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Synthesis and Electrical Conductivities of Poly(2,3,5,6-tetramethoxy-1,4-phenylenevinylene) and a Series of Poly(1,4-phenylenevinylene-*co*-2,3,5,6-tetramethoxy-1,4-phenylenevinylene)s

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ABSTRACT: Poly(2,3,5,6-tetramethoxy-1,4-phenylenevinylene) (PTMPV) and a series of poly(1,4-phenylenevinylene-*co*-2,3,5,6-tetramethoxy-1,4-phenylenevinylene)s (poly(PV-*co*-TMPV)) were prepared via the water-soluble precursor method. They were obtained in film form and could be readily doped with $FeCl_3$. A uniaxially drawn film (draw ratio = 10) of PTMPV can be doped with $FeCl_3$ to give a conductivity of 1.1×10^{-2} S cm^{-1} along the draw direction. In contrast, copolymers containing only intermediate levels of the TMPV unit are dopable with iodine, whereas those containing either a very low or a very high level of the TMPV unit are not dopable with the same dopant. The uniaxially drawn (drawn ratio = 10) copolymer film containing 13.3 mol % of the TMPV unit reveals the highest conductivities among the series, which are 7.2×10^2 and 5.2×10^{-1} S cm^{-1}, respectively, when doped with $FeCl_3$ and I_2. The infrared and UV–vis spectra of TMPV and its copolymers are presented. According to their IR spectra, the copolymers containing TMPV units show the presence of both *trans*- and *cis*-vinylene structures. The IR absorption intensity of the *cis*-vinylene configuration increases with increasing content of the TMPV unit.

Introduction

Poly(1,4-phenylenevinylene) (PPV) and its derivatives can be readily prepared in high molecular weight through the water-soluble precursor route.[1–7] These sulfonium precursor polymers are converted into extended π-conjugated structures by thermal elimination reaction. PPV and its derivatives thus prepared display a wide range of electrical conductivities after doping with various dopants,[1–15] and they also possess high nonlinear optical (NLO) activities.[16–21] Substitution on the phenylene rings of PPV with different electron-donating[6,7,11,14,15] or electron-withdrawing groups[22–24] has a significant influence on the electronic structure of the resulting polymer and thus affects the electrochemical and optical properties thereof.

It is well known that PPV films can be easily doped with strong oxidizing agents such as AsF_5 to produce highly conducting materials,[1,2,4,5] but they cannot be effectively doped with weaker oxidizing dopants such as I_2. Also, the precursor polymer films can easily be stretched before or during the thermal elimination to the final polyconjugated films.[4] Substituted PPV containing electron-donating groups, however, shows easy dopability to I_2, leading to high electrical conductivity.[6,7,11–15] For example, poly(2,5-dimethoxy-1,4-phenylenevinylene)[6,7] (PDMPV) can be readily doped with I_2, producing a conductive material whose maximum conductivity reaches the order of 10^2 S cm^{-1}. The presence of strong electron donors facilitates oxidation of the π-system by weak oxidants.

Poly(2-methoxy-1,4-phenylenevinylene)[14] (PMPV), having only one methoxy substituent on each phenylene ring, was reported to show a diminished susceptibility toward I_2 when compared with PDMPV, which contains two methoxy groups on each phenylene unit. As a result I_2-doped PMPV exhibits a lower electrical conductivity ($\sim$1.0 S cm^{-1}) than I_2-doped PDMPV does.

Up to now, there has not been any report on the synthesis and electrical properties of poly(2,3,5,6-tetramethoxy-1,4-phenylenevinylene) (PTMPV), containing four methoxy groups on each phenylene ring. We, therefore, became interested in synthesis and structural and electrical properties of PTMPV. A series of poly(1,4-phenylene-

