Synthesis of Poly[(2-(2-(4-cyanophenyl)ethenyl)-5-methoxy-1,4-phenylene)vinylene] and Poly(1,4-phenylenevinylene) Copolymers: Electrical and the Second- and Third-Order Nonlinear Optical Properties

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ABSTRACT: Poly[(2-(2-(4-cyanophenyl)ethenyl)-5-methoxy-1,4-phenylene)vinylene] (PCEMPV) and a series of copolymers containing 1,4-phenylenevinylene (PV) units were synthesized through a water-soluble precursor route, and their electrical and second- and third-order nonlinear optical properties were studied. The PCEMPV films could not be doped with I_2 but could be doped with $FeCl_3$ to show an electrical conductivity of 5.0×10^{-3} S/cm. The conductivities of $FeCl_3$-doped copolymer films ranged from 8.0×10^{-3} to 6.5 S/cm depending on their copolymer compositions. The electro-optic properties of corona-poled copolymer films containing 32 mol % of the CEMPV unit were investigated by using a reflection measurement technique, and they showed electo-optic coefficients of 1.2 ± 0.3 pm/V. No significant decay of the electro-optic responses was observed for over 2600 h at room temperature. Most significant is the fact that these polymers showed no detectable decay and no tendency of relaxation for 150 h even at 100 °C. The third-order nonlinear optical susceptibility, $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$, was also investigated by the degenerate four wave mixing (DFWM) technique at 602 nm. The $\chi^{(3)}$ values of PCEMPV and 32-poly(PV-*co*-CEMPV) were 8.3×10^{-11} and 3.0×10^{-10} esu, respectively.

Introduction

Conjugated polymers are currently attracting much interest as materials for a wide variety of applications including lightweight batteries, electronic and nonlinear optical (NLO) devices, and even as potential replacements for metal wires.[1,2] Especially, interests in poly(1,4-phenylenevinylene) (PPV) and its derivatives have been spawned in recent years by the recognition that these polymers reveal high electrical conductivities after doping,[3-5] high second-[6,8] and third-order optical nonlinearity,[9-11] good processibility and high film quality, etc. Also the photoluminescence and electroluminescence of these polymers have been extensively studied for the realization of light-emitting devices and large-area multicolor display.[12-14] Up to now, many second-order NLO polymers have been developed, but their thermal stability after poling has been one of the major problems to be improved for practical device applications. Electro-optic responses of the poled polymers decay slowly at elevated temperature because of the relaxation of the dipole alignment induced by the electric field. Various approaches have been proposed to improve the thermal and temporal stability. Cross-linking NLO chromophores to a polymer matrix[15,16] or doping NLO chromophores into highly stable polymers such as polyimide[17,18] are examples of these approaches. PPV derivatives can be used as good materials for thermally stable NLO device applications because they have a highly rigid backbone structure and good thermal stability up to 300 °C. Attaching donor and acceptor groups or NLO chromophores to PPV as side chains or directly to the polymer backbone may result in highly stable materials, and this was demonstrated indeed. Recently, we reported the second-order nonlinear optical properties of poly[(2-cyano-5-methoxy-1,4-phenylene)-vinylene] (PCMPV) and copolymers with PPV.[6,7] The electro-optic response was stable up to 100 °C when the materials were poled during elimination. We have also reported earlier the synthesis,[8,19] electrical conductivity,[19] and second-harmonic generation (SHG) activities[8] of poly-[(2-methoxy-5-nitro-1,4-phenylene)vinylene-*co*-(2-methoxy-1,4-phenylene)vinylene]s [poly(MNPV-*co*-MPV)]. Particularly, poly (MNPV-*co*-MPV) containing 67.5 mol % of the MNPV unit exhibited no relaxative SHG of $\chi^{(2)} = 1.0 \times 10^{-8}$ esu even when the sample film was heated to 100 °C. This polymer was obtained in a poled state by heating its organic-soluble precursor film in an electric field of 10^5 V/cm.[8] In this article, we report the synthesis of new PPV derivatives containing a stilbene moiety with both electron-donating methoxy and electron-withdrawing nitrile groups. Poly[2-(2-(4-cyanophenyl)ethenyl)-5-methoxy-1,4-phenylene)vinylene] (PCEMPV) and a series of copolymers with PPV were synthesized through a water-soluble precursor route and electrical conductivities were measured at room temperature. The electro-optic properties of poled copolymers were studied and the third-order nonlinear optical susceptibility of PCEMPV was determined by using a degenerate four wave mixing technique at 602 nm. The synthetic methods, spectroscopic studies, and electrical conductivities of analogous

