Synthesis of Poly(2-methoxy-5-methyl-1,4-phenylenevinylene) and Its Poly(1,4-phenylenevinylene) Copolymers: Electrical and Third-Order Nonlinear Optical Properties

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ABSTRACT: Asymmetrically disubstituted poly(2-methoxy-5-methyl-1,4-phenylenevinylene) (PMMPV) and a series of poly(1,4-phenylenevinylene-*co*-2-methoxy-5-methyl-1,4-phenylenevinylene)s (poly(PV-*co*-MMPV)) were synthesized through a water-soluble precursor route. These polymers were characterized using UV–visible, FT-IR spectroscopy, and a DSC, TGA thermal analyzer. The electrical conductivities of the polymers were investigated by the four-in-line method at room temperature. A PMMPV film can be stretched up to 5 times and doped with $FeCl_3$ and I_2 to give electrical conductivities of 27 and 7.4 S/cm, respectively, along the drawn direction. In copolymers, as the content of the MMPV unit increases, the electrical conductivity steadily increases. The $\chi^{(3)}$ $(-3\omega; \omega, \omega, \omega)$ value of PMMPV was determined by the third harmonic generation (THG) technique at 1907 nm, the fundamental wavelength. The measured $\chi^{(3)}$ value was 7.5×10^{-12} esu.

Introduction

The field of organic conjugated polymers such as polyacetylene, polyaromatics, poly(heteroaromatics), poly(1,4-phenylenevinylene), and polyaniline, etc., has emerged as one of the most exciting and interdisciplinary areas in the last few decades because they show not only high electrical conductivity but also optical nonlinearity and luminescent property.[1,2]

Among them, the interest in poly(1,4-phenylenevinylene) (PPV) and its derivatives has been increased because they have high environmental and thermal stability, good processibility, and high film quality, etc. They can be readily prepared in high molecular weight through the water-soluble precursor route.[3] This route has allowed for preparation of a number of derivatives, including alkoxy-, alkyl-, and halogen-substituted derivatives.[4–9] The substitution on the phenylene ring of the monomer with different types of substituents shows a significant difference in the electronic structure of the corresponding polymer[4–14] and thus affects the nonlinear optical and electrical properties of the polymer.

PPV films can be easily doped with strong oxidizing agents such as AsF_5 and $FeCl_3$ to give high electrical conductivity, but they cannot be effectively doped with weaker oxidizing dopants such as I_2. The presence of strong electron-donating substituents on the phenylene ring leads to the reduction in band gap and ionization potential of the conjugated polymers, which facilitates oxidation with weak oxidants such as I_2. For example, poly(2,5-dimethoxy-1,4-phenylenevinylene) (PDMPV) can be doped with I_2 to give an electrical conductivity of 10^1 S/cm, whereas the precursor polymer of PDMPV cannot be drawn to any extent during or prior to the elimination reaction.[15] The drawability of the precursor polymer is also an important factor in electrical conductivity because the drawn films exhibit about 10 times higher conductivity along the drawn direction than undrawn ones.

There have been many reports about the asymmetrically substituted PPV derivatives such as methoxy-,[16] methoxy/*n*-butoxy-,[17] trimethylsilyl/cholesteroxy-,[18] and methoxy/cyano-substituted[19,20] derivatives, etc. Generally, asymmetrically substituted PPV derivatives can be easily stretched. For example, poly(2-methoxy-1,4-phenylenevinylene) (PMPV) films can be readily stretched to show the electrical conductivity of 10^0 S/cm after I_2 doping.[16] Despite stretching the PMPV film, its electrical conductivity is not higher than that of PDMPV. It can be explained that PMPV having only one methoxy substituent on each phenylene ring has a higher oxidation potential to oxidative doping than PDMPV which contains two methoxy groups on each phenylene ring, and this results in the lower susceptibility of PMPV toward I_2.

Therefore, we have been interested in the synthesis of PPV derivatives which can be easily stretched and have a low oxidation potential to oxidative doping. Asymmetrically disubstituted poly(2-methoxy-5-methyl-1,4-phenylenevinylene) (PMMPV) is one of the candidates. In this paper, we report the synthesis, electrical conductivity, and third-order nonlinear optical properties of PMMPV and its PPV copolymers, poly(1,4-phenylenevinylene-*co*-2-methoxy-5-methyl-1,4-phenylenevinylene) (poly(PV-*co*-MMPV)). The synthetic routes and polymer structures are shown in Schemes 1 and 2.

