Macromolecules

Volume 27, Number 19 September 12, 1994

Synthesis and Characterization of Poly[(2-(2-phenylethenyl)-1,4-phenylene)vinylene], Poly[(2-methoxy-5-(2-phenylethenyl)-1,4-phenylene)vinylene], and Their Copolymers Containing 1,4-Phenylenevinylene Units

Jung-Il Jin,* Young-Hun Lee, Chi-Kyun Park, and Byung-Ki Nam

Department of Chemistry, College of Sciences, Korea University,
1-Anam Dong, Seoul 136-701, Korea

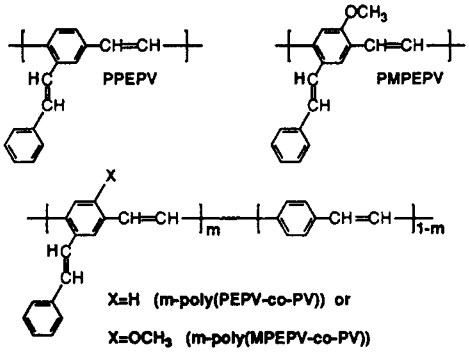
Received February 1, 1994; Revised Manuscript Received June 13, 1994®

ABSTRACT: Poly[(2-(2-phenylethenyl)-1,4-phenylene)vinylene] (PPEPV), poly[(2-methoxy-5-(2-phenylethenyl)-1,4-phenylene)vinylene] (PMPEPV), and their copolymers containing 1,4-phenylenevinylene (PV) units [poly(PEPV-*co*-PV)s and poly(MPEPV-*co*-PV)s] were synthesized via water soluble, polyelectrolyte precursor polymers. Electronic spectral characteristics of the polymers clearly demonstrate that the cross-conjugation between the main chain and the pendant 2-phenylethenyl (β-styryl) unit is insignificant. Electrical conductivities of $FeCl_3$-doped PPEPV and PMPEPV were on the order of 10^{-4} S cm^{-1}, which were lower than those of copolymers containing PV units. This is ascribed to the charge-transfer interactions between the dopants and styryl units in the side branch. The MPEPV copolymer containing about 93 mol % of PV unit, however, exhibited an electrical conductivity of about 5 S cm^{-1}, when it was doped with $FeCl_3$. The PEPV copolymer containing 85 mol % PV unit showed an electrical conductivity (0.24 S cm^{-1}) of 1 order of magnitude lower. In general, doping with I_2 resulted in lower electrical conductivities than doping with $FeCl_3$.

Introduction

A wide variety of polyconjugated polymers has been reported in recent years with regard to their synthesis, electrical properties, nonlinear optical properties, and luminescence characteristics.[1-10] Among them poly(1,4-phenylenevinylene), PPV, possesses a unique structural feature: it can be taken as an alternating copolymer composed of 1,4-phenylene and vinylene units. Since the phenylene ring can be subjected to various chemical modifications to carry many different types of substituents, PPV is very versatile for derivatization. Alkoxy,[11-15] halogen,[16-10] nitro,[20-22] and nitrile[23] groups are some of the representative substituents that have been examined for their influence on the structures and properties of modified PPVs.

There has not yet been any report, however, describing the synthesis and properties of the substituted PPVs having a pendant β-styryl or 2-phenylethenyl structure attached to the phenylene rings of PPV. These compositions have a uniqe structure in that pendant groups can be cross-conjugated with the polyconjugated main chain. We have succeeded in the preparation of poly[(2-(2-phenylethenyl-1,4-phenylene)vinylene] (PPEPV), poly[(2-methoxy-5-(2-phenylethenyl)-1,4-phenylene)vinylene)] (PMPEPV), and their copolymers containing 1,4-phenylenevinylene (PV) units, whose structures are shown below:



This report describes synthetic methods of the above polymers, their structual characteristics, and electrical properties. Their electrical conductivities were investigated after they were doped with I_2 and $FeCl_3$.

Experimental Section

The chemical structure reference numbers refer to those structures detailed in the synthetic Scheme 1 and 2 in the Results and Discussion.

Synthesis of the Precursor Homopolymer and Copolymers of Poly[(2-(2-phenylethenyl)-1,4-phenylene)vinylene].

[®] Abstract published in *Advance ACS Abstracts,* July 15, 1994.

0024-9297/94/2227-5239$04.50/0

***trans*-2,5-Bis(bromomethyl)stilbene (2).** 2,5-Dimethylstilbene (1; 5.2 g, 25 mmol). *N*-bromosuccinimide (8.9 g, 50 mmol) and benzoyl peroxide (0.25 g, 1.03 mmol) were dissolved in 100 mL of CCl_4. The mixture was refluxed for 4 h under a N_2 atmosphere. The solid succinimide formed was removed by filtration. The solvent was removed using a rotatory evaporator. The residue was recrystallized three times from acetone. The product yield was 5.3 g (58%).

^{1}H-NMR (acetone-*d*$_6$): δ 7.3–7.9 (m, 10H, Ar and CH=CH), 4.9 (s, 2H, CH_2Br), 4.7 (s, 2H, CH_2Br). IR(KBr): 1633 (C=C stretch), 1601 and 1495 (Ar C=C stretch), 958 (*trans* vinylene =C—H out-of-plane bending), 648 cm^{-1} (C—Br stretch). Anal. Calcd for $C_{16}H_{14}Br_2$: C, 52.49; H, 3.82; Br, 43.69. Found: C, 52.54; H, 3.76; Br, 43.71.

Stilbene-2,5-dimethylene Bis(tetrahydrothiophenium bromide) (3). 2,5-Bis(bromomethyl)stilbene (4.0 g, 11 mmol) was dissolved in a mixture of 30 mL of methanol and 5.8 mL of tetrahydrothiophene. The mixture was stirred at 50 °C for 24 h. About three-quarters of the liquid was removed by distillation using a rotatory evaporator.

Cold acetone was poured into the concentrated solution, precipitating out the product. The solid was collected on a filter followed by washing with cold acetone. The solid was redissolved in a small volume of ethanol. The product was reprecipitated by addition of cold acetone and then was dried in a vacuum oven for 24 h. The yield was 5.2 g (87%).

^{1}H-NMR (D_2O): δ 7.3–7.9 (m, 10H, Ar and CH=CH), 4.8 (s, 2H, CH_2 Ph *ortho* to the styryl group), 4.6 s, 2H, CH_2Ph *meta* to the styryl group), 3.4–3.6 (m, 8H; S^+—CH_2), 2.4–2.2 (m, 8H, CH_2). IR (KBr): 1633 (C=C stretch), 1603 and 1497 (Ar C=C stretch), 966 (*trans* vinylene =C—H out-of-plane bending), 743 and 694 cm^{-1} (monosubstituted aromatic C—H out-of-plane bending).

Precursor Polymers 5. Bis(sulfonium salt) **3** (1.35 g, 2.5 mmol) was dissolved in 50 mL of a *N,N*-dimethylformamide/water (v/v = 2/8) mixture of 0 °C. With vigorous stirring 1.8 mL of 0.8 M aqueous NaOH (0.58 equiv) was added. Just after the addition of NaOH solution was complete, an additional 20 mL of DMF was added to prevent polymers formed from precipitation. The mixture was stirred about an additional 4 min and then was neutralized with 1 M aqueous HCl.

The conversion was calculated from the amount of HCl required for neutralization and was found to be 85.7%. After neutralization, the mixture was dialyzed for 3 days against distilled water using a dialysis tube (Sigma) with a molecular weight cutoff at 12 000. Copolymers were prepared in a similar way by varying the mole ratio of **3** and **4** in the feed. When the mole ratios of **4** to **3** were 90:10, 75:25, and 50:50 in the feed, the conversions were found to be 66, 68, and 78%, respectively. Copolymers remained soluble in the solution of a DMF/H_2O (v/v = 2/8) mixture, and therefore, addition of additional DMF was not required during polymerization.