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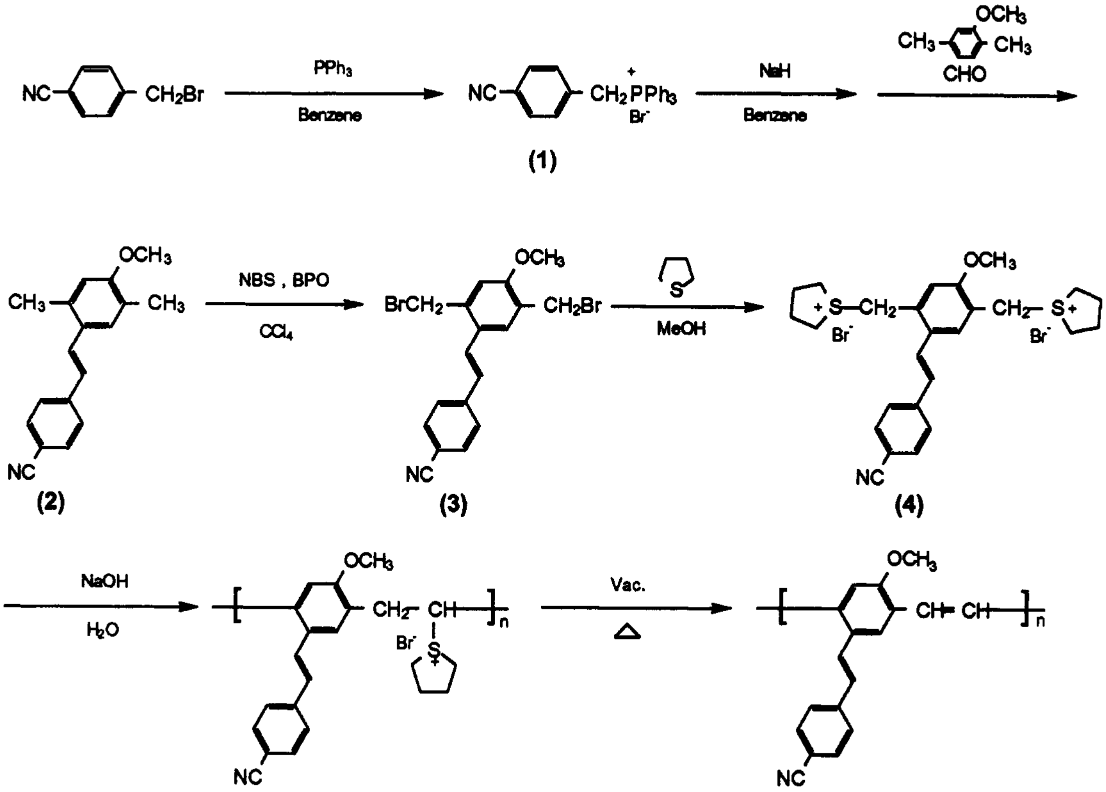
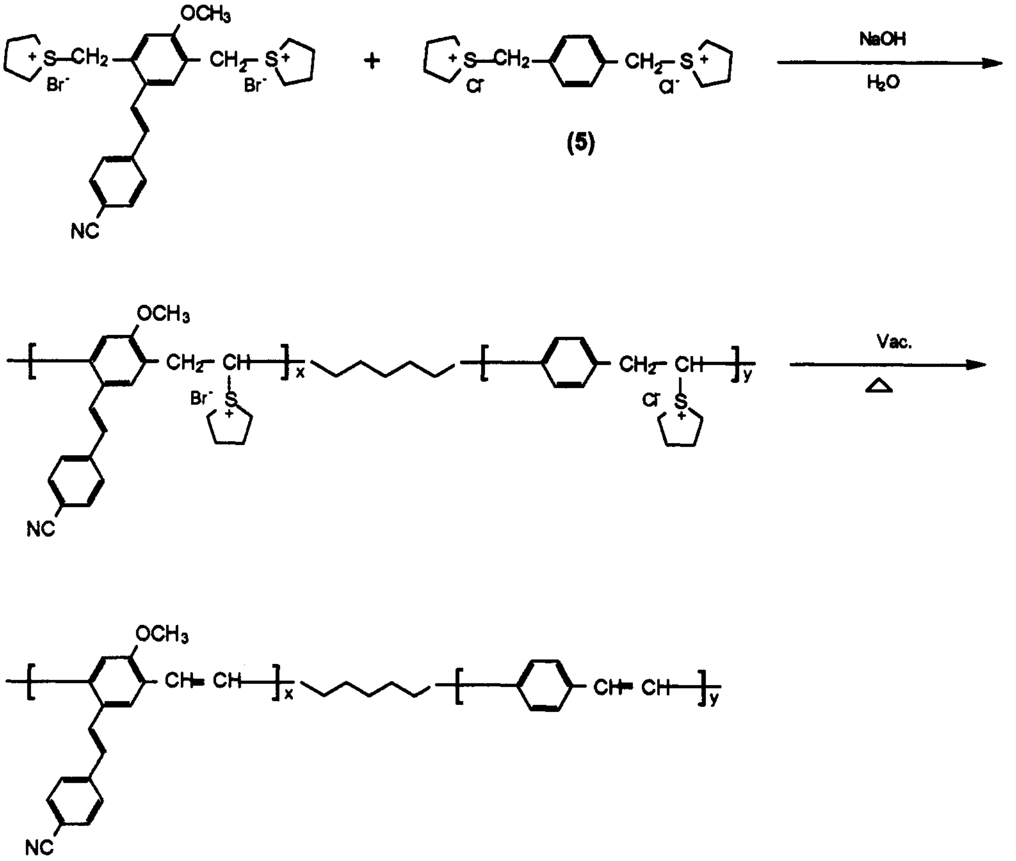
Scheme 1



Scheme 2



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 have been reported earlier by us.[20] The synthetic routes and polymer structures are shown in Schemes 1 and 2.