Experimental Section

Instrumentation. The synthesized compounds were identified by ^1H-NMR spectra that were obtained using a Bruker AM 200 spectrometer. Melting points were determined using an Electrothermal Model 1307 digital analyzer. FT-IR spectra were measured by a Bomem Michelson Series FT-IR spectrophotometer, and UV–visible spectra were obtained with a Shimadzu UV-3100S. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of precursor polymers were performed under a nitrogen atmosphere at a heating rate

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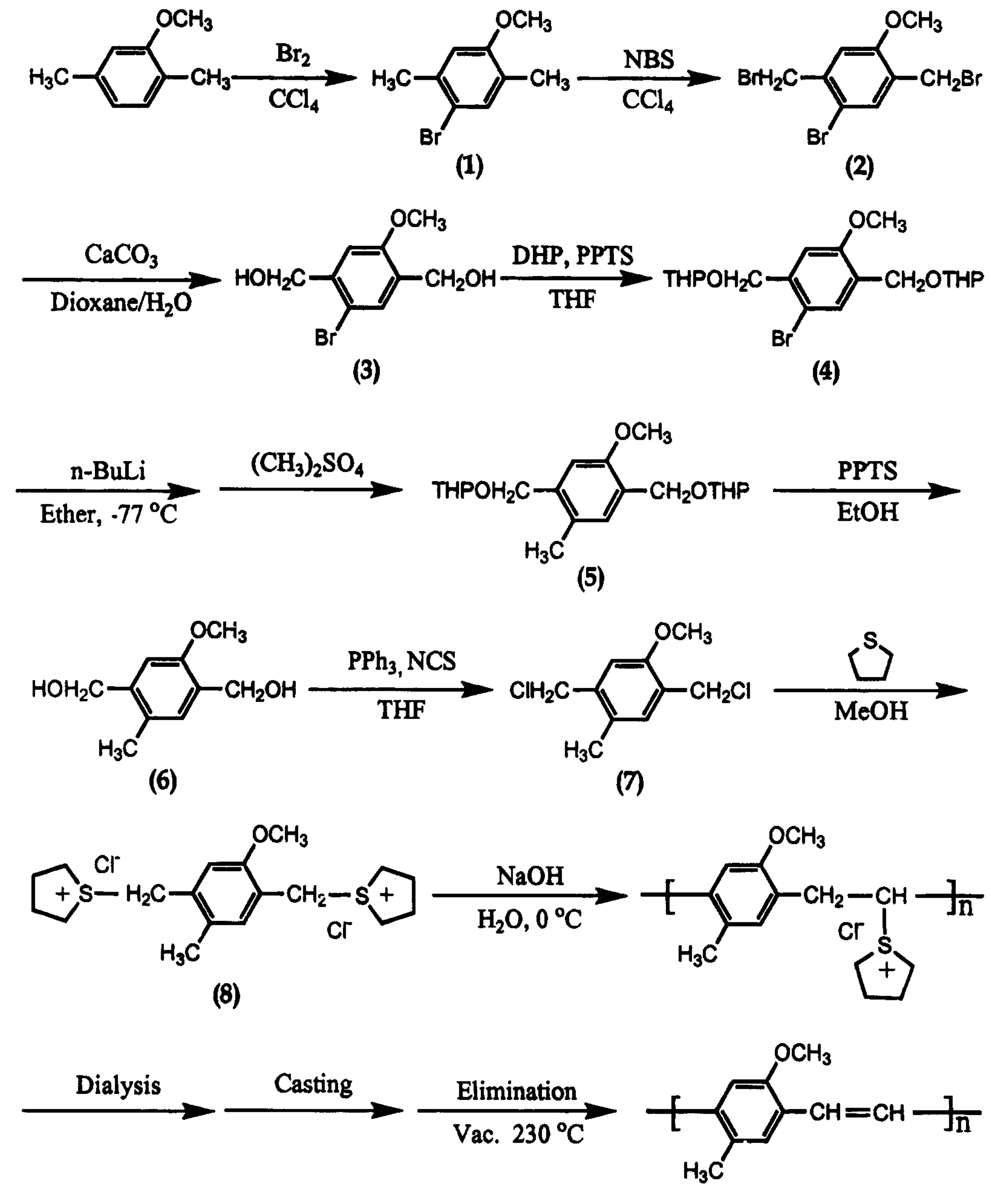
Scheme 1



PMMPV

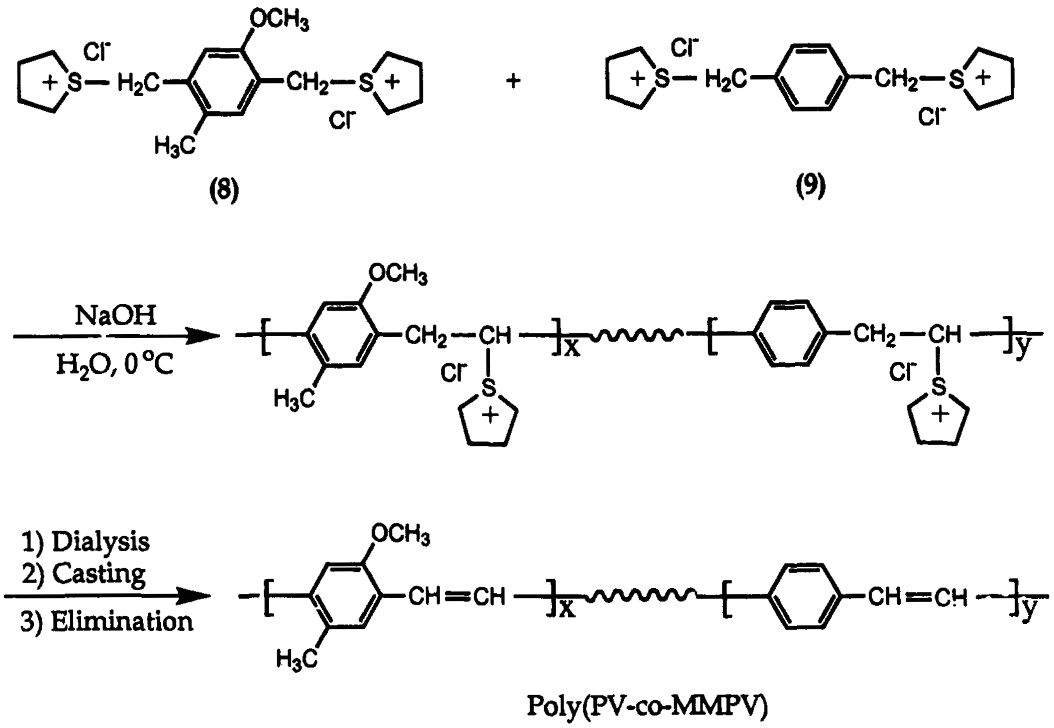
of 10 °C/min with a Dupont 9900 analyzer. Elemental analyses were performed by the Analytical Department of the Korea Research Institute of Chemical Technology. Electrical conductivities of doped polymer films were measured by the four-in-line probe method at room temperature. The third-order nonlinear optical coefficient of the final polymer was measured by the third harmonic generation (THG) technique with a Nd:YAG laser system. The thicknesses of the spin-coated polymers were measured using the Alpha step 200 profilometer. The photoluminescence spectrum of the PMMPV film was obtained using a Perkin-Elmer LS-50 luminescence spectrometer.