Poly[(2-(2-phenylethenyl)-1,4-phenylene)vinylene] (PPEPV) and Copolymers [Poly(PEPV-*co*-PV)] (6). The films of the precursor polymers were cast either from DMF solution of the homopolymer or from the aqueous solutions of the copolymers. The films were clamped between two Teflon sheets in a glass tube and subjected to thermal elimination in vacuo (10^{-2} Torr) at 180 °C for 8 h, at 230 °C for 4 h, and finally at 240 °C for 10 min.

When required, the films (ca. 1 cm × 5 cm strips) were uniaxially stretched manually at 100–120 °C over a zone-heating Pyrex tube before the final thermal elimination. A zone-heating apparatus was constructed using a Pyrex tube (diameter, 4 cm; length, 20 cm) through which a resistive nichrome heating wire was fixed. A thermocouple was attached to the central surface of the tube to monitor the temperature. Power was supplied to the nichrome wire using a transformer. A film was slowly stretched by hand to the desired draw ratio on the tube surface preheated to 100–120 °C. The thickness of the final polymer films ranged from about 5 to 50 μm. Actual compositions of the copolymers are shown in Table 1.

Synthesis of Precursor Homopolymer and Copolymers of Poly[{(2-methoxy-5-(2-phenylethenyl)-1,4-phenylene)vinylene}-*co*-1,4-phenylenevinylene]. *trans*-4-Methoxy-2,5-dimethylstilbene (8). Sodium (6.30 g, 0.274 mol) was dissolved in 250 mL of absolute ethanol. To this solution was added 71.04 g (0.183 mol) of benzyltriphenylphosphonium chloride. After the solution became clear, 30.0 g (0.183 mol) of 2,5-dimethylanisaldehyde was added. The mixture was then refluxed for 12 h, after which it was poured into 1.5 L of distilled water. The precipitate was washed twice with distilled water and dried in a vacuum oven. The crude product was subjected to *n*-hexane extraction. The volume of the *n*-hexane solution was reduced by distillation under a reduced pressure. Methanol was added to the solution, precipitating out the product, which was collected and recrystallized from methanol. The product yield was 21.0 g (48.1%), mp 67 °C.

^{1}H-NMR (acetone-*d*$_6$): δ 7.2–7.63 (m, 7H, Ar), 7.00 and 6.70 (s, 2H, CH=CH), 3.77 (s, 3H, OCH_3), 2.27 (s, 6H, CH_3). IR (KBr): 3041 (Ar C—H stretch), 1985 (aliphatic C—H stretch), 1616 and 1467 (Ar C=C stretch), 972 cm^{-1} (*trans* vinylene =C—H out-of-plane bending). Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.93; H, 7.57.

2,5-Bis(bromomethyl)-4-methoxystilbene (9). 4-Methoxy-2,5-dimethylstilbene (**8**; 18.72 g, 7.85 × 10^{-2} mol), *N*-bromosuccinimide (29.35 g, 0.165 mol), and benzoyl peroxides (6.50 g, 26.8 mmol) were dissolved in 250 mL of CCl_4. The mixture was refluxed under a N_2 atmosphere for 4 h. The succinimide formed was removed by filtration, and the CCl_4 in the filtrate was evaporated using a rotatory evaporator. To the sticky residue was added 10 mL of an ethyl acetate/*n*-hexane (v/v = 1/1) mixture, which resulted in the formation of the precipitate. The precipitate was collected on a filter and recrystallized from ethyl acetate. The yield was 14.0 g (45%), mp 173–174 °C.

^{1}H-NMR ($CDCl_3$): δ 7.17–7.56) (m, 7H, Ar), 7.03 and 7.779 (s, 2H, CH=CH), 4.50 (d, 4H, CH_2Br), 3.83 (s, 3H, OCH_3). IR (KBr): 1610 and 1467 (Ar C=C stretch), 1217 (CH_2Br bending), 966 (*trans* vinylene =C—H out-of-plane bending), 692 cm^{-1} (CH_2—Br stretch). Anal. Calcd for $C_{17}H_{16}Br_2O$: C, 51.54; H, 4.07. Found: C, 51.21; H, 4.02.

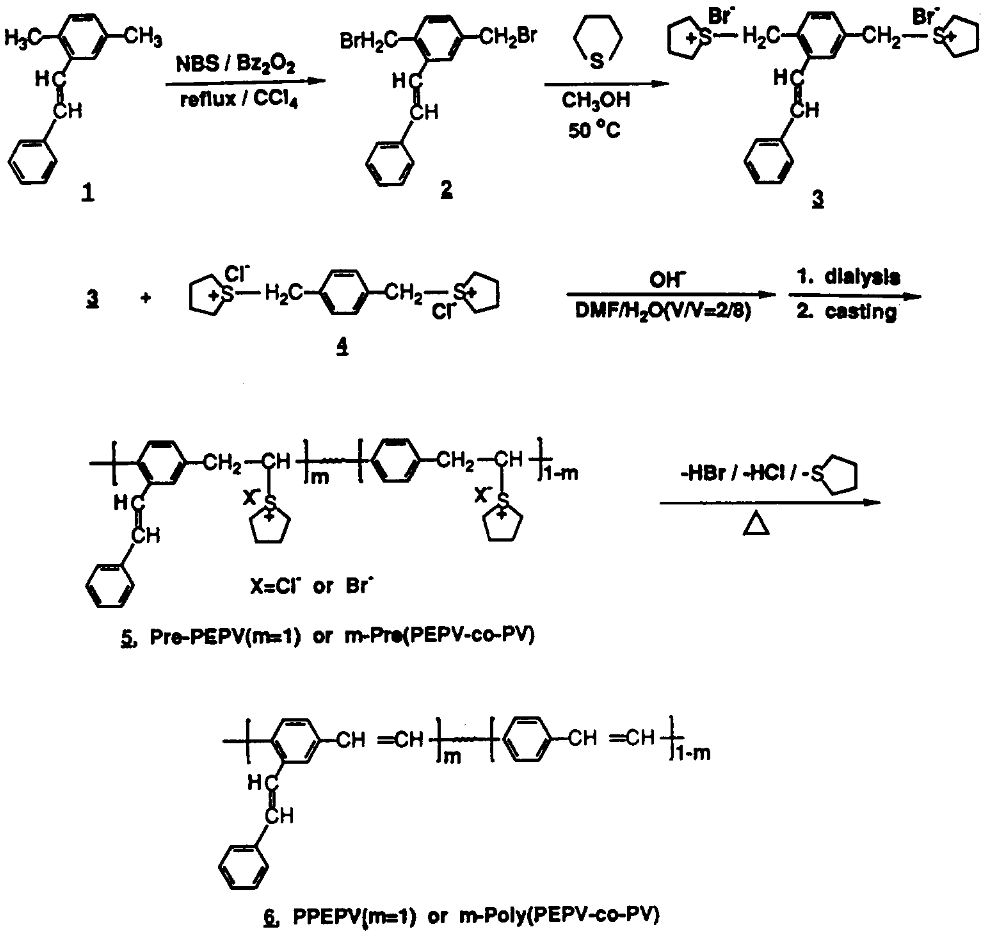
(2-Methoxy-5-(2-phenylethenyl)phenylene)-1,4-dimethylene Bis(tetrahydrothiophenium bromide (10). 2,5-Bis(bromomethyl)-4-methoxystilbene (**9**; 5.0 g, 1.26 × 10^{-2} mol) and 8.90 g (0.101 mol) of tetrahydrothiophene were reacted in 80 mL of methanol at 50 °C for 24 h. The reaction solvent was removed by distillation under reduced pressure. Addition of cold dry acetone to the residue precipitated out the product. The crude product was redissolved in 10 mL of dry methanol and then cold dry acetone was added to precipitate the product. The precipitate was thoroughly washed with cold dry acetone and dried in vacuo. The product yield was 5.99 g (83.0%).