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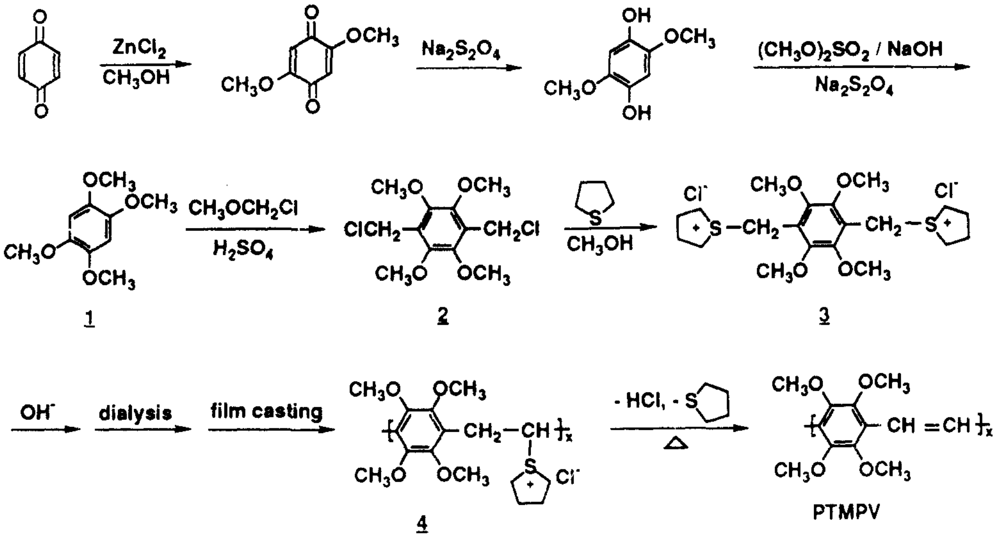
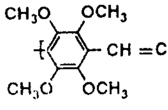
Scheme I

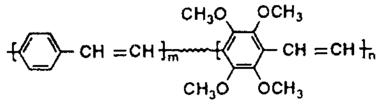


vinylene-*co*-2,3,5,6-tetramethoxy-1,4-phenylenevinylene) (poly(PV-*co*-TMPV)) were also prepared. The dependence of electrical conductivity on polymer composition was investigated. As recently reported by us,[8,22-25] inclusion of a low level of substituted 1,4-phenylenevinylene units in PPV, regardless of the electron-donating or electron-withdrawing power of the substituent, tends to improve the doping ability of I_2 and $FeCl_3$ and thus enhances the electrical conductivity of doped materials.

The structures of PTMPV and copolymers prepared and characterized in this study are as follows:



PTMPV



Poly(PV-co-TMPV)

The values *m* and *n* describe the compositional ratio of the two repeating units in the copolymer. For simplicity, copolymers containing *n* mol % of TMPV unit are designated as *n*-poly(PV-*co*-TMPV) in this article. For example, 75-poly(PV-*co*-TMPV) stands for the copolymer containing 75 mol % of TMPV unit.

Experimental Section

Monomer Synthesis. 1,2,4,5-Tetramethoxybenzene (1) was prepared from benzoquinone following the literature method.[27] 1,4-Bis(chloromethyl)-2,3,5,6-tetramethoxybenzene (2) was prepared by reacting 1,2,4,5-tetramethoxybenzene with chloromethyl methyl ether containing concentrated H_2SO_4. Into a three-neck, round-bottomed flask containing 20 mL of chloromethyl methyl ether were charged 2.0 g (0.01 mol) of tetramethoxybenzene and 4 mL of concentrated H_2SO_4. The mixture was refluxed for 4 h in the flask, which was equipped with a dry ice condenser. The precipitate formed was collected on a filter. White powder was obtained after sublimation at 100 °C under reduced pressure (ca. 0.2 Torr). The yield of 2 was 1.02 g (34%), mp 127.5 °C. ^{1}H-NMR ($CDCl_3$): 4.7 (4 H, s, CH_2Cl), 3.9 ppm (12 H, s, OCH_3). IR (KBr): 1059 (Ar-O-C), 660 cm^{-1} (C-Cl). Anal. Found: C, 49.21; H, 5.41; Cl, 24.24. Calcd: C, 48.81; H, 5.42; Cl, 24.06.