1-Bromo-4-methoxy-2,5-dimethylbenzene (1). A total of 30.0 g (220 mmol) of 2,5-dimethylanisole was dissolved in 150 mL of carbon tetrachloride, and 40.5 g (250 mmol) of Br_2 was added dropwise to the solution at 0 °C. When dropping was finished, the mixture was stirred at room temperature for 2 h. The reaction was quenched by an aqueous NaOH solution, and then organic layer was extracted by methylene chloride. The extract was dried over anhydrous magnesium sulfate, and the solvent was removed by a rotary evaporator. The product was obtained by vacuum distillation, and the yield was 45.0 g (95.1%): ^{1}H-NMR ($CDCl_3$) δ 7.3 (s, 1H), 6.7 (s, 1H), 3.8 (s, 3H), 2.4 (s, 3H), 2.2 (s, 3H); bp 85 °C (ca. 0.5 Torr). Anal. Calcd for $C_9H_{11}OBr$: C, 46.38; H, 4.76. Found: C, 46.19; H, 4.65.

1-Bromo-2,5-bis(bromomethyl)-4-methoxybenzene (2). Compound **2** was prepared by reacting 20.0 g (93.0 mmol) of **1** with 36.4 g (200 mmol) of *N*-bromosuccinimide (NBS) in 150 mL of carbon tetrachloride. A small amount of benzoyl peroxide was added as an initiator. The reaction mixture was refluxed for 3 h under a nitrogen atmosphere. The completion of the reaction was indicated by the appearance of succinimide and consumption of the NBS. Succinimide was filtered out, and a crude solution was concentrated under reduced pressure. The white solid product was obtained by precipitation in *n*-hexane, and the yield was 24.3 g (70.1%): ^{1}H-NMR ($CDCl_3$) δ 7.5 (s, 1H), 6.9 (s, 1H), 4.5 (s, 2H), 4.4 (s, 2H), 3.9 (s, 3H); mp 137 °C. Anal. Calcd for $C_9H_9OBr_3$: C, 25.32; H, 2.12. Found: C, 25.48; H, 2.30.

1-Bromo-2,5-bis(hydroxymethyl)-4-methoxybenzene (3). A mixture of 16.0 g (42.9 mmol) of **2** and an excess of $CaCO_3$ in 140 mL of dioxane and 100 mL of water was refluxed for 15 h. When the reaction was finished, the extra $CaCO_3$ was quenched by a HCl solution. The white solid product was obtained by precipitation in water and dried in vacuum oven.

Scheme 2



The product yield was 8.5 g (80%): ^{1}H-NMR (DMSO-d_6) δ 7.5 (s, 1H), 7.1 (s, 1H), 5.5 (t, 1H), 5.2 (t, 1H), 4.5 (m, 4H), 3.8 (s, 3H); mp 151–152 °C. Anal. Calcd for $C_9H_{11}O_3Br$: C, 40.78; H, 4.18. Found: C, 40.62; H, 4.09.

1-Bromo-2,5-bis[(tetrahydropyran-2-yloxy)methyl]-4-methoxybenzene (4). A total of 1.6 g of pyridinium *p*-toluenesulfonate (PPTS) and 8.2 g (96 mmol) of 3,4-dihydropyran (DHP) were added to the solution of 8.0 g (32 mmol) of **3** in 100 mL of methylene chloride, and then the mixture was refluxed for 4 h. The mixture was washed with water, and the organic layer was dried with magnesium sulfate. The volatiles were removed under reduced pressure, and the product was separated by the column chromatography. The white solid was obtained, and the yield was 11.3 g (85%): ^{1}H-NMR ($CDCl_3$) δ 7.5 (s, 1H), 7.0 (s, 1H), 4.7 (m, 4H), 4.5 (m, 2H), 3.9 (m, 2H), 3.8 (s, 3H), 3.5 (m, 2H), 1.5–1.8 (m, 12H); mp 84–86 °C. Anal. Calcd for $C_{19}H_{27}O_5Br$: C, 52.67; H, 6.28. Found: C, 52.49; H, 6.16.