^{1}H-NMR (D_2O): δ 7.07–7.82 (m, 9H, Ar and CH=CH), 3.96 (s, 3H, OCH_3), 3.35 (m, 8H, S^+—CH_2), 2.30 (m, 8H, CH_2). IR (KBr): 300(Ar C—H stretch), 2947 (aliphatic C—H stretch), 1620 (ethylene C=C stretch), 151(Ar C=C stretch), 972 cm^{-1} (*trans* vinylene =C—H out-of-plane bending).

Precursor Polymers of Poly[(2-methoxy-5-(2-phenylethenyl)-1,4-phenylene)-vinylene] and Copolymers 11. The bis(sulfonium salt) monomer *10* (0.73 g, 1.3 mmol) prepared above was dissolved in 10 mL of a mixture of distilled water and DMF (v/v = 1/1). To this solution was added at room temperature 1.39 mL of 0.918 M tetramethylammonium hydroxide. The mixture was stirred for 1.5 h at room temperature. And then the solution was titrated to pH 7.0 with 1 M HCl. The conversion estimated from the quantity of HCl solution required for neutralization was 77%. After neutralization, the whole mixture was dialyzed against distilled water for 3 days using a dialysis tube (Sigma) with a molecular weight cutoff of 12 000. The precursor copolymers were synthesized in the same way by varying the feed mole ratio of the two sulfonium salts **10**:**4** = 50:50, 33:67, 20:80, and 10:90. The conversion for each case was 78, 87, 86, and 85%.

Poly[(2-methoxy-5(2-phenylethenyl)-1,4-phenylene)vinylene] (PMPEPV) and poly[{(2-methoxy-5-(2-phenylethenyl)-1,4-phenylene)vinylene}-*co*-1,4-phenylenevinylene] (Poly(MPEPV-*co*-PV)) (12). The precursor polymers were cast into films at 0.5-Torr pressure from the dialyzed aqueous solutions. The films were subjected to thermolysis for 1 h at 200 °C and then 5 h at 230 °C in vacuo (10^{-2} Torr). The thickness of the final polymer films ranged from 7 to 37 μm. Actual compositions of the copolymers are shown in Table 2.

Scheme 1. Synthetic Route to Poly[(2-(2-phenylethenyl)-1,4-phenylene)vinylene] (PPEPV) and Poly[{(2-(2-phenylethenyl)-1,4-phenylene)vinylene}-*co*-1,4-phenylenevinylene] [poly(PEPV-*co*-PV)]



Synthesis of the Precursor Homopolymer of PPV and Its Conversion to PPV. The synthetic method of the PPV precursor was the same as described earlier by us.[20] The only change made was a shorter polymerization time (20 min). Conversion of the precursor polymer to PPV was conducted in vacuo (10^{-2} Torr) at 300 °C for 1 h.

Characterization. The structure of the intermediates and the precursor and final polymers were verified by IR (Alpha Centauri FT-IR of Mattson Co.) and NMR (AM 300 spectrometer of Bruker) spectroscopy and by elemental analysis (Perkin-Elmer Model 240 elemental analyzer). The UV-vis spectrum was recorded on a Hewlett Packard 8452A spectrophotometer. Solution viscosity values of the precursor polymers were measured at 30 °C in the presence of 0.05 M Na_2SO_4. An Ostwald-Fenske type viscometer was used. Thermal analysis of the precursor polymers was performed in a N_2 atmosphere on a differential scanning calorimeter (DuPont 910) and also on a thermogravimetric analyzer (Mettler 3000) with a heating role of 10 °C/min.

Doping and Electrical Conductivity Measurement. Conductivities of doped polymer films were measured by the usual four-in-line probe method.[24] The polymer films attached to the platinum wire electrodes using carbon paste in a vacuum line were doped at room temperature with I_2 vapor at the pressure of 10^{-3} Torr. The samples were doped until they revealed a maximum conductivity. Doping of the polymer films with $FeCl_3$ was conducted by immersing the films in a nitromethane solution saturated with the salt. The film surface was rinsed with fresh nitomethane before applying the vacuum. And the degree of doping in both cases was calculated from the weight pickup.

Results and Discussion

Syntheis of Polymers. Poly[(2-(2-phenylethenyl)-1,4-phenylene)vinylene] (PPEPV) and the copolymers containing 1,4-phenylenevinylene (PV) units were prepared via the route shown in Scheme 1. The symbol of "*m*" in the equations stands for the mole fraction of the structural unit carrying the 2-phenylethenyl substituent.

2,5-Dimethylstilbene (1) was converted to the bis(bromomethyl) compound 2 by reacting with *N*-bromosuccinimide in the presence of benzoyl peroxide. And then compound 2 was reacted with tetrahydrothiophene in methanol to form the bis(sulfonium salt) monomer 3. Since sulfonium salt monomer 3 is only slightly soluble in water, polymerization of 3 or the mixture of 3 and 4[4,5] was conducted in a mixed solvent of DMF and H_2O (v/v = 2/8) in the presence of 0.58 equiv of NaOH. The polymerization results are summarized in Table 1. The monomer conversions to precursor polymers were relatively high in spite of rather short reaction times; the conversion decreased somewhat with decreasing mole fraction of monomer 3 in the feed.

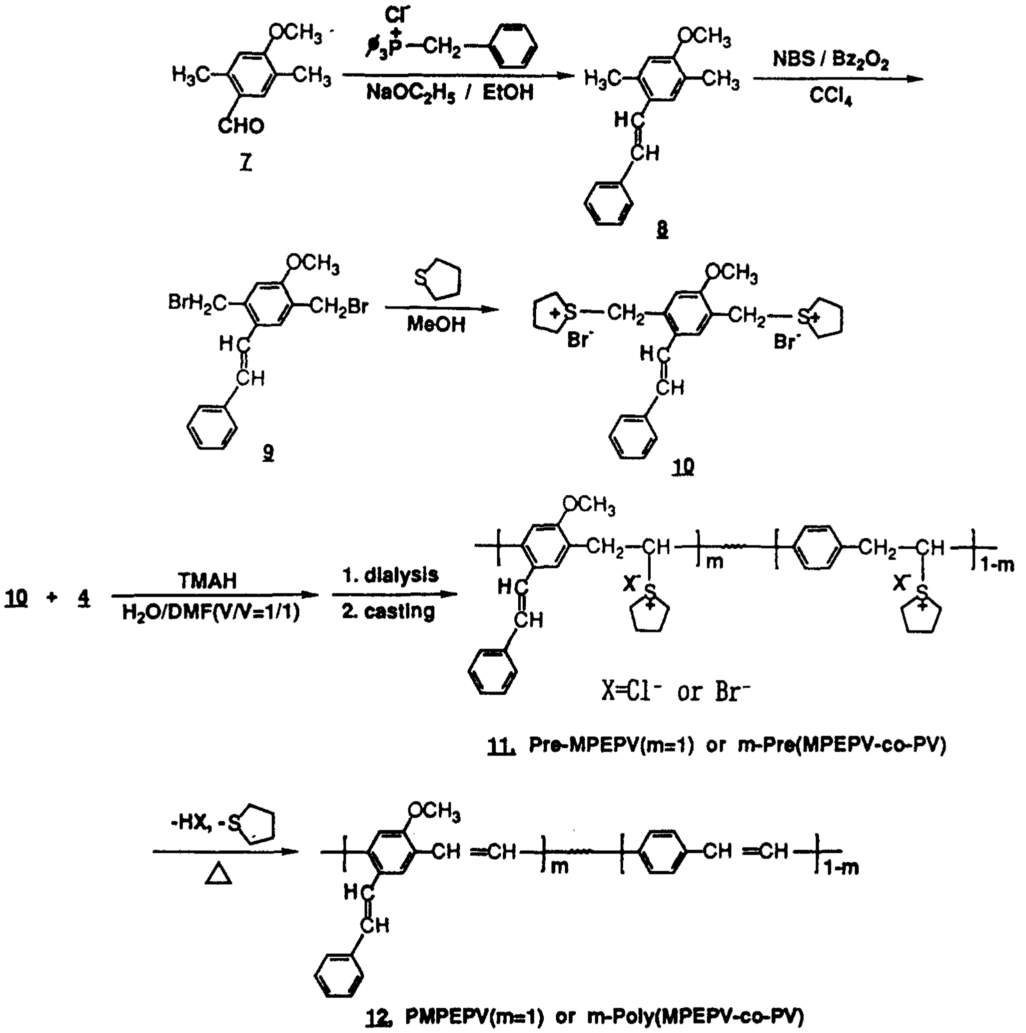
The solution viscosity values of the precursor polymers measured for aqueous solutions in the presence of Na_2SO_4 are very high with the exception of that of PPEPV (0.65) and increase steadily with the content of unsubstituted monomer 4 in the feed. The polymer yield is higher for PPEPV (47%) than the yields for the copolymers containing lower levels of the substituted PEPV unit. For example, the yields of 38-poly(PEPV-*co*-PV) and 15-poly(PEPV-*co*-PV) were 34 and 35%, respectively. The polymer yields were estimated from the weights of polyconjugated polymers obtained after thermal elimination of the dialyzed precursors. Since the precursor polymers were dialyzed against the distilled water using a dialysis tube with a molecular weight cutoff of 12 000, the highest polymer yield for PPEPV tells us that a higher fraction of pre-PEPV 5 formed was of a molecular weight