Compound 2 (0.75 g, 1.6 mmol) and tetrahydrothiophene (0.80 g, 9.0 mmol) were reacted for 20 h at 50 °C in 15 mL of methanol, after which the solution was concentrated by distilling out two-thirds of the solvent. The residue was poured into dry acetone at 0 °C, and the white precipitate formed was thoroughly washed with dry acetone and dried. The yield of 3 was 1.12 g (93%). ^{1}H-NMR (D_2O): 4.5 (4 H, s, CH_2Cl), 3.9 (12 H, s, OCH_3), 3.5–3.4 (8 H, m, S^+–CH_2), 2.4–2.2 ppm (8 H, m, CH_2). IR (KBr): 3418 (OH), 1057 cm^{-1} (Ar-O-C). Anal. Found: C, 50.71; H, 6.77; Cl, 15.31; S, 13.30. Calcd: C, 50.95; H, 6.84; Cl, 15.04; S, 13.60.

Compound 5 was prepared similarly from 1,4-bis(chloromethyl)benzene and tetrahydrothiophene following the literature method.[4,26]

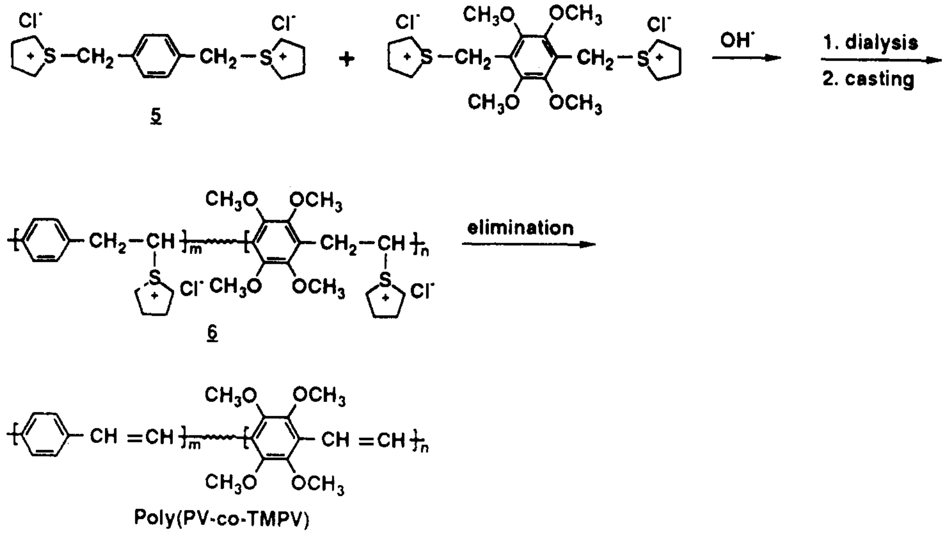
Polymerization. The procedures used for the preparation of homopolymer and copolymers were the same as reported by us[3,8,10,23-25] and others.[1,2,6,7] A mixture of the bis-sulfonium salt monomer (0.4 M) and sodium hydroxide (0.4 M) in aqueous solution was stirred for 0.5 h under a nitrogen atmosphere at 0 °C. A homogeneous viscous polymer solution was obtained. For the copolymers, the total moles of the two bis-sulfonium monomers, 3 and 5, were kept constant (0.4 M), but their mole ratio was varied. At the end of the polymerization the solution was dialyzed against deionized distilled water using a dialysis tube (Sigma) with a molecular weight cutoff at 12 000. A fluorescent, viscous solution was obtained after 3 days of dialysis. The films cast from this precursor polymer solution were subjected to thermal elimination in vacuo (10^{-2} Torr) at 230 °C for 19 h to transform into the polyconjugated polymer. The precursor polymer could be easily stretched uniaxially up to a draw ratio of 10 (L/L_0 = 10) at 110–130 °C over a zone-heating glass tube. The final film had a golden brown to yellow color, depending on the elimination conditions and composition. Typical film thickness was about 8–12 μm.