1-Methoxy-2,5-bis[(tetrahydropyran-2-yloxy)methyl]-4-methylbenzene (5). A total of 9.2 g (22 mmol) of **4** was dissolved in 150 mL of dried ether, and 26.0 mL (66.0 mmol) of *n*-BuLi was added to this solution at −77 °C. After 1 h of reaction, 7.0 mL (66 mmol) of dimethyl sulfate was added to the reaction mixture and the reaction was carried out at −77 °C for 2 h. The reaction was quenched by water, and the organic layer was dried with magnesium sulfate. The white solid product was obtained by column chromatography, and the yield was 4.6 g (60%): ^{1}H-NMR ($CDCl_3$) δ 7.2 (s, 1H), 6.9 (s, 1H), 4.7 (s, 4H), 4.5 (m, 2H), 3.9 (m, 2H), 3.8 (s, 3H), 3.5 (m, 2H), 2.3 (s, 3H), 1.8–1.5 (m, 12H); mp 66–67 °C. Anal. Calcd for $C_{20}H_{30}O_5$: C, 68.55; H, 8.63. Found: C, 68.47; H, 8.71.

1,4-Bis(hydroxymethyl)-2-methoxy-5-methylbenzene (6). A mixture of 4.5 g (13 mmol) of **5** and 0.3 g (1 mmol) of PPTS in 100 mL of ethanol was reacted at 55 °C for 12 h. The volatiles were removed under reduced pressure, and then a white solid was obtained. This solid was purified by washing with methylene chloride. The yield was 1.8 g (79%): ^{1}H-NMR (DMSO) δ 7.1 (s, 1H), 6.9 (s, 1H), 5.0 (t, 1H), 4.8 (t, 1H), 4.4 (m, 4H), 3.7 (s, 3H), 2.1 (s, 3H); mp 80–81 °C. Anal. Calcd for $C_{10}H_{14}O_3$: C, 65.92; H, 7.74. Found: C, 65.85; H, 7.76.

1,4-Bis(chloromethyl)-2-methoxy-5-methylbenzene (7). The reaction of 1.6 g (9.0 mmol) of **6**, 3.2 g (27 mmol) of *N*-chlorosuccinimide, and 5.7 g (22 mmol) of triphenylphosphine dissolved in 100 mL of THF was carried out at room temperature for 12 h. The product was separated by column chromatography and then white solid was obtained. The yield was 1.6 g (82%): ^{1}H-NMR ($CDCl_3$) δ 7.2 (s, 1H), 6.8 (s, 1H), 4.6 (s, 2H), 4.5 (s, 2H), 3.9 (s, 3H), 2.3 (s, 3H); mp 109–110 °C. Anal. Calcd for $C_{10}H_{12}O_1Cl_2$: C, 54.82; H, 5.52. Found: C, 54.75; H, 5.59.

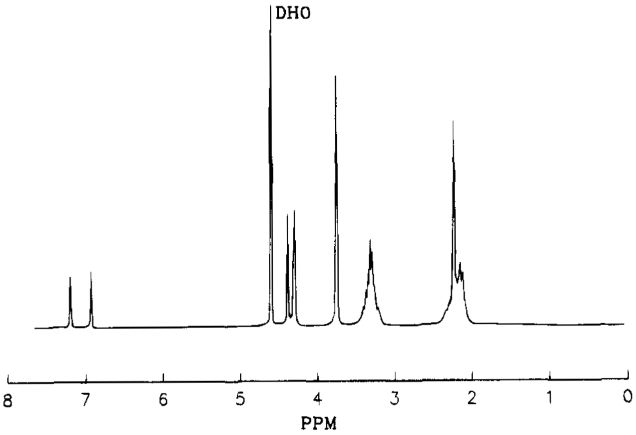


Figure 1. ^{1}H-NMR spectrum of salt monomer **8** (solvent: D_2O).

1-Methoxy-4-methyl-2,5-phenylenebis(methylenetetrahydrothiophenium) Dichloride (8). A total of 1.5 g (7.0 mmol) of compound **7** and excess tetrahydrothiophene were reacted at 50 °C for 24 h in 20 mL of methanol. As the reaction proceeded, this suspension changed to the clear solution. The final salt monomer (**8**) was obtained by concentration of the reaction solution, precipitation in cold acetone, filtration, and vacuum drying. The product yield was 1.9 g (70%): ^{1}H-NMR (D_2O) δ 7.2 (s, 1H), 6.9 (s, 1H), 4.4 (s, 2H), 4.3 (s, 2H), 3.7 (s, 3H), 3.4–3.2 (m, 8H), 2.2 (s, 3H), 2.3–2.0 (m, 8H) (Figure 1); mp 240–241 °C (dec). Anal. Calcd for $C_{18}H_{28}OCl_2S_2$: C, 54.69; H, 7.14. Found: C, 54.47; H, 7.09. The salt monomer for PPV (**9**) was prepared similarly from α,α'-dichloro-*p*-xylene and tetrahydrothiophene following the literature method.[21,22]