Table 1. Synthesis of PPEPV and Poly(PEPV-*co*-PV)

polymer[a]	feed ratio[b] 3:4	actual ratio[b] m:1 − m	monomer conversion (mol %)	η_{inh}[c] (dL/g)	polymer[d] yield (%)
PPEPV	100:0	1.00:0	85.7	0.65	47
57-poly(PEPV-*co*-PV)	50:50	0.57:0.43	78.3	2.46	44
38-poly(PEPV-*co*-PV)	25:75	0.38:0.62	68.1	4.57	34
15-poly(PEPV-*co*-PV)	10:90	0.15:0.85	66.4	8.40	35

[a] The numbers in the experssion of copolymers indicate the mole percent of the PEPV unit incorporated into the final polymers. [b] Mole ratios. [c] The viscosity values of precursor polymers were measured for aqueous solutions of 2 g/dL at 30 °C in the presence of Na_2SO_4. [d] The values were estimated from the weight of the final polyconjugated polymers obtained after thermolysis of the dialyzed precursor polymers.

Scheme 2. Synthetic Route to Poly[(2-methoxy-5-(2-phenylethenyl)-1,4-phenylene(vinylene) [PMPEPV] and Poly[{(2-methoxy-5-(2-phenylethenyl)-1,4-phenylene)vinylene-*co*-1,4-phenylenevinylene] [poly(MPEPV-*co*-PV)]



higher than 12 000 when compared with copolymer precursors, i.e., pre(PEPV-*co*-PV)s.

The compositions of the copolymers were determined spectroscopically from their absorbance at 296 nm, and a calibration curve, was constructed to show a relationship between the composition of precursor mixtures consisting of PPEPV (i.e., pre-PEPV) and PPV precursors and their absorbance at 296 nm. The PPV precursor polymer (i.e., 5 with n = 0) was separately prepared under the same polymerization conditions as described in the Experimental Section. The compositions of the copolymers thus estimated are included in Table 1. The data in Table 1 clearly show that the copolymers contain consistently higher levels of the 2-phenylethenyl substituted monomer unit than the mole fraction of the substituted monomer (3) in the feed. This suggests that the substituted monomer (3) is more reactive than the unsubstituted monomer (4). This is in line with our earlier observations[13-15] that the electron-donating substituents on the phenylene ring of the bis(sulfonium salt) monomers enhance the reactivity in copolymerizations. In general, film quality such as uniformity and integrity was superior when the copolymers contained higher levels of the unsubstituted 1,4-phenylenevinylene (PV) unit.

The synthetic scheme for the preparation of poly[(2-methoxy-5-(2-phenylethenyl)-1,4-phenylene)vinylene] (PMPEPV) and the copolymers [poly(MPEPV-*co*-PV)] containing the PV unit is shown in Scheme 2.

In order to prepare compound 8, 2,5-dimethylanisaldehyde prepared separately from 2,5-dimethylanisole and *N*-phenyl-*N*-methylformamide via the Vilsmeier–Haack reaction[25,26] was condensed with benzyltriphenylphosphonium chloride in the presence of sodium ethoxide (Wittig reaction).[27,28] Compound 8 was then subjected to benzylic bromination using *N*-bromosuccinimide. Bis(bromomethyl) compound 9 was converted to monomer

Table 2. Synthesis of PMPEPV and Poly(MPEPV-*co*-PV)

polymer[a]	feed ratio[b] 10:4	actual ratio[b] m:1 − m	monomer conversion (mol %)	η_{inh}[c] (dL/g)	polymer[d] yield (%)
PMPEPV	100:0	1.00:0	76.5	0.41	70
62-poly(MPEPV-*co*-PV)	50:50	0.62:0.38	77.8	0.36	63
25-poly(MPEPV-*co*-PV)	33:67	0.25:0.75	86.6	1.40	62
17-poly(MPEPV-*co*-PV)	20:80	0.17:0.83	86.2	2.74	56
7-poly(MPEPV-*co*-PV)	10:90	0.07:0.93	85.0	9.20	38
PPV	0:100	0:1.00	38.9	2.10	20

[a] The numbers in the experssion of copolymers indicate the mole percent of the MPEPV unit incorporated into the final polymers. [b] Mole ratios. [c] The viscosity values were measured for aqueous solutions of 2 g/dL at 30 °C in the presence of Na_2SO_4. [d] The values were estimated from the weight of the final polyconjugated polymers obtained after thermolysis of the dialyzed precursor polymers.

10 by reacting with tetrahydrothiophene.

Homopolymerization of monomer **10** as well as copolymerization of mixtures of monomers **10** and **4** was conducted in a mixed solvent of H_2O/DMF (v/v = 1/1) in the presence of tetramethylammonium hydroxide. After the polymerization reactions were stopped by neutralizing the mixture with 1 M HCl, the whole mixture was dialyzed in the same way as already described in the synthesis of pre-PEPV and copolymer precursors **5**. The polymerization results are summarized in Table 2.

Monomer conversions are high. And the polymer yields estimated from the weights of the final polyconjugated polymers obtained through thermolysis of dialyzed precursor polymers diminish with the increasing fraction of unsubstituted monomer **4** in feed. This is in direct contrast to the higher solution viscosity values of the precursor polymers containing a higher fraction of the unsubstituted PV monomer unit. In other words, we observe that a parallelism does not hold between the solution viscosity values of the precursors and the polymer yields in the previous and present series of copolymers. One of the possible conjectures to explain this phenomenon can be put forward on the basis of the poor solubility of the precursor polymers containing higher levels of the styryl substituent. That is, the low solution viscosity values for the precursor polymers of PPEPV and PMPEPV could have at least partially been derived from their poor solubility in water due to the presence of the hydrophobic styryl structure in the repeating unit. When the viscosity of the precursor polymer of PPEPV (i.e., pre-PEPV) was measured in DMF in the absence of any salt, the inherent viscosity value obtained was 37, whereas in water it was only 1.8. Therefore, we believe that the solvent effect might have caused the lower viscosity values for the precursor polyelectrolytes of the homopolymers and the copolymers containing high levels of the substituted unit.

Thermal Elimination of Precursor Polymers to the Final Polyconjugated Polymers. Thermal properties of the precursor polymers were examined under a N_2 atmosphere by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The heating rate was maintained at 10 °C/min for both analyses, and some of the representative thermograms are shown in Figure 1 and 2.