Analysis. Melting points were determined using a Fisher-Johns melting point apparatus. Elemental analyses were performed by the Analytical Department of the Korea Research Institute of Chemical Technology, Korea. Viscosities of the precursor polymers were measured at 25 °C using a Ubbelohde-type viscometer for aqueous solutions containing 0.05 M Na_2SO_4. ^{1}H-NMR spectra were recorded on a Bruker AM300 spectrometer, and IR spectra were obtained on a Mattson Alpha Centauri FT-IR instrument. UV-vis spectra were recorded on a Hewlett-Packard 8452A spectrometer. The differential scanning calorimetric (DSC) thermograms were recorded on a DuPont DSC 910 instrument, and thermogravimetry (TG) was performed on a Mettler 3000 thermal analyzer. A heating rate of 10 °C/min was utilized for both analyses. Conductivities were measured by the usual four-in-line probe method. Doping the polymer films with I_2 was performed in a vacuum chamber at a pressure of 10^{-3} Torr. For $FeCl_3$ doping, the films were soaked at room temperature in a 0.05 M $FeCl_3$ solution in nitromethane. Doped films were washed with fresh nitromethane before drying. Graphite Elecrodag was used for contact between Pt electrodes and sample films.

Results and Discussion

Synthesis. Synthetic routes to monomer 3, PTMPV, and poly(PV-*co*-TMPV) are shown in Schemes I and II. To prepare monomer 3, 1,4-bis(chloromethyl)-2,3,5,6-

Scheme II



tetramethoxybenzene (2) first had to be synthesized by chloromethylation of 1,2,4,5-tetramethoxybenzene (1). 1,2,4,5-Tetramethoxybenzene could be easily prepared from benzoquinone.[27] Although the chloromethyl groups in 2 are surrounded by two adjacent methoxy groups, its reaction with tetrahydrothiophene proceeded smoothly to give 3 in a high yield. It is conjectured that the cyclic structure of tetrahydrothiophene makes the reaction system free from the severe steric hindrance of the four methoxy substituents flanking the two chloromethyl groups.

Polymerization of monomer 3 alone or a mixture of monomers 3 and 5 was carried out at 0 °C under a nitrogen atmosphere. Table I summarizes the data for conversion of monomers to precursor polymers and their solution viscosities. Data for conversions were obtained by titration of the final polymerization solution with 1.0 M HCl. Solution viscosities (2.7–4.8 dL/g) of dialyzed polymers as given in Table I suggest that the molecular weights of the obtained polymers are very high. Solution viscosities were measured in the presence of 0.05 M Na_2SO_4 to suppress the possible complication arising from the extended conformation in dilute solutions of polyelectrolyte chains.[28]

The degree of monomer conversions (50–89%) to precursor polymers is comparable to those reported for other similar polymerization systems.[4,5,21] Use of more concentrated monomer solutions and longer reaction time could result in higher conversions, but we did not try to improve reaction conditions to increase conversions. As shown in Table I, the contents of TMPV units incorporated into the copolymers are consistently significantly higher than those in the monomer feed mixtures, suggesting that the reactivity of TMPV monomer 3 is greater than unsubstituted PV monomer 5. Conversion of monomers and solution viscosity of precursor polymers increase with the content of 3 units in the precursor polymer, indicating that the presence of electron-donating methoxy groups in 3 facilitates chain propagation.

Table I
Monomer Conversions, Precursor Polymer Yields, and Solution Viscosities

polymn system[a]	feed molar ratio 5:3	mole ratio of $m{:}n$ in polymer	monomer conv, mol %	η_{inh}, dL/g	polymer yield,[b] %
PTMPV	0:100	0:100	89	4.80	43
75-poly(PV-co-TMPV)	50:50	24.9:75.1	78	3.59	38
37-poly(PV-co-TMPV)	80:20	62.8:37.2	63	3.23	34
13-poly(PV-co-TMPV)	90:10	86.7:13.3	56	2.87	30
12-poly(PV-co-TMPV)	95:5	88.0:12.0	54	2.91	31
6-poly(PV-co-TMPV)	98:2	94.3:5.7	50	2.73	28

[a] The numerical values stand for the mole percent of TMPV units incorporated into the copolymers. [b] The values were estimated from the weight of polyconjugated polymers obtained after final thermal elimination.