Polymerization. The procedures used for the preparation of homopolymer and copolymers were the same as reported by us[6,22] and others.[21] The monomer sulfonium salt solution was polymerized in a 1.0 N NaOH solution at 0 °C. A

Table 1. Monomer Conversions and Polymer Yields of PMMPV and Copolymers

polymer[a]	feed molar ratio (**8**:**9**)	actual ratio (MMPV[b]: PV[c])	monomer convn (%)	polymer yield (%)
PMMPV	100:0	100:0	93	67
88-poly(PV-*co*-MMPV)	83:17	88:12	90	50
77-poly(PV-*co*-MMPV)	50:50	77:23	84	45
47-poly(PV-*co*-MMPV)	17:83	47:53	82	21
38-poly(PV-*co*-MMPV)	9:91	38:62	81	31

[a] The numerical values stand for mol % of MMPV units in the final copolymers, and these values were determined from the results of the elemental analyses. [b] MMPV: 2-methoxy-5-methyl-1,4-phenylenevinylene unit. [c] PV: 1,4-phenylenevinylene unit.

homogeneous and viscous solution was obtained. For the copolymers, the total moles of the two monomers (**8** and **9**) were kept constant, but their mole ratios were varied. The polymerization reaction was quenched by neutralization with 0.5 N HCl, and the precursor polymer solutions were dialyzed against deionized water for 5 days to remove unreacted monomers and low molecular weight oligomers using a dialysis tube with a molecular weight cutoff at 12 000. The films cast or spin-coated from these aqueous precursor polymer solutions were subjected to thermal elimination in vacuo (10^{-2} Torr) at 230 °C for 12 h to transform them into the final polyconjugated polymer films. If desired, the precursor polymer films were uniaxially drawn at 120 °C using a zone-heating apparatus.

Results and Discussion

For the first time, the salt monomer of PMMPV (**8**) was synthesized from 2,5-dimethylanisole through the somewhat long synthetic steps as shown in Scheme 1. It was necessary to build the functional group on the benzylic position and then to protect this functional group for the introduction of the methyl group to the phenylene ring. Tetrahydropyran was used as a protection group because this group could be easily attached and detached and the protected compound could be readily handled as a solid form at room temperature. The deprotection was carried out, and then the final salt monomer was synthesized in moderate yield.

Table 1 summarizes the data for the actual ratio of the copolymers which was calculated from elemental analysis data, the conversions of monomers to precursor polymers, and the polymer yields. The conversions were calculated by the backtitration of the polymerized precursor solution, and the polymer yields were estimated gravimetrically from the weight of the cast film. The degrees of monomer conversions are very high, ranging from 81 to 93%, and the polymer yields are comparable to or slightly higher than those reported for other similar polymerization systems.[7,8,15,16] Both the monomer conversion and the polymer yield are increased as the feed ratio of the MMPV unit is increased. This indicates that the presence of electron-donating groups in **8** facilitates chain propagation in the polymerization step. As shown in Table 1, the contents of the MMPV unit in the polymer chain are higher than those in the monomer feed ratio, indicating that the reactivity of the MMPV monomer (**8**) is greater than that of the PV monomer (**9**). There is some different placement of the substituents, OMe and Me, in the polymer backbone because of the asymmetric substitution. It can be expected that there is no regiospecific placement of OMe and Me groups in the polymer. The fact that asymmetric substitution gives regioscrambling in the PPV derivative synthesized through the precursor method is reported by others.[20]

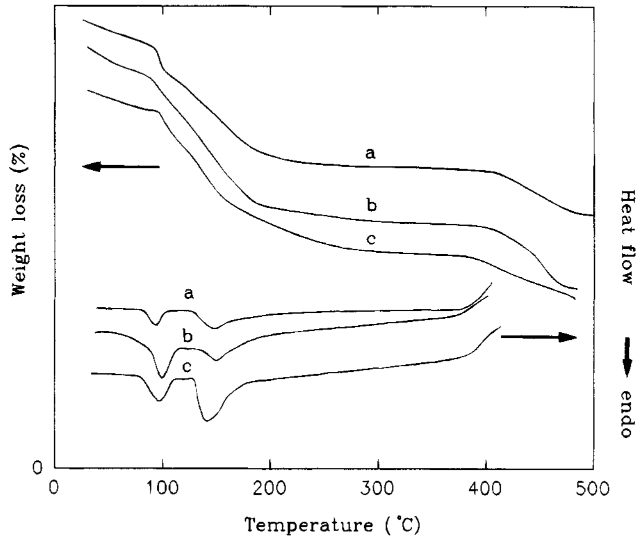


Figure 2. TGA and DSC thermograms of precursor polymers of (a) PMMPV and (b) 88- and (c) 77-poly(PV-*co*-MMPV).