As one can see from their thermograms, both series of precursor polymers undergo a strong endothermic weight loss around 100 °C due to the evaporation of adsorbed water followed by further endothermic weight loss over a wider temperature range (ca. 100–200 °C). The latter arises from thermolysis of the precursor polyelectrolytes to the final polyconjugated polymers, resulting from the loss of hydrogen halide(s) and tetrahydrothiophene. They finally exhibit a continuous weight loss starting from about 300 °C (for PPEPV and PMPEPV) or higher temperatures (for copolymers) depending on their composition. The weight loss at a high temperature is ascribed to thermal degradations. The actual thermolysis conditions for the present precursor polymers described in the Experimental

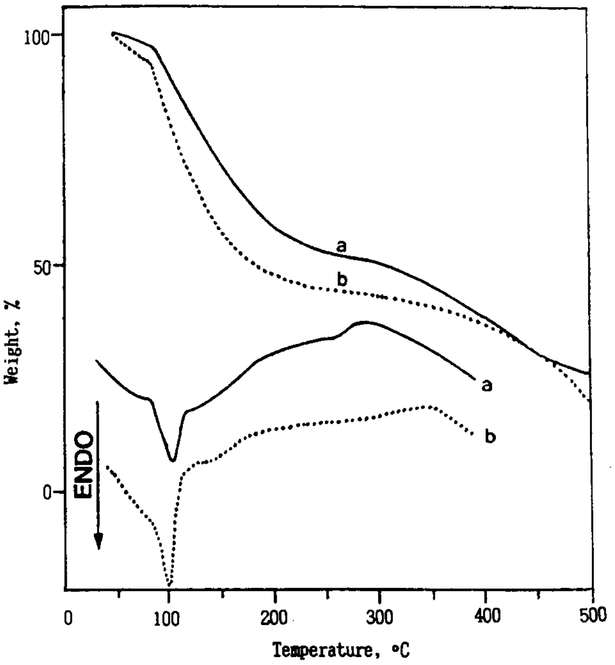


Figure 1. TGA and DSC thermograms of the precursor polymers of (e) PPEPV and (b) 38-poly(PEPV-*co*-PV).

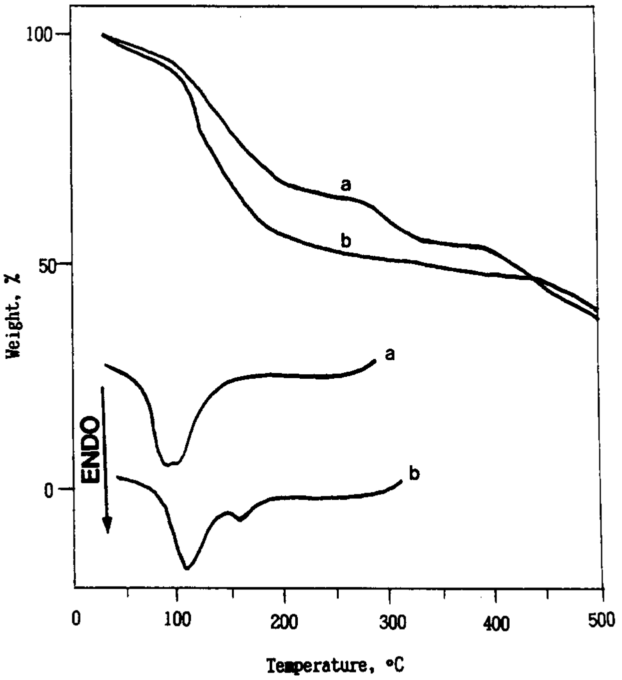


Figure 2. TGA and DSC thermograms of the precursor polymers of (a) PMPEPV and (b) 25-poly(MPEPV-*co*-PV).

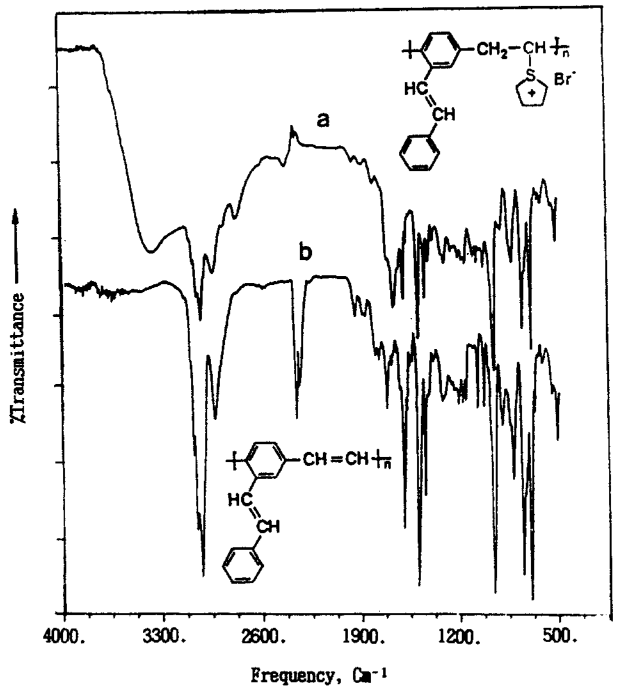


Figure 3. IR spectra of (a) the precursor homopolymer Pre-PEPV and (b) the corresponding polyconjugated polymer, PPEPV.

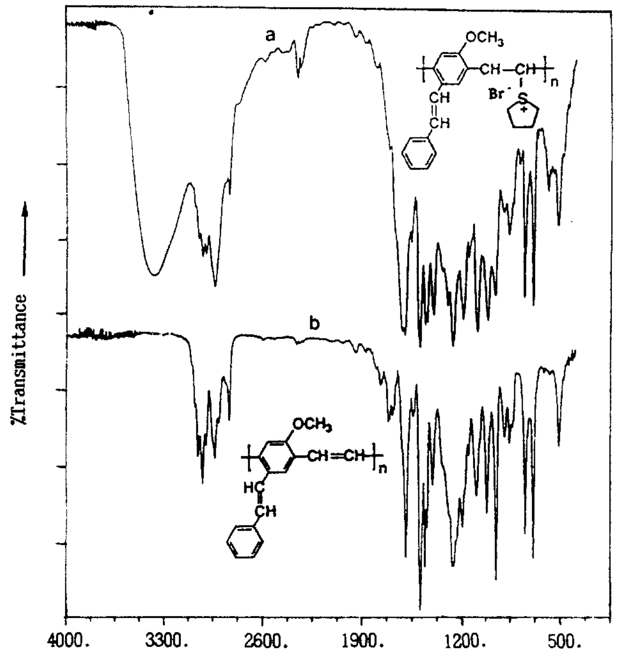


Figure 4. IR spectra of (a) the precursor homopolymer Pre-MPEPV and (b) the corresponding polyconjugated polymer, PMPEPV.

Section were selected after examining the IR spectra of the final polymers obtained under various conditions.

The FT-IR spectra of the precursor homopolymers and the final polyconjugated polymers obtained from them are shown in Figure 3 and 4. The broad and strong absorptions by the precursor polymers at 3100–3600 cm^{-1} are due to the presence of adsorbed water. Since the precursor polymers contain stilbene moieties, their IR spectra reveal a sharp absorption peak at 970 cm^{-1} due to the out-of-plane bending vibration of the *trans*-vinylene C—H bonds.[29,30] The copolymers containing higher levels of 2-phenylethenyl-substituted units, for example, PPEPV (Figure 3b), 57-poly(PEPV-*co*-PV) (Figure 5a), PMPEPV (Figure 4b), and 25-poly(MPEPV-*co*-PV (Figure 5b), exhibit three sharp absorption peaks at about 1500, 750, and 690 cm^{-1}. The first one corresponds to the absorption mode due to aromatic C=C stretching and the other two to out-of-plane wagging vibrations of aromatic C—H bonds.[31] These absorption peaks appear in the precursor polymers as well as in the final eliminated polymers. In addition, in the case of PMPEPV and poly-(MPEPV-*co*-PV) (Figure 5b) we can observe another strong absorption peak at 1285 cm^{-1}, which corresponds to the C—O stretching mode between the aromatic carbon and methoxy oxygen.