Experimental Section

Synthesis of Triphenyl(4-cyanobenzyl)phosphonium Bromide (1). A mixture of 20 g (102 mmol) of 4-cyanobenzyl bromide and 32 g (122 mmol) of triphenylphosphine in 150 mL of dry benzene was heated at 70 °C for 12 h with stirring. The mixture was allowed to cool to room temperature, and the white powder

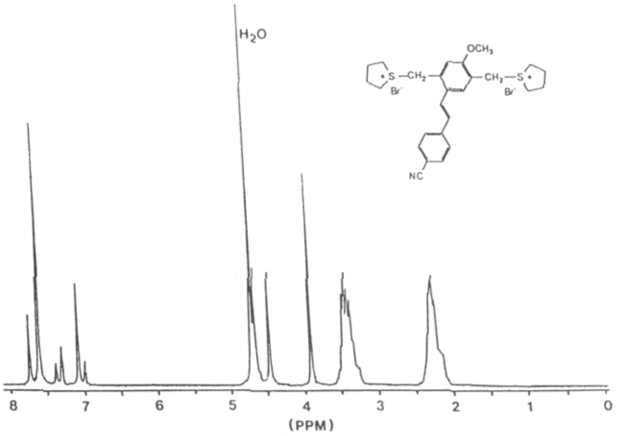


Figure 1. ^{1}H-NMR spectrum of salt monomer 4 (solvent: D_2O).

was filtered, washed with diethyl ether, and dried in a vacuum oven. The product yield was 44.4 g (95%): ^{1}H-NMR (200 MHz, DMSO) δ 7.90 (m, 3H), 7.74 (m, 14H), 7.20 (q, 2H), 5.45 (d, 2H); mp 330 °C (dec).

4′-Cyano-4-methoxy-2,5-dimethylstilbene (2). A mixture of 20 g (43.6 mmol) of phosphonium salt 1 and a slightly excess of sodium hydride in 150 mL of dry benzene was refluxed for 3–4 h, and then 7.2 g (43.6 mmol) of 2,5-dimethyl-4-methoxybenzaldehyde was added. The reaction mixture was refluxed for 12 h. After extraction with ethyl acetate, the extract was dried over anhydrous magnesium sulfate and the solvent was removed by distillation. The residue was recrystallized from methanol, and a yellow trans isomer was obtained. The product yield was 6.7 g (58%): ^{1}H-NMR (DMSO) δ 7.82 (s, 4H), 7.56 (d, 1H), 7.53 (s, 1H), 7.16 (d, 1H), 6.83 (d, 1H), 3.84 (s, 3H), 2.46 (s, 3H), 2.20 (s, 3H); mp 113–114 °C.

4′-Cyano-4-methoxy-2,5-bis(bromomethyl)stilbene (3). Compound **3** was prepared by reacting 5.0 g (19.0 mmol) of **2** with 7.1 g (40.0 mmol) of *N*-bromosuccinimide in 40 mL of carbon tetrachloride. A small amount of benzoyl peroxide was added as an initiator. The reaction mixture was refluxed at 90 °C for 3 h under a nitrogen atmosphere. When the reaction was finished, a yellow solid product and succinimide were precipitated. The reaction mixture was concentrated completely and washed with methanol. After filtration and vacuum drying, a yellow milky-colored solid was obtained. The product yield was 3.2 g (40%): ^{1}H-NMR (DMSO) δ 7.92 (s, 1H), 7.85 (m, 4H), 7.60 (d, 1H), 7.25 (d, 1H), 7.19 (s, 1H), 4.99 (s, 2H), 4.65 (s, 2H), 3.90 (s, 3H); mp 230 °C.

[(2-(2-(4-Cyanophenyl)ethenyl)-5-methoxy-1,4-phenylene)-dimethylene]bis(tetrahydrothiophenium bromide) (4). Compound **3** (3.0 g, 7.1 mmol) and excess tetrahydrothiophene were reacted for 24 h at 50 °C in 30 mL of methanol. The final salt monomer **4** was obtained by concentration of the reaction solution, precipitation in cold acetone, filtration, and vacuum drying. The product yield was 3.4 g (80%): ^{1}H-NMR (D_2O) δ 7.73 (s, 1H), 7.60 (s, 4H), 7.34 (d, 1H), 7.07 (s, 1H), 7.03 (d, 1H buried), 4.70 (s, H_2O), 4.66 (s, 2H), 4.46 (s, 2H), 3.90 (s, 3H), 3.45–3.25 (m, 8H), 2.45–2.12 (m, 8H) (m, 8H) (Figure 1); mp 239–240 °C (dec). The salt monomer for PPV, **5**, was prepared similarly from α,α′-dichloro-*p*-xylene and tetrahydrothiophene following the literature method.[21]