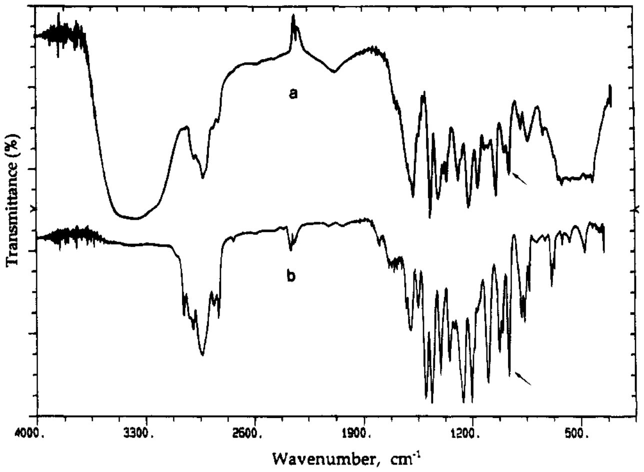


Figure 3. FT-IR spectra of (a) precursor and (b) final eliminated PMMPV.

The thermal analyses of the precursor polymers were performed to find the temperature at which the elimination reaction occurred. Figure 2 shows the DSC and TGA thermograms of the same precursor polymers. Two endotherm peaks appeared. The low-temperature endotherm peak at 100 °C corresponds to the loss of absorbed water during film casting and the higher temperature one between 120 and 170 °C to the elimination reaction of HCl and tetrahydrothiophene. The TGA thermograms are well-consistent with the DSC results. The weight loss of absorbed water appeared below 100 °C. The elimination reaction was found between 100 and 200 °C. The polymers were stable up to 400 °C, and above that temperature, decomposition occurred. The analyses of DSC of the fully eliminated films show that no melt transition occurred. This is due to the high rigid nature of the polymer chains. From these thermal analyses, the elimination reactions of the polymers were finished before 200 °C. So elimination reaction of the precursor polymers was performed at 230 °C.

Figure 3 shows IR spectra of the films of PMMPV and its precursor polymer. The precursor polymer film exhibits a broad absorption at 3100−3600 cm^{-1} due to absorbed water, which disappeared in the spectrum of the final polyconjugated polymer. A strong absorption peak appeared at 960 cm^{-1} after elimination, indicating that the vinylene C=C bonds formed have the trans

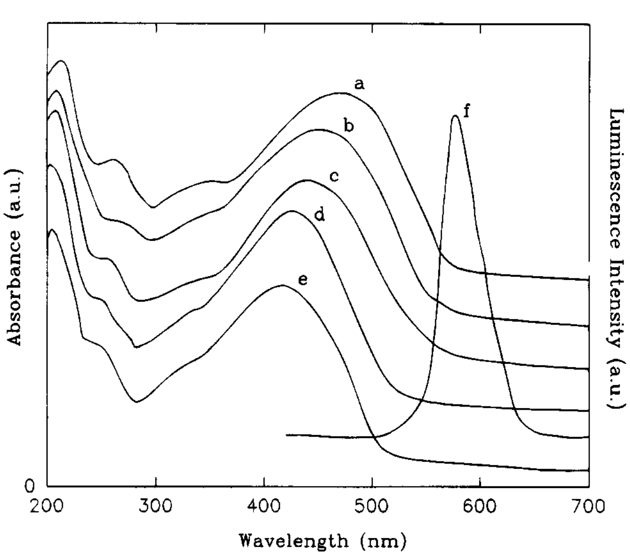


Figure 4. UV–visible spectra of (a) PMMPV and (b) 88-, (c) 77-, (d) 47-, and (e) 38-poly(PV-*co*-MMPV), and (f) a photoluminescence spectrum of PMMPV.

Table 2. Maximum Conductivities of $FeCl_3$- and I_2-Doped PMMPV and Copolymers

	electrical conductivity (S/cm)			
	$FeCl_3$ doping		I_2 doping	
polymer	undrawn	drawn (5 times)	undrawn	drawn (5 times)
PMMPV	3.6	27	0.52	7.4
88-poly(PV-*co*-MMPV)	1.4	25	4.2×10^{-2}	5.3
77-poly(PV-*co*-MMPV)	3.5×10^{-2}	4.2	7.2×10^{-3}	1.4
47-poly(PV-*co*-MMPV)	4.1×10^{-3}	1.1	1.1×10^{-3}	0.75
38-poly(PV-*co*-MMPV)	1.6×10^{-3}	0.87	6.8×10^{-4}	0.65

configurations. The IR spectrum of the precursor polymer also shows a small, but sharp absorption peak at the same position. This results from a premature elimination reaction that occurred during film casting.

UV–visible spectra of PMMPV and its PPV copolymers are presented in Figure 4. The broad, long-wavelength absorptions around 350–560 nm are due to $\pi-\pi^*$ transitions of the polyconjugated systems. The maximum absorption peak for $\pi-\pi^*$ transition and the band edge were found at 460 and 560 nm for PMMPV. The maximum absorption peak value and the band edge for PMMPV are placed between those of PMPV and PDMPV, and it is closer to those of PMPV than those of PDMPV. This suggests that the electron-donating effect of the methyl group is not strong as we expected. The maximum absorption peak of the copolymers is gradually blue shifted as the content of the PV monomer is increased.