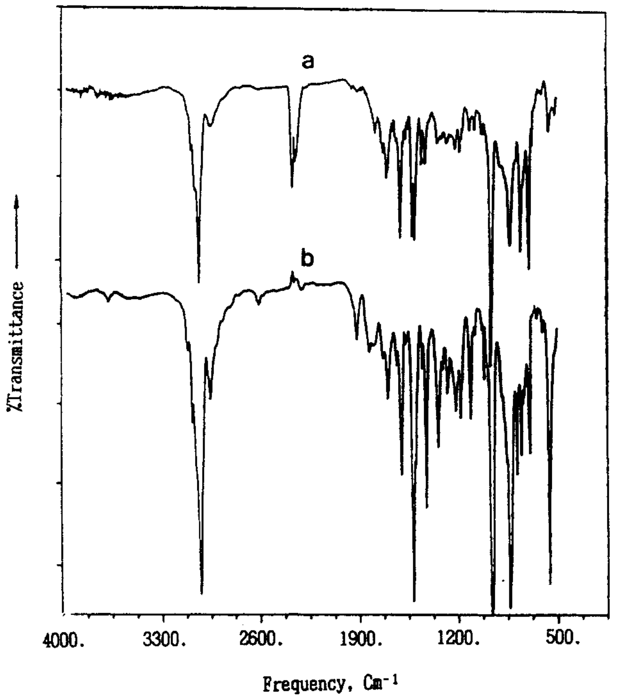


Figure 5. IR spectra of (a) 57-poly(PEPV-*co*-PV) and (b) 25-poly(MPEPV-*co*-PV).

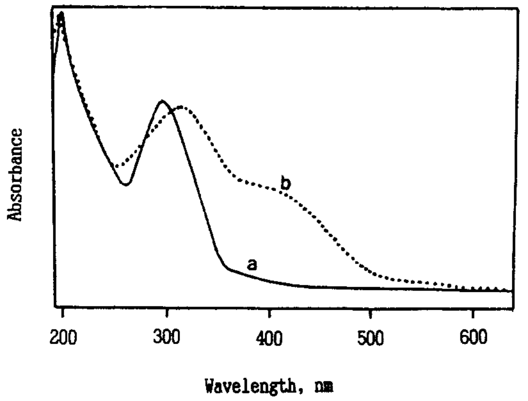


Figure 6. UV–vis spectra of (a) Pre-PEPV and (b) PPEPV.

UV–Vis Spectral Characteristics of the Polymers. Figure 6 compares UV–vis spectra of the precursor polymer (pre-PEPV) and PPEPV. And Figure 7 shows a series of spectra obtained for poly(PEPV-*co*-PV)s. The precursor polymer exhibits an absorption peak over 250–350 nm whose λ_{max} is located at 296 nm, which is practically the same as observed for *trans*-stilbene.[32] The unique absorption of the precursor polymers at this position enabled us to determine spectroscopically the actual compositions of the copolymers, as summarized in Table 1.

PPEPV obtained from the thermolysis of the precursor polymer shows two major absorptions, one around 314 nm and another around 405 nm. The first one can be taken as an absorption arising from the π–π^* transition of the

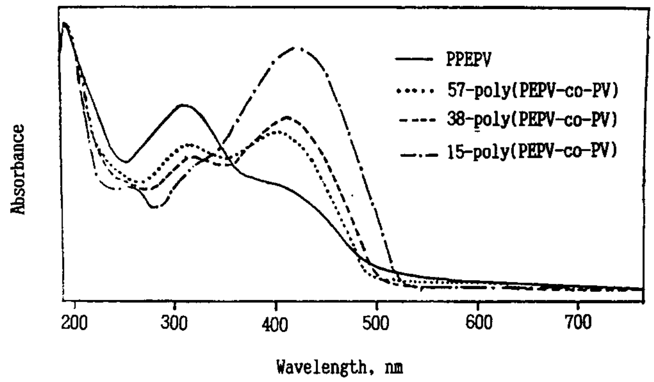


Figure 7. UV–vis spectra of poly(PEPV-*co*-PV)s.

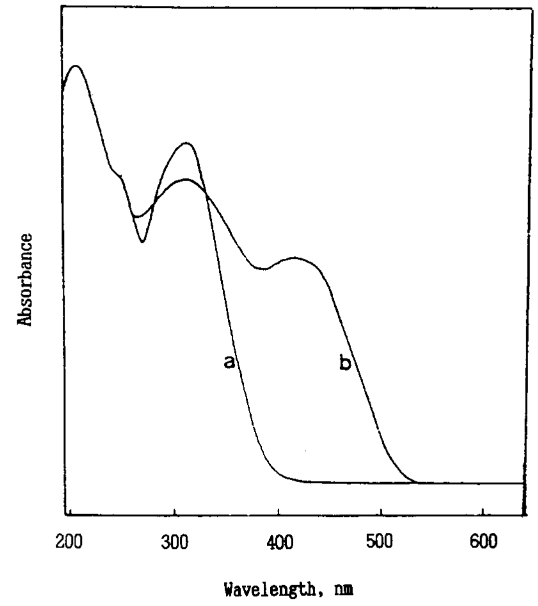


Figure 8. UV–vis spectra of (a) Pre-MPEPV and (b) PMPEPV.

trans-stilbene-like structure involving the 2-phenylethenyl group, while the second one can be due to the π–π^* transition of the π-electron system along the main chain. It is very interesting to note that the original absorption of λ_{max} at 296 nm in the precursor polymer has been shifted only slightly to 314 nm and, moreover, the π-system of the main chain reveals an independent absorption whose λ_{max} position is located at 405 nm. The λ_{max} position for the π–π^* transition, however, has moved slightly to a shorter wavelength when compared with that (ca. 420 nm)[14] of PPV.

According to the spectra of copolymers, i.e., poly(PEPV-*co*-PV)s, shown in Figure 7, the λ_{max} position for the π–π^* transition of the main chain π-system appears to shift steadily but only slightly to a longer wavelength with increasing content of the unsubstituted PV unit. The λ_{max} position of 15-poly(PEPV-*co*-PV) is 420 nm, which is about the same as for PPV. Such spectral changes imply that there is only a meager perturbation or cross-conjugation between the main chain π-system and side chain styryl π-electrons.

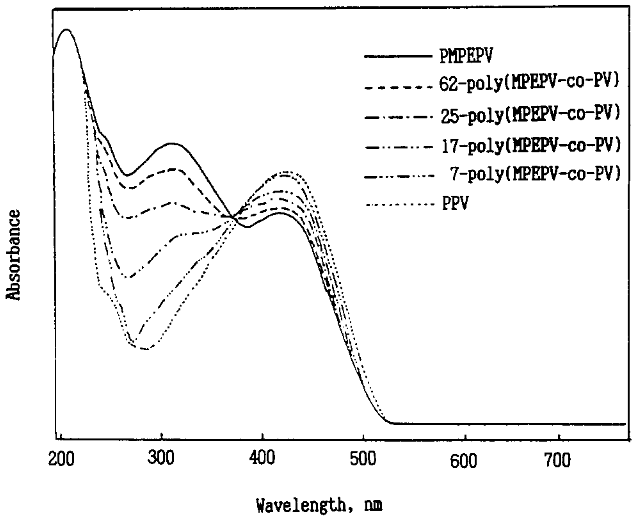


Figure 9. UV–vis spectra of poly(MPEPV-*co*-PV)s.