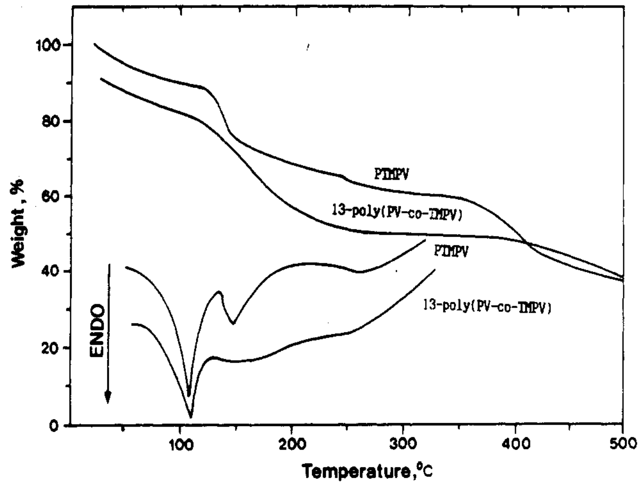


Figure 1. DSC and TGA thermograms of TMPV and 13-poly(PV-co-TMPV).

Thermal Elimination to Polyconjugated Polymers. Thermal analyses of the elimination reactions of the precursor polymers were studied by DSC and thermogravimetry (TG) with a heating rate of 10 °C/min. Representative DSC and TG thermograms are given in Figure 1. DSC thermograms exhibit two major endothermic processes at about 110 and 150 °C. The low-temperature endotherm corresponds to evaporation of absorbed water, and the higher temperature endotherm to the elimination of tetrahydrothiophene and HCl. A major weight loss up to about 130 °C is mainly due to the loss of absorbed water, and elimination of tetrahydrothiophene and HCl occurs from 130 to about 230 °C. To ensure complete reaction, thermal eliminations were conducted for 20 h at 230 °C.

The FT-IR spectra of the eliminated films are shown in Figure 2. In the case of PPV, it is known that thermal elimination of precursor polymers results in the formation of predominantly *trans*-vinylene structure. Figure 2 compares the IR spectra of PTMPV, 75-poly(PV-co-TMPV), and 12-poly(PV-co-TMPV). All of them reveal a strong absorption at 964 cm^{-1} due to the out-of-plane

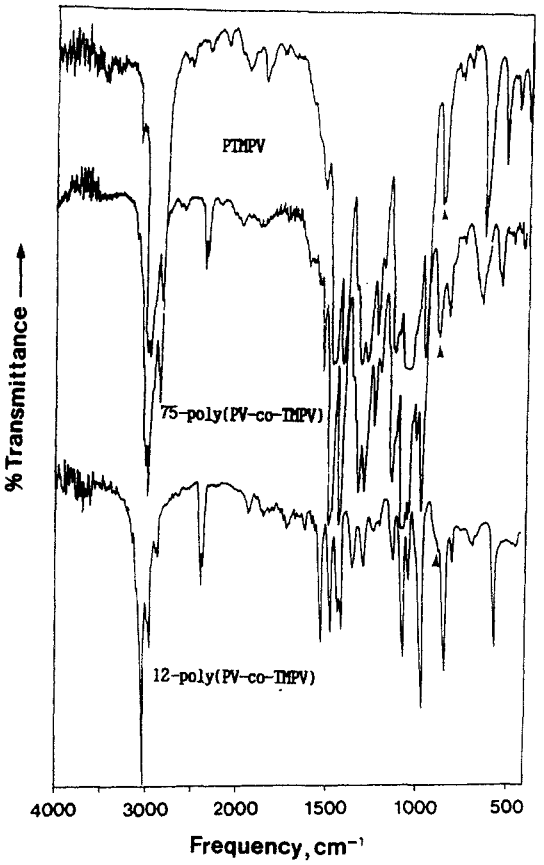


Figure 2. IR spectra of PTMPV and poly(PV-*co*-TMPV)s.

