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Synthesis and electrical properties of poly[2-(2-(4-trifluoromethyl)phenyl)ethenyl-1,4-phenylenevinylene] and PPV copolymers

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Summary

Poly[2-(2-(4-(trifluoromethyl)phenyl)ethenyl)-5-methoxy-1,4-phenylenevinylene] (PFEMPV) and a series of PPV copolymers containing 1,4-phenylenevinylene (PV) units were synthesized through a water-soluble precursor route, and their electrical and third-order nonlinear optical properties were studied. The PFEMPV films could not be doped with I_2, but $FeCl_3$-doped films showed an electrical conductivity of 5.0×10^{-4} S/cm. The conductivities of $FeCl_3$-doped copolymer films ranged from 2.0×10^{-3} to 2.0 S/cm depending on their copolymer compositions. The third-order nonlinear optical susceptibility, $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$, was also investigated by the degenerate four wave mixing technique at 602 nm. The $\chi^{(3)}$ value of PFEMPV was 6.9×10^{-11} esu. The photoluminescence spectrum of PFEMPV shows its emission maximum at 550 nm.

Introduction

The field of organic conjugated polymers such as polyacetylene, polyaromatics, polyheteroaromatics, poly(p-phenylenevinylene) and polyaniline, etc. has emerged as one of the most exciting and interdisciplinary areas in last a few decades because of their possible applications to the electronic and photonic devices.[1-5] Among them, interests in poly(1,4-phenylenevinylene) (PPV) and its derivatives have been increased because these polymers show high electrical conductivity[6,7], third-order optical nonlinearity[8,9] and good film quality, in addition to good processibility from the water-soluble precursor polymer. Also the study on photoluminescence (PL) and electroluminescence (EL) of these polymers is one of the hot current issues in these days for realization of large area multicolor display and various light-emitting devices.[10,11] Substitution on the phenylene ring of PPV with different types of substituents shows significant differences in electronic structures and morphologies of the corresponding polymers and thus affects the electrical, optical and other physical properties of the resulting polymers. We reported the synthesis and properties

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of PPV derivatives containing both electron donating and electron withdrawing groups. Especially, poly(2-cyano-5-methoxy-1,4-phenylenevinylene) (PCMPV)[12,13] and poly[2-(2-(4-cyanophenyl)ethenyl)-5-methoxy-1,4-phenylenevinylene] (PCEMPV)[9] and their copolymers with PPV showed the 2nd-order nonlinear optical properties with good thermal stability up to 100 °C when the materials were poled during elimination.

In this article, we report the synthesis of new PPV derivatives containing stilbene moiety attached both electron donating and withdrawing groups. Poly[2-(2(4-(trifluoromethyl)phenyl)ethenyl)-5-methoxy-1,4-phenylenevinylene] (PFEMPV) and a series of PPV copolymers were synthesized through a water-soluble precursor route. The electrical conductivities and third-order nonlinear optical properties of these polymers were studied. The synthetic routes and polymer structures are shown in scheme 1 and 2.

Experimental part

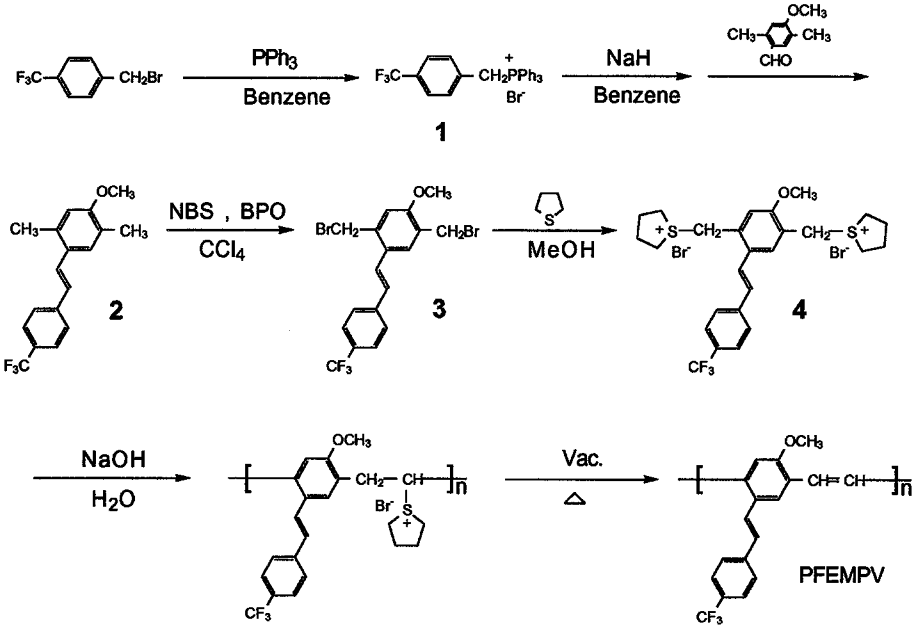
Monomer Synthesis

Triphenyl[4-(trifluoromethyl)benzyl]phosphonium bromide (1). A mixture of 20 g (83.7 mmol) of 4-(trifluoromethyl)benzyl bromide and 26.4 g (101 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 was filtered, washed with diethyl ether, and dried in a vacuum oven. The product yield was 40 g (95%) : mp 257-258 °C (dec) : ^{1}H-NMR (200 MHz, DMSO-d_6) δ 7.90 (m, 3H), 7.76 (m, 14H), 7.2 (d, 2H), 5.43 (d, 2H). Elem anal. Calcd: C, 62.27; H, 4.19. Found: C, 62.64; H, 4.19.