We observe similar phenomena for PMPEPV and copolymers. Figure 8 compares the UV–vis absorption spectra of PMPEPV and its precursor. The precursor shows an absorption of λ_{max} at 310 nm, which corresponds to a π–π^* transition of the *trans*-4-methoxystilbene moeity.[33] The formation of a polyconjugated main chain through thermolysis of the precursor brings about an additional absorption peak whose λ_{max} is positioned at 420 nm. This additional absorption is due to a π–π^* transition of π-electrons in the main chain. Figure 9 shows absorption spectra of poly(MPEPV-*co*-PV)s, and the general feature of the copolymers' spectra is very similar to the features of poly(PEPV-*co*-PV)s, as shown in Figure 7. Here again, utilizing the absorption intensity at 310 nm, we could determine the actual compositions of the precursor polymers. And the values agreed with those estimated from elemental analysis.

Electrical Conductivity. Electrical conductivities of the polymers, before as well as after having been doped, were measured using a four-in-line probe method.[24] Table 3 summarizes draw ratios, degrees of doping, and the maximum conductivities of poly(PEPV-*co*-PV)s. Doping with I_2 was performed in a vacuum chamber at the pressure of 10^{-3} Torr. For $FeCl_3$ doping an acetonitrile solution was used at room temperature. All of the undoped polymer films had conductivities less than 10^{-7} s cm^{-1}, but their conductivities increased rapidly on doping. The data shown in Table 3 reveal a couple of very interesting points. The degree of doping increases steadily with increasing content of PEPV unit for both I_2 and $FeCl_3$ dopants. But, surprisingly enough, the conductivity value decreases as the content of PEPV unit in the copolymers is increased. The PPEPV film, when doped with I_2, showed a maximum conductivity of 6.1×10^{-5} S cm^{-1} for the unstretched sample and 2.7×10^{-4} S cm^{-1} for the stretched sample ($L/L_0 = 6$) along the drawing direction. The stronger oxidant $FeCl_3$ produced conductivities considerably higher; the conductivities of $FeCl_3$-doped samples were higher just about by 1 order of magnitude than those of I_2-doped films. The copolymer containing 15 mol % of PEPV unit, i.e., 15-poly(PEPV-*co*-PV), could be only slightly doped either with I_2 or with $FeCl_3$, but its electrical conductivity was the highest among the compositions examined in the present series. The conductivity of the $FeCl_3$-doped sample stretched to a draw ratio of $L/L_0 = 6$ was 5.7 S cm^{-1}.

The seemingly anomalous, inverse relationship between the degrees of doping and the conductivity values of this series certainly appears perplexing. We believe that the possible charge-transfer type interaction between the dopants and the pendant substituent groups (—CH═CH—Ph) is the major reason for this observation.[34,35] The pendant group can form, a π-complex with the dopants of Lewis acid character, which is expected to increase the apparent degree of doping for the copolymers containing a greater amount of the pendant group. This, however, is expected to convert the electron-donating

Table 3. Maximum Conductivities of PPEPV and Poly(PEPV-*co*-PV)s

polymer[a]	dopant	draw ratio L/L_0	deg of doping dopant/repeat unit (I_3^- or $FeCl_4^-$/RU)[b]	conductivity (S cm^{-1})
PPEPV	I_2	1	0.34	6.1×10^{-5}
		6	0.37	2.7×10^{-4}
	$FeCl_3$	1	0.31	7.5×10^{-4}
		6	0.33	2.4×10^{-3}
57-poly(PEPV-*co*-PV)	I_2	1	0.18	1.4×10^{-4}
		6	0.22	7.2×10^{-4}
	$FeCl_3$	1	0.20	1.5×10^{-3}
		6	0.25	7.3×10^{-3}
38-poly(PEPV-*co*-PV)	I_2	1	0.13	6.3×10^{-4}
		6	0.10	4.1×10^{-3}
	$FeCl_3$	1	0.08	7.0×10^{-3}
		6	0.08	4.7×10^{-2}
15-poly(PEPV-*co*-PV)	I_2	1	0.04	2.0×10^{-2}
		6	0.05	2.4×10^{-1}
	$FeCl_3$	1	0.03	2.4×10^{-1}
		6	0.04	5.7

[a] The numbers in the expression of copolymers indicate the mole percent of the PEPV unit in the final polymers. [b] RU stands for the average repeating unit.

Table 4. Elemental Analysis and Maximum Conductivities of PMPEPV and Poly(MPEPV-*co*-PV)s

	elemental content (theoretical content) (wt %)		max conductivity (S cm^{-1})		deg of doping[c]	
polymer[a]	C	H	I_2	$FeCl_3$	I_2	$FeCl_3$
PMPEPV	87.59 (87.15)	5.91 (6.02)	1.9×10^{-5}	2.2×10^{-4}	0.73	0.23
62-poly(MPEPV-*co*-PV)	88.60 (88.60)	5.14 (6.00)[b]	3.9×10^{-4}	8.7×10^{-3}	0.51	0.13
25-poly(MPEPV-*co*-PV)	91.10 (91.10)	5.87 (5.96)[b]	1.4×10^{-3}	3.6×10^{-2}	0.47	0.13
17-poly(MPEPV-*co*-PV)	91.90 (91.90)	5.80 (5.95)[b]	2.5×10^{-3}	0.31	0.37	0.13
7-poly(MPEPV-*co*-PV)	93.00 (93.00)	5.65 (5.94)[b]	8.6×10^{-3}	5.0	0.32	0.12

[a] The numbers in the expression of copolymers indicate the mole percent of MPEPV unit in the final polymers. [b] Calculated values for the actual compositions estimated from the carbon contents determined by elemental analyses. [c] I_3^- or $FeCl^-_3$ per average repeating unit estimated from the weight gain on doping.

substituents into electron-attracting ones. The latter, in turn, would cause a lower electrical conductivity.

Earlier, we[36] made an analogous observation in the electrical conductivities of poly((2-methyl-5-(methylthio)-1,4-phenylene)vinylene) and copolymers containing PV units. In this case, the n electrons of the methylthio substituents are able to make charge-transfer interactions with the dopants. As a result, the substituent attains electron-attracting power upon doping. Therefore, the degree of doping for poly(2-methoxy-5-(methylthio)-1,4-phenylene)vinylene) was the highest among the series, but its electrical conductivity value was the lowest. In short, the charge-transfer interactions between a dopant and pendant substituent apparently result in a high degree of doping but can diminish electrical conductivity due to the resulting change in the electronic property of the substituent. The higher electrical conductivity values for the stretched films along the drawing direction is very well-known and is due to the improved contact between polymer chains owing to an improved chain orientation.[16,37] Alignment of the conjugated chain sequences may also make charge transport more efficient down the chain direction.[37] For the present series, the conductivity values of the stretched films are 5–10 times those of unstretched ones.

The maximum electrical conductivities of doped poly[(2-methoxy-5-(2-phenylethenyl)-1,4-phenylene)vinylene], PMPEPV, and copolymers containing the unsubstituted PV unit, i.e., poly(MPEPV-*co*-PV)s, are summarized in Table 4. The dependence of electrical conductivity values on composition and the nature of dopants is very similar to those described above for PPEPV and poly(PEPV-*co*-PV)s. Even the inverse relationship between the degree of doping and conductivity is again observed for this series. The electrical conductivities of doped films, however, are higher approximately by 1 order of magnitude than those for the previous series. This means that the methoxy group in the phenylene ring of the (2-methoxy-5-(2-phenylethenyl)1,4-phenylene)vinylene (MPEPV) unit exerts a positive electronic effect on the electrical conductivities of the doped polymers. It is possible here again that the charge-transfer interactions between the methoxystilbene moiety and the dopants reduce the ease of oxidation of the main chain by the oxidants, when the copolymers contain high levels of the methoxystilbene unit.