The interests in electroluminescence of PPV derivatives have been spawned in recent years. Therefore, the photoluminescence spectrum was obtained for characterizing the polymer as electroluminescence devices (Figure 4). The excitation wavelength is 400 nm, and the emission maximum is 570 nm which corresponds to the orange color.

Electrical Conductivity of the Polymers. Table 2 shows the draw ratios and the maximum conductivities of $FeCl_3$- and I_2-doped PMMPV and copolymers. Efforts have been made to synthesize PPV derivatives which can be readily doped with various dopants and stretched for high electrical conductivity such as PMPV and poly(2-*n*-butoxy-5-methoxy-1,4-phenylenevinylene) (PBMPV), etc. PMPV and PBMPV can be easily stretched and doped with I_2 to show the electrical conductivities of 10^0 and 10^2 S/cm, respectively.[16,17] As a part of the synthesis of well dopable and stretchable PPV derivatives, PMMPV was synthesized through somewhat long synthetic steps. The PMMPV film, which was stretched 5 times, showed the electrical conductivities of 27 and 7.4 S/cm, respectively, when doped with $FeCl_3$ and I_2. These values are slightly higher than those of the PMPV film, but lower than those of the PDMPV film. PMMPV has the methoxy and methyl substituents at the 2 and 5 positions of the phenylene ring, whereas PDMPV has the two methoxy groups at the same positions. There are two distinct properties between them. First, the precursor film of PMMPV could be easily drawn up to a draw ratio of 5, whereas that of PDMPV could not be drawn. This result is explained by the fact that there is good polymer chain packing in PDMPV due to the symmetry of the two methoxy substituents, while the chain packing abilities between the polymer chains are significantly reduced in asymmetrically disubstituted PMMPV. Second, the electrical conductivity value of the PDMPV film is higher than that of the PMMPV film because the two strong electron-donating methoxy groups in PDMPV lead to the reduction in band gap and ionization energy of the conjugated polymer chains, to enhance the electrical conductivity more than the case of PMMPV. Especially the electrical conductivity of a 5 times stretched PMMPV film is lower than that of an unstretched PDMPV film. This means that the electrical conductivity is more strongly affected by the electron-donating power of the methoxy groups than the polymer chain drawability. Also, we concluded that the drawability of the PPV derivatives strongly depends upon the structural symmetry of the substituents at the 2,5-positions of the phenylene ring of the polymer main chain. For example, monoalkoxy-substituted PPVs and asymmetrically disubstituted PPVs such as PMMPV and PBMPV could be easily stretched, but symmetrically disubstituted PPVs such as PDMPV and poly[2,5-bis(trimethylsilyl)-1,4-phenylenevinylene] could not be stretched.[23] In copolymers, as the content of the MMPV unit in the copolymer increases, the electrical conductivity steadily increases as shown in Table 2. It is expected that the presence of the strong electron-donating methoxy and weak electron-donating methyl groups reduces the oxidation potential of the polymer chain, resulting in increased dopability. Therefore, the electrical conductivities of the MMPV unit rich polymers are higher.

Third-Order Nonlinear Optical Susceptibility. To determine the third-order nonlinear optical susceptibility of the PMMPV film, the third harmonic generation (THG) intensity of the polymer was measured as a function of the angle of incidence. The THG intensity from the BK-7 glass substrate was also measured as a reference. Figure 5 shows Maker-fringe patterns of the polymer and BK-7 glass substrate. The $\chi^{(3)}$ value of the PMMPV was calculated by comparing the measured THG peak intensity of the film and that of the substrate using the equation reported elsewhere, assuming the film thickness to be much thinner than the coherence length of the film.[24,25] We also assumed that the effect of the refractive index difference between the PMMPV and the substrate for $\chi^{(3)}$ calculation is negligible. The measured $\chi^{(3)}$ value was 7.5×10^{-12} esu at 1.91 μm. This $\chi^{(3)}$ value is slightly lower than that of PDMPV, 5.4×10^{-11} esu at 1.85 μm reported by Kaino et al., and slightly higher than that of PPV, 3.0×10^{-12} esu at 1.91 μm reported by us.[26,27] This result is explained by the band-gap energy difference of the polymers. It is well-

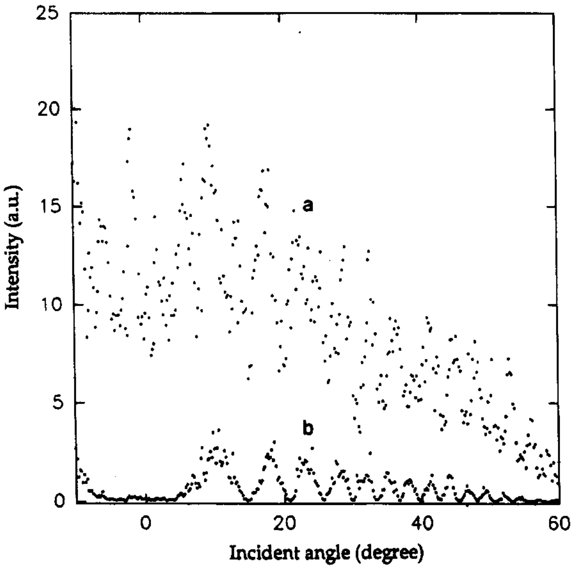


Figure 5. Maker-fringe patterns of (a) PMMPV and (b) BK-7 glass.

known that the $\chi^{(3)}$ value is inversely proportional to the sixth power of the band-gap energy. The positions of the absorption edges are 610 nm for PDMPV, 550 nm for PMMPV, and 530 nm for PPV, respectively. So, the order of the band-gap energies is PDMPV < PMMPV < PPV. This order of the band-gap energies is well consistent with that of the $\chi^{(3)}$ values. The trend of increasing third-order nonlinearities shows important contributions derived from the electron-donating substituents at the 2,5-positions in PPV.