Polymerization. Synthetic methods for the homopolymer and copolymers were the same as those reported by us and others.[22–24] The monomer sulfonium salt solution was polymerized in a 1.0 N NaOH solution at 0 °C. A homogenous and viscous solution was obtained. For the copolymers, the total moles of the two monomers were kept constant, but their mole ratios were varied. The reaction was quenched by neutralization with 0.5 N aqueous HCl, and the neutralized polyelectrolyte precursor solutions were dialyzed against deionized water for 7 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 from these aqueous precursor polymer solutions were subjected to thermal elimination in vacuo (10^{-2} Torr) at 210 °C for 10 h to transform them into the final polyconjugated polymer films (thickness 10–20 μm).

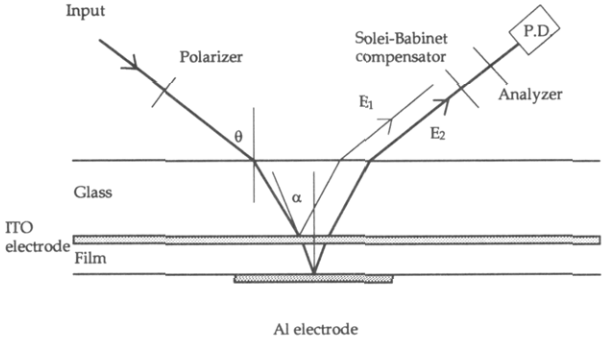


Figure 2. Optical configuration of the experimental setup for the reflection measurement technique.

Characterization. Melting points were determined using a Electrothermal Model 1307 digital analyzer. ^{1}H-NMR spectra were recorded on a Bruker AM 200 spectrometer. FT-IR spectra were recorded on a Bomem Michelson Series FT-IR spectrophotometer, and UV–visible spectra were obtained with a Shimadzu UV-3100S. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate 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. Thicknesses of the polymer films were measured by using an Alpha Step 200 profilometer. Refractive indices were measured by a prism coupling method. Electrical conductivities of doped polymer films were measured by the four-in-line probe method at room temperature.

Measurement of Electro-optic Coefficient. The electro-optic coefficient of the poled polymer was measured by using the reflection measurement technique.[25,26] Figure 2 shows a schematic diagram of the optical configuration of the experimental setup. A He–Ne laser beam (632.8 nm) is incident on the back side of the glass substrate at an angle θ. It propagates through the substrate, the ITO glass, and the polymer layer and is then reflected back out into the air by the top aluminum electrode. The polarization of the input beam is set at 45° to the plane of incidence so that the parallel (p-wave) and perpendicular (s-wave) components of the optical field are equal in amplitude. The reflected beam propagates through a Solei-Babinet compensator, an analyzer, and into a detector. The modulation in the beam is measured using a lock-in amplifier.

Measurement of Third-Order Nonlinear Susceptibility, $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$. The experimental setup used for degenerate four wave mixing (DFWM) utilized a laser system in which the IR output of a mode-locked continuous wave (CW) Nd:YAG laser was first compressed in a grating fiber compressor and then frequency-doubled to sync-pump a CW dye laser. The dye pulses were subsequently amplified by frequency-doubled pulses from a 30 Hz Q-switched pulsed Nd:YAG laser to generate around 400 fs nearly transform-limited pulses with an energy of 0.4 mJ at 602 nm. A peak power density of around 400 MW/cm^2 was used in our study. The beams in the forward wave geometry for DFWM were focused onto the film. The four-wave mixing signal was detected by a photodiode and processed by a boxcar averager.

Results and Discussion

Table 1 summarizes the data for monomer conversions to precursor polymers, polymer yields, and the compositions of the final copolymers as calculated from elemental analyses. The data for monomer conversions were obtained by back-titration of the precursor polymer solution. The polymer yields were estimated gravimetrically from the weight of cast films. The degrees of monomer conversions to precursor polymers are very high, ranging from 82 to 95%, and the polymer yields (42–60%) are comparable to or slightly higher than those reported for other similar polymerization systems.[19,27,28] Both the degrees of conversion and the polymer yields are increased

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

polymer[a]	feed monomer ratio (5:4)	actual ratio (PV[b]:CEMPV[c])	monomer conv (%)	polymer yield (%)
PCEMPV	0:100	0:100	95	60
88-poly(PV-*co*-CEMPV)	17:83	12:88	92	57
63-poly(PV-*co*-CEMPV)	50:50	37:63	90	53
32-poly(PV-*co*-CEMPV)	83:17	68:32	87	48
21-poly(PV-*co*-CEMPV)	91:9	79:21	82	42

[a] The numerical values stand for mole percent of CEMPV units in the final copolymers, and these values were calculated from the results of the elemental analyses (C, H, N). [b] PV: 1,4-phenylenevinylene unit. [c] CEMPV: (2-(2-(4-cyanophenyl)ethenyl)-5-methoxy-1,4-phenylene)vinylene unit.