Lastly, the PPV copolymers containing less than 20 mol % of either (2-(phenylethenyl)-1,4-phenylene)vinylene (PEPV) or (2-methoxy-5-(2-phenylethenyl)-1,4-phenylene)vinylene (MPEPV) comonomer unit exhibit electrical conductivities up to 5 S cm^{-1}. The values are much higher than the conductivity values ($\sim 10^{-5}$ S cm^{-1}) for I_2- or $FeCl_3$-doped PPV measured by us under the same conditions employed for the present investigation. It should be remembered we have earlier reported higher values of electrical conductivity for PPV copolymers containing various substituted PV units regardless of the nature of the substituents, especially when the contents of the comonomers were low. This is explained by the morphological changes and disturbances of the π-electron distribution brought about by the presence of the substituents in the comonomer units.[38,39]

Conclusion

A series of new PPV derivatives and their copolymers consisting of a π-conjugated main chain carrying β-styryl substituents have been synthesized. They were prepared via soluble polyelectrolyte precursors. Their UV–vis spectra clearly show two distinct absorption peaks: one for the π–π^* transition of the main chain π-system occurring over a longer wavelength (λ_{max}: 405–420 nm) region and the other for the π–π^* transitions of the stilbene-like moieties occurring over a shorter wavelength (λ_{max}: 295–310 nm) region. This can be taken as a strong implication that there is only a minor perturbation between the two π-systems and that the linear conjugation is much more efficient in stabilizing the molecules. Since the π-electrons of stilbene moieties reveal only very little cross-conjugation with the π-electrons along the main chain, this type of polymer may be an interesting material that would emit luminescent light of different wavelengths depending on the magnitude of the applied photochemical or electrical energy.

The seemingly contradictory, inverse relation between the degree of doping and the electrical conductivity is ascribed to the charge-transfer type interaction of the pendant, side chain π-systems (π-donor) with the dopant molecules (π-acceptor). The PPV copolymers containing low levels of the 2-phenylethenyl-substituted comonomer unit exhibit much enhanced electrical conductivity, when they were doped with both $FeCl_3$ and I_2. As the content of the substituted comonomer unit increases, the electrical conductivity drops quickly, reaching the conductivities of the homopolymers. The same trend is observed for PMPEPV and poly(MPEPV-*co*-PV)s, and their conductivities after doping are higher than those of the other series due to the positive electronic effect of the methoxy groups on the phenylene units along the main chain.

Acknowledgment. We gratefully acknowledge the support of this work by the Korea Science & Engineering Foundation.

References and Notes

(1) Chiang, C. K.; Drug, M. A.; Gau, S. C.; Heeger, A. J.; Louis, E. J.; MacDiarmide, A. G.; Park, Y. W.; Shirakawa, H. *J. Am. Chem. Soc.* **1978**, *100*, 1013.
(2) Naarmann, H.; Theophilou, N. *Synth. Met.* **1987**, *22*, 1.
(3) Chien, J. C. W. *Polyacetylene-Chemistry, Physics, and Material Science*; Academic Press: New York, 1984.
(4) Gagnon, D. R.; Capistran, J. D.; Karasz, F. E.; Lenz, R. W. *Polym. Bull.* **1984**, *12*, 293.
(5) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Polym. Commun.* **1984**, *25*, 327.
(6) Diaz, A. F.; Kanazawa, K. K.; Gardini, G. D. *J. Chem. Soc., Chem. Commun.* **1979**, 635.
(7) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Organic Molecules and Polymers*; John Wiley and Sons, Inc.: New York, 1991.
(8) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987; Vols. 1 and 2.
(9) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Bruns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.
(10) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47.
(11) Han, C. C.; Lenz, R. W.; Karasz, F. E. *Polym. Commun.* **1987**, *28*, 261.
(12) Liang, W. B.; Lenz, R. W.; Karasz, F. E. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 2867.
(13) Jin, J.-I.; Park, C.-K.; Shim, H.-K; Park, Y.-W. *J. Chem. Soc., Chem. Commun.* **1989**, 1205.
(14) Jin, J.-I.; Park, C.-K.; Shim, H.-K. *Macromolecules* **1993**, *26*, 1799.
(15) Jin, J.-I.; Park, C.-K.; Shim, H.-K. *Polymer*, in press.
(16) Jin, J.-I.; Kim, J.-C.; Shim, H.-K. *Macromolecules* **1992**, *25*, 5519.
(17) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Synth. Met.* **1987**, *17*, 639.
(18) McCoy, R. K.; Karasz, F. E.; Sarker, A.; Lahti, P. M. *Chem. Mater.* **1991**, *3*, 941.
(19) Gregorius, R. Ma.; Lahti, P. M.; Karasz, F. E. *Macromolecules* **1992**, *25*, 6664.
(20) Jin, J.-I.; Yu, S.-H.; Shim, H.-K. *J. Polym. Sci., Part B: Polym. Phys.* **1993**, *31*, 87.
(21) Jin, J.-I.; Lee, Y.-H.; Shim, H.-K. *Macromolecules* **1993**, *26*, 1805.
(22) Jin, J.-I.; Lee, Y.-H. *Mol. Cryst. Liq. Cryst.*, in press: Presented at the German-Korean Symposium on Developments and Trends in Polymer Material Science, Max-Plank Institute für Polymerforschung, Mainz, Germany, June 28–June 30, 1993.
(23) Shim, H.-K.; Hwang, D.-H.; Lee, K.-S. *Makromol. Chem.* **1993**, *194*, 1115.
(24) Harris, F. K. *Electrical Measurement*; John Wiley & Sons, Inc.: New York, 1952. Gagnon, D. G. Ph.D. Thesis, University of Massachusetts, Amherst, MA, Sept 1986, pp 64–67.
(25) *Organic Syntheses*; Rabjohn, N., Ed.; John Wiley & Sons, Inc.: New York, 1963; Collective Vol. IV, pp 331–333.
(26) Vilsmeier, A.; Haack, A. *Chem. Ber.* **1927**, *60*, 119.
(27) Wittig, G.; Schölkopf, U. *Chem. Ber.* **1954**, *87*, 481.
(28) Wittig, G. *Acc. Chem. Res.* **1974**, *7*, 6.
(29) Gagnon, D. R.; Capistran, J. D.; Karasz, R. E.; Lenz, R. W. *Polymer* **1987**, *28*, 567.
(30) Pavia, D. L.; Lampman, G. M.; Kriz, G. S., Jr. *Introduction to Spectroscopy*; W. B. Saunders Co.: Philadelphia, PA, 1979; p 37.
(31) Reference 30, p 39.
(32) Stern, E. S.; Timmons, C. J. *Electronic Absorption Spectroscopy in Organic Chemistry*, 3rd ed.; Edward Arnold Ltd.: London, 1970; p 116.
(33) *Handbook of Spectroscopy*; Robinson, J. W., Ed.; CRC Press: Cleveland, OH, 1974; Vol. II, p 144.
(34) Refer to Yamashita, S. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 1212 (for the charge-transfer complexation between iodine and stilbenes).
(35) For complex formation between iodine and styrenes, refer to: MulliKen, R. S.; Person, W. B. *Molecular Complexes*; Wiley-Interscience: New York, 1969; Chapter 10.
(36) Jin, J.-I.; Park, C.-K.; Shim, H.-K.; *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29* (1), 93.
(37) Karasz, F. E.: Capistran, J. D.; Gagnon, D. R.; Lenz, R. W. *Mol. Cryst. Liq. Cryst.* **1985**, *118* (1–4), 327.
(38) Jin, J.-I.; Shim, H.-K.; Park, C.-K.; Kang, H.-J.; Yu, S.-H.; Kim, J.-C. *Synth. Met.* **1991**, *41*–43, 271.
(39) Jin, J.-I.; Park, C.-K.; Lee, Y.-H. *Macromolecules* **1992**. Kahovec, J., Ed.; VSP: Netherland, 1993; pp 279–290.