs. Simple electronic effects of the two opposing substituents cannot explain such a noticeable blue shift in the UV–vis absorption spectra of poly(PV-*co*-MNPV)s.

Finally, Table II includes the conductivity data of uniaxially stretched ($L/L_0 = 5$) films doped with $FeCl_3$. In general, the conductivity of stretched samples along the drawing direction is much higher than that of the original sample. Improved chain orientation by stretching is expected to lead to better contacts between polymer chains, which, in turn, will result in enhanced conductivity. Anisotropy in conductivity and increased conductivity of stretched film samples were reported earlier by us[6,20] and others[3] for many other related compositions.

## Conclusions

We successfully synthesized poly(2-methoxy-5-nitro-1,4-phenylenevinylene) (PMNPV) and poly(1,4-phenyl-

**Table II**
**Elemental Analysis and Conductivity of Polymers**

| polymer | feed ratio *m*:*n* | actual ratio[a] *m*:*n* | elem content,[b] wt % |  |  | max conductivity, S $cm^{-1}$ |  | deg of doping[d] |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  | C | H | N | $I_2$ | $FeCl_3$[c] | $I_2$ | $FeCl_3$ |
| PMNPV | 100:0 |  |  |  |  | $1.38 \times 10^{-7}$ | $1.15 \times 10^{-5}$ | 0.07 | 0.14 |
| 55-poly(PV-*co*-MNPV) | 50:50 | 55.2:44.8 | 75.61<br>(75.83) | 4.97<br>(4.85) | 4.36<br>(4.36) | $1.9 \times 10^{-7}$ | $6.0 \times 10^{-4}$ | 0.05 | 0.16 |
| 35-poly(PV-*co*-MNPV) | 33:67 | 35.4:64.6 | 82.32<br>(82.22) | 5.22<br>(5.13) | 2.81<br>(2.81) | $7.4 \times 10^{-5}$ | $4.4 \times 10^{-1}$<br>(1.7) | 0.16 | 0.30 |
| 8-poly(PV-*co*-MNPV) | 25:75 | 8.4:91.6 | 91.31<br>(91.40) | 5.75<br>(5.66) | 0.66<br>(0.66) | $2.5 \times 10^{-4}$ | $3.0 \times 10^{1}$<br>($1.5 \times 10^{2}$) | 0.14 | 0.27 |
| 4-poly(PV-*co*-MNPV) | 10:90 | 3.9:96.1 | 92.78<br>(93.00) | 5.84<br>(5.65) | 0.31<br>(0.31) | $5.2 \times 10^{-3}$ | $2.2 \times 10^{1}$<br>($3.8 \times 10^{2}$) | 0.14 | 0.26 |
| PPV | 0:100 | 0:100 |  |  |  | $5.8 \times 10^{-6}$ | $1.7 \times 10^{-5}$ | 0.09 | 0.02 |

[a] Actual compositions were estimated from the experimentally determined nitrogen contents of the copolymers. [b] The values in parentheses are those calculated for the actual compositions estimated from the experimentally found nitrogen contents. [c] The values in parentheses are those for uniaxially stretched ($L/L_0 = 5$) films along the stretch direction. [d] $I_3^-$ or $FeCl_4^-$ per average repeating unit estimated from the weight gain on doping.

enevinylene-*co*-2-methoxy-5-nitro-1,4-phenylenevinylene)s (poly(PV-*co*-MNPV)s) via the standard water-soluble precursor route. These polymers contain electron-donating methoxy groups as well as electron withdrawing nitro substituents, which are expected to induce very strong second-order NLO activity. Inclusion of the MNPV unit results in a fast decrease in the solution viscosities of dialyzed precursor polymers, indicating that the substituent bis-sulfonium monomer **6** retards the chain propagation or favors chain termination or both. UV–vis spectra of PMNPV and poly(PV-*co*-MNPV)s show that the presence of the two substituents on the phenylene rings causes a much higher degree of blue shift than that expected from their combined electronic effect of opposing character. This may be taken as a suggestion that the two bulky substituents partially destroy the coplanarity of the $\pi$-system by steric hindrance, which would result in reduced overlapping of $\pi$-electrons.

Incorporation of low levels (ca. 4–10 mol %) of 2-methoxy-5-nitro-1,4-phenylenevinylene units improves remarkably the doping ability of $I_2$ and $FeCl_3$. Electrical conductivity also exhibits a maximum at around these levels of MNPV content and then diminishes at higher levels. Uniaxial stretching of polymer films increased conductivity further due to improved chain orientation and, thus, interchain contacts.

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## References and Notes

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(21) After we finished the present studies we found in a subsequent investigation that a direct nitration of 2,5-bis(bromomethyl)-anisole using fuming nitric acid/acetic anhydride at 0 °C produces 2,5-bis(bromomethyl)-4-nitroanisole. $^1$H-NMR ($CDCl_3$) $\delta$ 8.18 (s, H, aromatic H ortho to $NO_2$), 7.00 (s, 1 H, aromatic H ortho to $OCH_3$), 4.87 (s, 2 H, benzylic $CH_2$ ortho to $NO_2$), 4.48 (s, 2 H, benzylic $CH_2$ ortho to $OCH_3$), 4.02 (s, 3 H, $OCH_3$); mp 94–95 °C. This compound can be converted to the corresponding bis-sulfonium salt, which can be utilized in the preparation of PMNPV and copolymers.
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