Conclusion

Asymmetrically disubstituted poly(2-methoxy-5-methyl-1,4-phenylenevinylene) (PMMPV) and a series of copolymers containing PV units were synthesized via the water-soluble precursor route. The PMMPV film, which was stretched 5 times, shows the electrical conductivities of 27 and 7.4 S/cm, respectively, when doped with $FeCl_3$ and I_2. These values are slightly higher than those of the PMPV film and lower than those of the PDMPV film. In copolymers, as the content of the MMPV unit in the copolymer increases, the electrical conductivity steadily increases. The $\chi^{(3)}$ value of PMMPV was 7.5×10^{-12} esu which was determined by the third harmonic generation (THG) technique at 1907 nm, the fundamental wavelength.

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References and Notes

(1) Bredas, J. L.; Silbey, R. *Conjugated polymers*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1991.
(2) Prasad, P. N.; Williams, D. J. *Introduction to nonlinear optical effects in molecules and polymers*; John Wiley & Sons, Inc.: New York, 1991.
(3) Wessling, R. A.; Zimmerman, R. G. U.S. Patent 3,401,152, 1968; U.S. Patent 3,706,667, 1972.
(4) Hoerhold, H.; Helbig, N. *Makromol. Chem., Macromol. Symp.* **1987**, *12*, 229.
(5) Murase, I.; Ohnishi, T.; Noguchi, T.; Hirooka, M. *Synth. Met.* **1987**, *17*, 639.
(6) Shim, H. K.; Hwang, D. H.; Lee, J. I.; Lee, K. S. *Synth. Met.* **1993**, *55–57*, 908.
(7) Kang, I. N.; Lee, G. J.; Kim, D.; Shim, H. K. *Polym. Bull.* **1994**, *33*, 89.
(8) Jin, J. I.; Park, C. K.; Shim, H. K. *Macromolecules* **1993**, *26*, 1799.
(9) Shim, H. K.; Noh, H. G. *Mol. Cryst. Liq. Cryst.* **1994**, *247*, 23.
(10) Lenz, R. W.; Han, C. C.; Strenger-Smith, J.; Karasz, F. E. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 3241.
(11) Liang, W. B.; Lenz, R. W.; Karasz, F. E. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 2867.
(12) McCoy, R. K.; Karasz, F. E.; Sarker, A.; Lahti, P. B. *Chem. Mater.* **1991**, *3*, 941.
(13) Jin, J. I.; Shim, H. K.; Park, C. K.; Kang, H. J.; Yu, S. H.; Kim, J. C. *Synth. Met.* **1991**, *41–7*, 271.
(14) Gagnon, D. R.; Capistran, J. D.; Karasz, F. E.; Lenz, R. W. *Polym. Bull.* **1984**, *12*, 293.
(15) Jen, R. Y.; Shacklette, L. W.; Elsenbaumer, R. *Synth. Met.* **1987**, *22*, 179.
(16) Shim, H. K.; Hwang, D. H.; Lee, K. S. *Makromol. Chem.* **1993**, *194*, 1115.
(17) Jin, J. I.; Park, C. K.; Shim, H. K.; Park, Y. W. *J. Chem. Soc., Chem. Commun.* **1989**, 1205.
(18) Hoger, S.; Mcnamara, J. J.; Schricker, S.; Wudl, F. *Chem. Mater.* **1994**, *6*, 171.
(19) Shim, H. K.; Kang, S. W.; Hwang, D. H. *Bull. Korean Chem. Soc.* **1993**, *14*, 43.
(20) Lahti, P. M.; Sarker, A.; Garay, R. O.; Lenz, R. W.; Karasz, F. E. *Polymer* **1994**, *35*, 1312.
(21) Gagnon, D. R.; Capistran, J. P.; Karasz, F. E.; Lenz, R. W. *Polymer* **1987**, *28*, 567.
(22) Jin, J. I.; Park, C. K.; Shim, H. K. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 93.
(23) Hwang, D. H.; Shim, H. K. *Macromolecules*, submitted for publication.
(24) Kaino, T.; Kubodera, K.; Tomaru, S.; Kurihara, T.; Saito, S.; Tsutsui, T.; Tokito, S. *Electron. Lett.* **1987**, *23*, 1095.
(25) Kubodera, K. *Nonlinear Opt.* **1991**, *1*, 71.
(26) Kaino, T.; Kobayashi, H.; Kubodera, K.; Tokito, S. *Appl. Phys. Lett.* **1989**, *54*, 1619.
(27) Hwang, D. H.; Lee, J. I.; Lee, M.; Shim, H. K. *Bull. Korean Chem. Soc.* **1994**, *15*, 25.

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