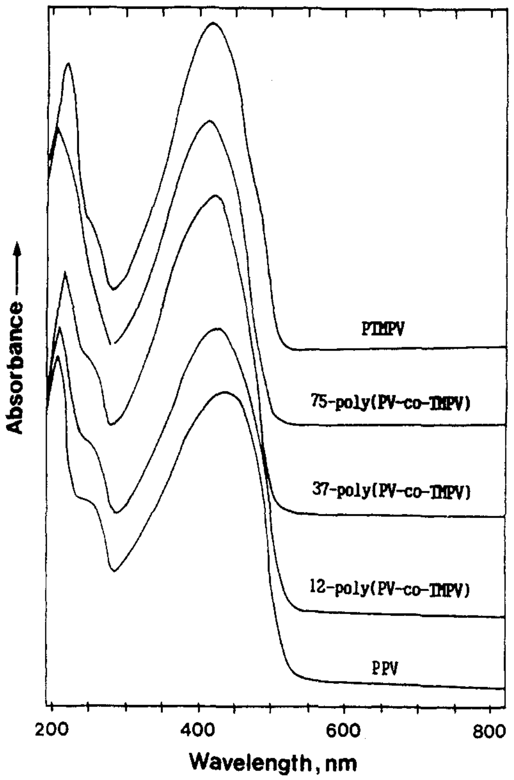


Figure 3. UV–vis spectra of PPV, poly(PV-*co*-TMPV)s, and PTMPV.

bending vibration of the *trans*-vinylene C–H bond and another absorption at 882 cm^{-1} that is known to be due to the *cis*-vinylene C–H out-of-plane bending mode.[29] Figure 2 also shows a gradual decrease in the intensity of the absorption band at 882 cm^{-1} with decreasing content of TMPV units in the copolymers. In other words, increasing the content of TMPV moieties in the copolymers results in the increase in the amount of *cis*-vinylene structure. The presence of four methoxy groups on the phenylene rings certainly restricts conformational rotation around C–C bonds of incipient vinylene groups being formed during the elimination process and, thus, brings about the formation of *trans*- as well as *cis*-vinylene groups. To examine the thermal stability or thermal isomerization of the *cis*-vinylene structure in TMPV copolymers, we compared the IR spectrum of a PTMPV film obtained by thermal elimination of the precursor polymer at 230 °C for 19 h with the IR spectrum of the same film after additional heat treatment at 300 °C for 4 h under a nitrogen atmosphere. We found that the two IR spectra were practically the same, indicating that the *cis*-vinylene structure, once formed, is not easily isomerized to the *trans*-vinylene structure even at an elevated temperature.

Figure 3 shows UV–vis spectra of thin films of PTMPV and copolymers. The profile of the absorption spectra and the maximum absorption positions of these polymer films are similar to those of PPV.[4] It is well known that the bathochromic shift by the two electron-donating methoxy groups on the phenylene rings in PDMPV is significant.[16] But, contrary to the original expectation, the maximum absorption and absorption edge positions (Figure 3) of the present PTMPV and copolymers are slightly, but definitely shifted to shorter wavelength relative to PPV. This suggests that the four methoxy groups in the TMPV unit reduce the effective π-conjugation between the phenylene and vinylene units. A molecular model clearly demonstrates that methoxy oxygens are in too close proximity to vinylene protons if the phenylene and vinylene units were assumed to be coplanar. To avoid such steric crowing, the phenylene rings have to twist around to a certain degree relative to each other and the π-system looses the coplanar overlapping. The l[illegible] complanarity would diminish the effective π-delocalization, resulting in a blue shift in the UV–vis spectra.

We reported earlier a similar phenomenon in the case of poly(1,4-phenylenevinylene-*co*-2,3,5,6-tetramethyl-1,4-phenylenevinylene)s. In addition, the above-mentioned structural characteristics of the present copolymers containing both *trans*- and *cis*-vinylene geometry can also be attributed partly to the diminished effectiveness in π-delocalization. A molecular model of the coplanar conformation of the tetramethoxyphenylene–*cis*-vinylene–tetramethoxyphenylene unit indicates that the two methoxy oxygens on the same side of the *cis*-vinylene structure are located too close to each other and, thus, to avoid such a steric and dipolar repulsion, the coplanar conformation has to be destroyed, leading to less efficient π-delocalization. However, due to the relatively strong electron-donating nature of the methoxy groups, the degree of blue shift by the TMPV unit is very slight.

Electrical Conductivity. Electrical conductivities of the polymers were measured using a four-in-line probe technique.[26] Table II summarizes the draw ratio, the degree of doping, and the maximum conductivity values obtained for the oriented as well as unoriented polymer films. We stopped doping the polymers after 20–60 s in a nitromethane solution of $FeCl_3$ depending on the thickness and composition of the films. Prolonged doping damaged the integrity of the films, and some of them even broke apart when left too long in the dopant solution. Doping with I_2 was performed in a vacuum chamber at a pressure of 10^{-3} Torr.