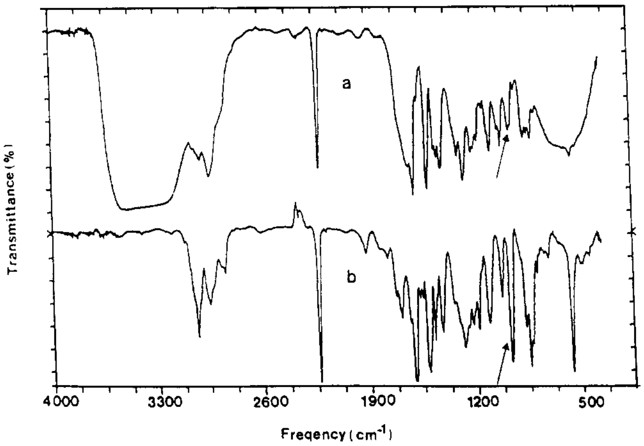


Figure 3. FT-IR spectra of (a) precursor and (b) final eliminated 32-poly(PV-*co*-CEMPV).

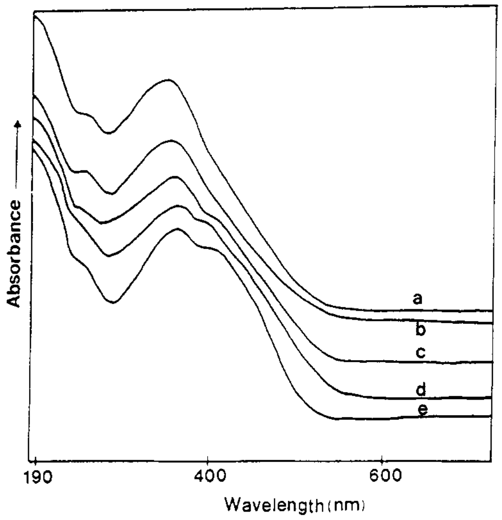


Figure 4. UV–visible spectra of (a) PCEMPV, (b) 88-poly(PV-*co*-CEMPV), (c) 63-poly(PV-*co*-CEMPV), and (d) 32-poly(PV-*co*-CEMPV), and (e) 21-poly(PV-*co*-CEMPV).

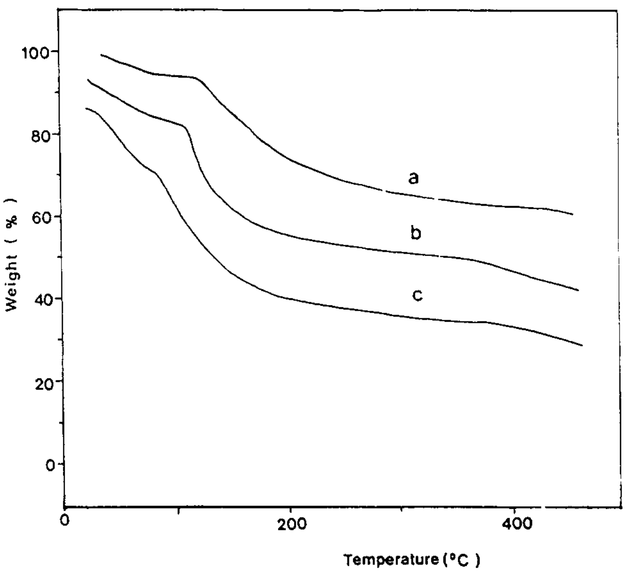


Figure 5. TGA thermograms of precursor polymers of (a) PCEMPV, (b) 63-poly(PV-*co*-CEMPV), and (c) 21-poly(PV-*co*-CEMPV).

by increasing CEMPV monomer ratio in the feed. Comparison of the values of the polymer yields with those of the monomer conversions indicates that a substantial amount of precursor polymers formed was removed during dialysis using a dialysis tube with a molecular weight cutoff at 12 000. Thus the molecular weight of these polymers must be reasonably high. The content of CEMPV units incorporated in the copolymers was higher than that in the feed monomer mixtures, suggesting that CEMPV monomer is more reactive than PV monomer. All of the precursor polymer solutions after dialysis appeared homogeneous and transparent.

The FT-IR spectrum of a copolymer containing 32 mol % of CEMPV units, 32-poly(PV-*co*-CEMPV), is compared with that of the corresponding precursor polymer film in Figure 3. The precursor polymer exhibits a broad absorption peak at 3100–3600 cm^{-1} due to absorbed water, which disappears in the spectrum of the eliminated film. A weak but sharp absorption of the precursor polymer at 960 cm^{-1} is due to the *trans*-vinylene =C–H out-of-plane bending mode of the stilbene double bond. The absorption intensity at this position is highly increased after elimination, suggesting that the generated double bonds in the main chain are also entirely of trans configuration. Both the precursor and the eliminated films exhibit sharp absorption peaks at 2223 cm^{-1} due to the nitrile groups.

Figure 4 shows the UV–visible spectra of PCEMPV and copolymer films. All of the polymers show the strong π–π^* transition of the *trans*-stilbene moiety at about 330 nm. As the content of CEMPV units in the copolymers increases, the position of maximum absorption slightly shifts to the shorter wavelength region. Especially, the absorption band due to the π–π^* transition of the main-chain double bonds of PCEMPV homopolymer film is buried in the strong absorption band of the *trans*-stilbene moiety, but definitely visible at around 410 nm. As shown in Figure 4, the absorption maximum is slightly moved to the longer wavelength region by increasing the PV unit, and the buried absorption band of the main-chain double bonds is separated from that of the stilbene moiety. The spectrum of the 21-poly(PV-*co*-CEMPV) copolymer film shows distinct two absorption bands due to the stilbene moiety (λ_{max} = 350 nm) and the main-chain double bond (λ_{max} = 410 nm), respectively.

Figure 5 shows the TGA thermograms of the precursor polymers. There are two regions in this thermogram, i.e., linear weight loss below 120 °C and steep weight loss above 120 °C. The weight loss in the low-temperature region below 120 °C corresponds to the loss of the absorbed water,

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

polymer	conductivity (S/cm)
PCEMPV	5.0×10^{-3}
88-poly(PV-*co*-CEMPV)	8.0×10^{-3}
63-poly(PV-*co*-CEMPV)	2.0×10^{-2}
32-poly(PV-*co*-CEMPV)	6.0×10^{-2}
21-poly(PV-*co*-CEMPV)	1.5×10^{-1}

and the higher temperature region corresponds to the elimination of tetrahydrothiophene and HCl or HBr. In these thermograms, PCEMPV and copolymers revealed good thermal stability up to 400 °C.

Electrical Conductivities of the Polymers. Table 2 shows the maximum conductivity values of $FeCl_3$-doped PCEMPV and copolymers. Substitution on the phenylene ring of PPV with different types of electron-donating or electron-withdrawing groups has a significant influence on the electronic structures and morphology of the resulting polymers.[19-24,27-29] For example, the PPV films are hardly doped with a weak oxidizing dopant like I_2.[30] In contrast, poly[(2,5-dimethoxy-1,4-phenylene)vinylene] (PDMPV) can be easily doped with I_2 and $FeCl_3$ to give electrical conductivities of 10^1–10^3 S/cm.[5] These high conductivities can be attributed to the electron-donating effect of the two methoxy groups. Similarly enhanced electrical conductivity was observed for I_2-doped poly[(2-*n*-butoxy-5-methoxy-1,4-phenylene)vinylene] (PBMPV).[31] By the way, the precursor polymers of PDMPV cannot be stretched to any extent, whereas the precursor polymer of PBMPV can be stretched. Recently, we reported the synthesis and electrical properties of electron-withdrawing group substituted PPV derivatives, such as poly[(2-methoxy-5-nitro-1,4-phenylene)vinylene] (PMNPV),[8,19] poly[(5-cyano-2-methoxy-1,4-phenylene)vinylene] (PCMPV),[32] and copolymers with PPV. The PMNPV and PCMPV films cannot be doped with I_2 but they can be readily doped with $FeCl_3$, though doped polymers exhibit very low electrical conductivities. Similar results were obtained with PCEMPV. The PCEMPV films could not be doped with I_2 but could be doped with $FeCl_3$. The electrical conductivity of the PCEMPV film was 5.0×10^{-3} S/cm. In copolymers, as the content of CEMPV unit in the copolymer increases, the electrical conductivity steadily decreases as shown in Table 2. It is originally expected that the presence of the strong electron-withdrawing nitrile group raises the oxidation potential of the polymer chain, resulting in reduced dopability. Therefore, the conductivity values of CEMPV-rich polymers are not so high. Unsubstituted PPV films showed relatively low electrical conductivities of 10^{-3}–10^{-4} S/cm after $FeCl_3$ doping.[33] Nevertheless, the copolymer films containing a small amount of bulky CEMPV units show significantly high conductivity values. This result can be explained by the morphological effect of the polymer chain. A small amount of CEMPV unit effectively breaks the dense packing structure of the PPV backbone and thus this makes it easier for the dopants to approach and oxidize the polymer chain. The inclusion of a small amount of a comonomer unit having a bulky substituent, regardless of its nature, into PPV enhances the dopability and, thus, electrical conductivity.[27,28] We believe that the doped PV unit largely contributes to the net conductivities of the copolymers.