The data shown in Table II reveal a few interesting points. *The copolymer films containing medium levels of*

Table II
Maximum Conductivities of I_2- and $FeCl_3$-Doped Polymers

polymer	dopant	draw ratio, L/L_0	deg of doping dopant/repeat unit (I_3^- or $FeCl_4^-$/RU)	conductivity, S cm^{-1}
PTMPV	I_2	1	*a*	*a*
		10	*a*	*a*
	$FeCl_3$	1	0.08	6.8×10^{-4}
		10	0.08	1.1×10^{-2}
75-poly(PV-*co*-TMPV)	I_2	1	*a*	*a*
		10	*a*	*a*
	$FeCl_3$	1	0.07	9.8×10^{-3}
		10	0.10	2.0×10^{-1}
37-poly(PV-co-TMPV)	I_2	1	0.11	7.2×10^{-4}
		10	0.13	5.2×10^{-2}
	$FeCl_3$	1	0.14	8.5×10^{-2}
		10	0.27	11
13-poly(PV-*co*-TMPV)	I_2	1	0.09	2.9×10^{-2}
		10	0.13	5.2×10^{-1}
	$FeCl_3$	1	0.16	38
		10	0.40	7.2×10^{2}
12-poly(PV-co-TMPV)	I_2	1	0.08	9.8×10^{-3}
		10	0.11	3.7×10^{-1}
	$FeCl_3$	1	0.14	6.3
		10	0.31	6.8×10^{2}
6-poly(PV-*co*-TMPV)	I_2	1	*a*	*a*
		10	*a*	*a*
	$FeCl_3$	1	0.06	19
		10	0.09	4.2×10^{2}

[a] The film was not doped even after treatment with dopant for 3 weeks.

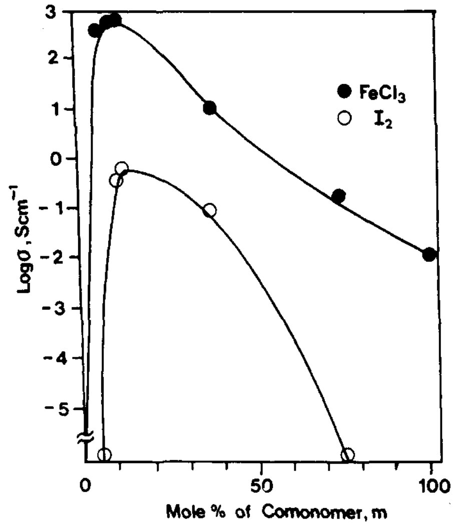


Figure 4. Maximum conductivities of stretched (L/L_0 = 10) poly(PV-*co*-TMPV)s doped with $FeCl_3$ and I_2.

the TMPV unit were readily doped with I_2 or $FeCl_3$, in contrast to the fact that PPV films are hardly doped with the same dopants. All of the undoped polymer films had conductivities less than 10^{-7} S cm^{-1}, but their conductivities increased rapidly on doping, especially with $FeCl_3$. The degree of doping and the conductivity value increase rapidly initially with increasing content of TMPV units in the copolymer, reaching the maximum at the composition containing about 13.3 mol % of TMPV units, followed by a gradual decrease with further increase in TMPV content (Figure 4). The copolymer film containing 13.3 mol % of TMPV units, when doped with $FeCl_3$, showed a maximum conductivity of 7.2×10^2 S cm^{-1} for the stretched sample (L/L_0 = 10) along the drawing direction and 38 S cm^{-1} for the unstretched sample, respectively.