Electro-optic Properties of 32-Poly(PV-*co*-CEMPV). For the electro-optic experiment, we chose 32-poly(PV-*co*-CEMPV) copolymer film because this polymer forms the high-quality films. Polymers with CEMPV contents >63% were somewhat brittle after elimination. Films were prepared by spin coating or casting from the precursor solutions dissolved in water. The solutions were first filtered to remove particle impurities, spun at 400–1000 rmp depending on the desired thicknesses, and finally dried in a vacuum oven to remove water. For electro-optic coefficient measurements, ITO glass plates were used as substrates. Corona discharge poling was employed to orient the NLO chromophores. In general, ionic polymers are difficult to pole because of their intrinsic ionic conductivity. Nevertheless, it has been reported that a significant poling-induced NLO chromophore alignment can be achieved in poled ionic polymers.[34-36] We adoped a two-stage poling process as schematically shown in Figure 6 based on the TGA thermogram. By keeping the film at 120 °C for 2 h under a corona field, the NLO chromophores are expected to be oriented with slow elimination. The dipole alignment formed during the time can be stabilized by the thermal elimination at 210 °C. After corona poling, a thick aluminum electrode was made on the top side of the corona-poled sample by thermal evaporation. The electro-optic coefficient was measured using the reflection measurement technique and calculated by the following equation:[25,26]

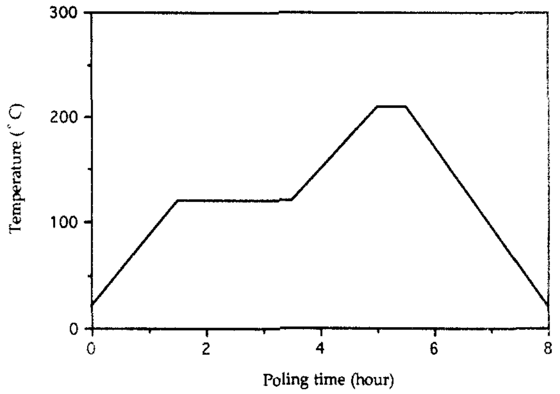


Figure 6. Schematic representation of the two-stage poling procedure.

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{(n^2 - \sin^2\theta)^{3/2}}{n^2 - 2\sin^2\theta} \frac{1}{\sin^2\theta} \qquad (1)$$

where λ is the optical wavelength, I_m is the amplitude of the modulation, I_c is the half-intensity point, V_m is the modulating voltage, and n is the refractive index. 32-Poly(PV-*co*-CEMPV) showed an electro-optic coefficient at 1.2 ± 0.3 pm/V. This value is comparable to that of poly[(2-cyano-5-methoxy-1,4-phenylene)vinylene] (PCMPV) and its copolymers reported before,[6,7] even though poly(PV-*co*-CEMPV) has a longer conjugation length than poly(PV-*co*-CMPV). This result can be explained by the orientation effect of the NLO chromophores incorporated in the polymer chain. The conjugation length of the CEMPV unit is more extended than that of the CMPV unit, but the CEMPV unit has some disadvantage in dipole alignment because it has a large steric hindrance for orientation in a rigid polymer backbone. In other words, under the same poling condition, the degree of orientation of the CEMPV unit is smaller than that of the CMPV unit. Figures 7 and 8 show the temporal and thermal stability of the electro-optic responses, respectively. No significant decay of the electro-optic responses was observed for over 2600 h at room temperature. Most significant is the fact that this polymer shows no detectable decay and no tendency of relaxation for 150 h even at 100 °C as shown in Figure 8. The thermal stability and NLO

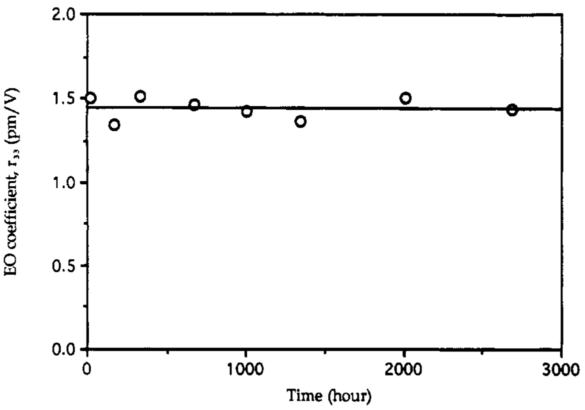


Figure 7. EO coefficients, r_{33}, of 32-poly(PV-*co*-CEMPV) measured as a function of time at room temperature under ambient conditions.

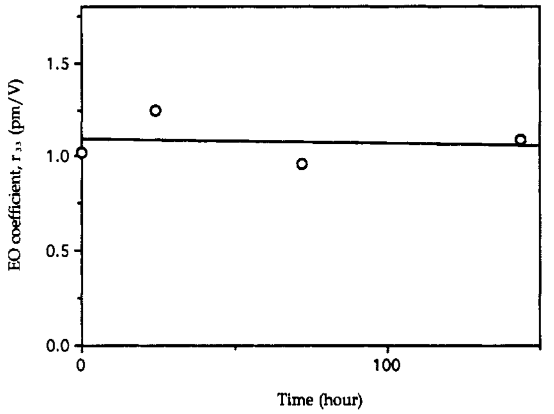


Figure 8. EO coefficients, r_{33}, of 32-poly(PV-*co*-CMSV) measured as a function of time at 100 °C under ambient conditions.

activity of PPV derivatives, as demonstrated in this paper and also in one of our earlier papers, suggest a new approach to obtain second-order nonlinear optical polymers with good thermal stability. By replacing the CN or OCH_3 group with stronger acceptors or donors and taking the optimum poling conditions, higher electro-optic coefficients may be achievable.