The weaker oxidant I_2, however, is much less efficient in doping and can dope only the copolymers containing more than 10 mol % of TMPV units. However, those containing very high levels of the TMPV unit as in 75-poly(PV-*co*-TMPV) and PTMPV are hardly doped with I_2. Moreover, the conductivities of I_2-doped polymers are considerably lower than those of $FeCl_3$-doped ones. In general, I_2-doped samples exhibit conductivities of about 3 orders of magnitude smaller than those of $FeCl_3$-doped samples. The conductivity values of I_2-doped poly(PV-*co*-TMPV)s are much lower than that of I_2-doped poly(1,4-phenylenevinylene-*co*-2,5-dimethoxy-1,4-phenylenevinylene) (poly(PV-*co*-DMPV)). In fact, it is known that PDMPV, containing only two methoxy groups on each phenylene ring, is readily doped with I_2, resulting in a maximum conductivity of 190 S cm^{-1}.[30] This is in great contrast to our present observation that PTMPV, containing four methoxy groups on each phenylene ring, is hardly doped with the same dopant. We[11] reported earlier that poly(2-butoxy-5-methoxy-1,4-phenylenevinylene) also is easily doped with I_2 to give a conductivity of 110 S cm^{-1} at room temperature. It was mentioned above that poly(2-methoxy-1,4-phenylenevinylene),[14] containing only one methoxy group on each phenylene ring, has a high enough affinity to I_2 and shows a conductivity of about 1.0 S cm^{-1} when doped with I_2.

Figure 4 represents the dependence of the conductivities of I_2- and $FeCl_3$-doped polymers on their composition, and it shows more or less parallelism for the two series. The sharp initial increase in electrical conductivity with increasing TMPV unit can be ascribed to the electron-donating property of the methoxy groups that facilitates easier oxidation of the polymer chain by the dopants. Another positive factor that can be envisaged is the morphological changes brought about by the substituents leading to easier access of doping species to polymer chains. For the copolymers containing higher levels of TMPV units and PTMPV itself, negative steric effects brought about by the TMPV units seem to be predominate over their electronic effects. This structural aspect was discussed above in detail. This structural characteristics will lead to a diminished dopability of the polymers and lower electrical conductivity of doped materials.

Lastly, conductivities of stretched films are higher by about 2 orders of magnitude along the draw direction than those of unstretched films. Better chain orientation and improved chain contact resulting from uniaxial stretching must be the main reasons for this observation, which were reported earlier for many other systems.

Conclusion

Poly(2,3,5,6-tetramethoxy-1,4-phenylenevinylene) (PTMPV) and random copolymers containing both 2,3,5,6-tetramethoxy-1,4-phenylenevinylene and 1,4-phenylenevinylene units were successfully synthesized via water-soluble polyelectrolyte precursors. The four methoxy groups in PTMPV fail to improve electrical conductivity after doping with I_2 relative to one or two methoxy groups in poly(2-methoxy-1,4-phenylenevinylene) (PMPV) and poly(2,5-dimethoxy-1,4-phenylenevinylene) (PDMPV), which reveal much more enhanced dopability to I_2 and, thus, higher conductivity than unsubstituted PPV. This seemingly contradictory phenomenon originates from the loss of coplanarity of the π-conjugated system due to the steric effect exerted by the four methoxy groups in PTMPV, which overwhelms the electron-donating electronic effect by the substituent. Moreover, TMPV units in PTMPV and copolymers lead to the formation of the *cis*-vinylene structure along the chain. Examination of molecular models and IR and UV–vis spectra of the polymers supports the above-mentioned interpretation. Inclusion of low levels of TMPV units in PPV copolymers facilitates doping with I_2 or $FeCl_3$ due to the positive electronic and morphological effect by the methoxy groups and increases the electrical conductivity of doped polymers steeply. When its content is relatively low, the TMPV unit certainly does not exert a strong steric effect. The conductivity of doped copolymers, however, gradually decreases with increasing content of the TMPV unit, after reaching maximum values at about the 13 mol % level of the TMPV moiety. This means that when a copolymer chain contains higher than about 13 mol % of the TMPV unit, the coplanar π-delocalized unit starts becoming shorter due to the steric crowding caused by the presence of the four methoxy groups in the TMPV unit. At the same time the content of the *cis*-vinylene structure appears to increase steadily with increasing content of the TMPV unit, which also is expected to increase the band-gap energy. In general, the stronger oxidant $FeCl_3$ is a more efficient dopant than I_2 and gives materials having higher conductivities. The present precursor polymers could be easily stretched uniaxially up to a draw ratio of 10 (L/L_0 = 10) before the final elimination reaction to polyconjugated materials. Stretched films exhibit much higher conductivities along the draw direction than unstretched samples. Better chain orientation and improved interchain contact can easily enhance the conductivity by an order of 2.

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