Third-Order Nonlinear Susceptibility of PCEMPV and 32-Poly(PV-*co*-CEMPV). The $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$ values of thin films of PCEMPV and 32-poly(PV-*co*-CEMPV) were evaluated by comparing the strength of the conjugated DFWM signal with that of THF at the same incident photon flux according to the following relationship:[9,37]

$$\frac{\chi_s^{(3)}}{\chi_t^{(3)}} = \left(\frac{n_s}{n_t}\right)^2 \frac{l_t}{l_s}\left(\frac{I_s}{I_t}\right)^{1/2} \frac{\alpha l_s}{\exp(-\alpha l_s/2)[1-\exp(-\alpha l_s)]} \qquad (2)$$

where n is the refractive index, l is the interaction length, α is the linear absorption coefficient of the polymer sample at 602 nm, and I is the intensity of the DFWM signal. The subscripts t and s refer to THF and the sample, respectively. The value of $\chi^{(3)} = 3.7 \times 10^{-14}$ esu was used as the reference value for THF. The subpicosecond response of the PCEMPV film sample is shown in Figure 9. The measured $\chi^{(3)}$ value for PCEMPV was 8.3×10^{-11} esu. This value is slightly smaller than that of PPV, 4.0×10^{-10} esu at 602 nm as reported by Singh et al.[38] Recently, we reported the third-order nonlinear optical properties of poly[(2-butoxy-5-methoxy-1,4-phenylene)vinylene] (PBMPV) and poly[(2-bromo-5-methoxy-1,4-phenylene)vinylene] (PBrMPV).[39] The measured $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$ values of PBMPV and PBrMPV were 2×10^{-9} and 9×10^{-10} esu, respectively. These results reflect that there is a significant contribution to $\chi^{(3)}$ values from the subsitutents at the 2 and 5 positions of the PPV phenylene ring. In the case of PBMPV, the electron-donating butoxy and methoxy groups enhance the π-electron density in the conjugated polymer chain and thus the $\chi^{(3)}$ value. However, in the case of PBrMPV, the weakly electron-attracting bromine group reduces the π-electron density, and so the $\chi^{(3)}$ value is smaller than that of PBMPV. In our experiment, though the conjugation length of PCEMPV is more extended than that of PPV by the introduction of the stilbene moiety, the strong electron-withdrawing nitrile group decreases the π-electron density and also disturbs the delocalization of the π-electrons in the conjugated polymer chain. Therefore the PCEMPV film is expected to have a smaller $\chi^{(3)}$ value than PPV. 32-Poly(PV-*co*-CEMPV) copolymer film shows the $\chi^{(3)}$ value of 3.0×10^{-10} esu. This value is higher than that of PCEMPV. One can expect that the copolymers reveal $\chi^{(3)}$ values between those of PCEMPV and PPV. All of the above observations are consistent with our conclusions.

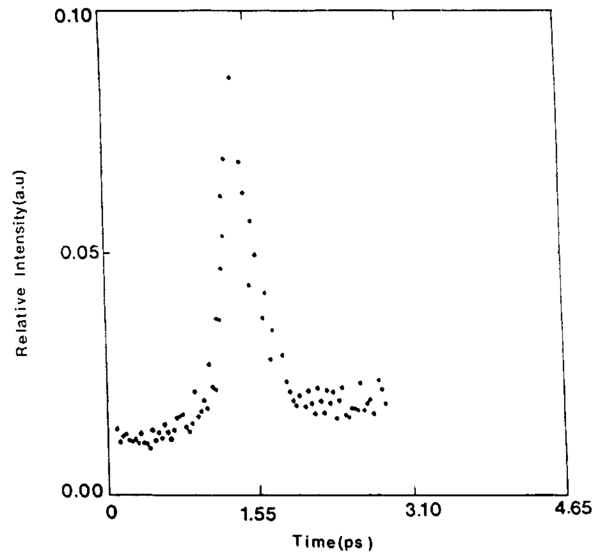


Figure 9. DFWM signal observed for PCEMPV as a function of the forward beam delay (wavelength 602 nm, 400 fs pulses).

Conclusion

Multifunctional PCEMPV and its copolymers were prepared via the water-soluble precursor route. Although the electrical conductivity of PCEMPV film was not high, the copolymer films showed high conductivity values depending on their copolymer compositions. The electro-optic property of poled 32-poly(PV-*co*-CEMPV) was investigated by using the reflection measurement technique. The electro-optic responses were stable even at 100 °C. The good thermal stability and mechanical strength of PPV and its derivatives and easy processibility from the precursor polymers suggest a new approach to the molecular design of poled electro-optic polymers. The PCEMPV and 32-poly(PV-*co*-CEMPV) films showed considerably high $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$ values, although the introduction of the CEMPV unit decreased the π-electron density and also disturbed the delocalization of the π-electrons in the conjugated polymer chain.

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