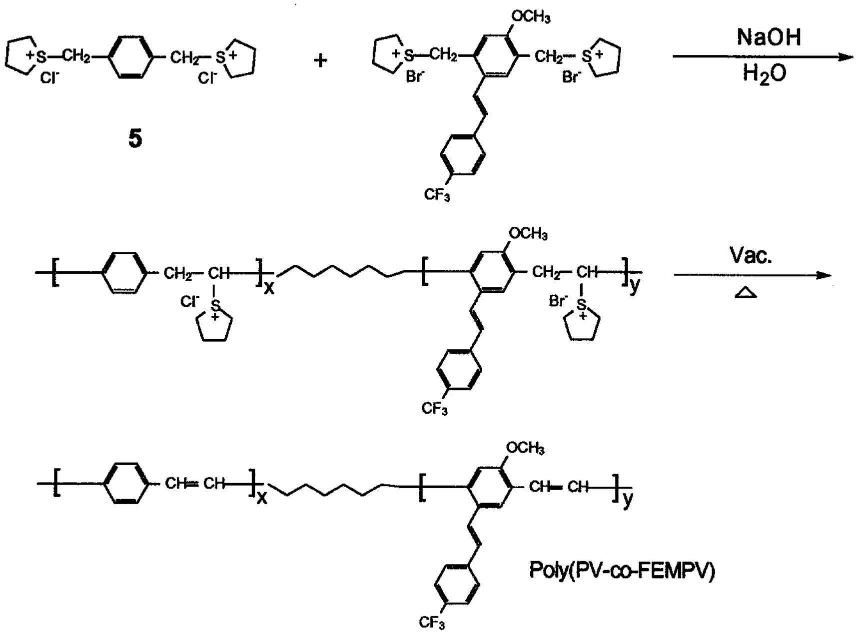
4′-Trifluoromethyl-4-methoxy-2,5-dimethylstilbene (2). A mixture of 20 g (40.0 mmol) of phosphonium salt **1** and a slight excess of sodium hydride in 150 mL of dry benzene was refluxed for 3-4 h, and then 6.6 g (40.0 mmol) of 2,5-dimethyl-4-methoxybenzaldehyde was added. The reaction mixture was refluxed 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 7.3 g (60%) : mp 101 °C : ^{1}H-NMR (DMSO-d_6) δ 7.79 (d, 2H), 7.68 (d, 2H), 7.52 (s, 1H), 7.49 (d, 1H), 7.09 (d, 1H), 6.79 (s, 1H), 3.79 (s, 3H), 2.41 (s, 3H), 2.15 (s, 3H). ^{13}C-NMR (DMSO-d_6) δ 157.35, 141.83, 135.15, 128.47, 127.34, 127.12, 126.98, 126.64, 125.43, 125.35, 125.29, 123.35, 121.72, 112.11, 55.13, 19.36, 15.65. Elem anal. Calcd: C, 70.56; H, 5.55. Found: C, 71.62; H, 6.14.

4′-Trifluoromethyl-4-methoxy-2,5-bis(bromomethyl)stilbene (3). Compound **3** was prepared by reacting 5.0 g (16.3 mmol) of **2** with 6.1 g (34.2 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 3.0 g (40%) : mp 178 °C : ^{1}H-NMR (DMSO-d_6) δ 7.93 (s,1H), 7.86 (d, 2H), 7.75 (d, 2H), 7.66 (d, 1H), 7.28 (d, 1H), 7.20 (s, 1H), 4.98 (s, 2H), 4.66 (s, 2H), 3.90 (s, 3H). ^{13}C-NMR (DMSO-d_6) δ 156.93, 141.46, 138.02, 128.59,

Scheme 1



Scheme 2



127.94, 127.03, 126.75, 125.63, 125.56, 121.75, 113.32, 55.95, 32.63, 29.29. Elem anal. Calcd: C, 46.56; H, 3.23. Found: C, 46.22; H, 3.15.

2-(4-(Trifluoromethyl)phenyl)ethenyl-5-methoxy-1,4-phenylenedimethylene bis(tetrahydrothiophenium bromide) (4). Compound 3 (3.0 g, 6.5 mmol) and excess tetrahydrothiophene were reacted for 24 h at 50 °C in 20 ml of methanol. The salt monomer 4 was obtained by concentration of the reaction solution, precipitation in cold acetone, filtration and vacuum drying. The product yield was 3.5 g (85%) : mp 201-202 °C (dec) : ^{1}H-NMR (D_2O) δ 7.60 (s, 1H), 7.52 (s, 4H), 7.27 (d, 1H), 7.96 (s, 1H), 7.94 (d, 1H), 4.69 (s, 2H), 4, 32 (s, 2H), 3.74 (s, 3H), 3.45-3.10 (m, 8H), 2.50-1.85 (m, 8H). Elem anal. Calcd: C, 48.74; H, 4.84. Found: C, 48.44; H, 4.79.

The salt monomer for PPV, 5, was prepared similarly from α, α'-dichloro-p-xylene and tetrahydrothiophene following the literature method.[6]

Polymerization

The 1.0 g (1.7 mmol) of monomer 4 was dissolved in 70 mL of deionized water. The salt monomer solution was polymerized in a 0.5 N NaOH solution at 0 °C. A homogeneous 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.

Analysis

Melting points were determined using a Electrothermal Model 1307 digital analyzer. ^{1}H-NMR and ^{13}C-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 ESCA analysis at 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 after doping. The photoluminescence spectra were recorded on a Perkin Elmer LS-50 fluorometer at room temperature utilizing a lock-in amplifier system with chopping frequency of 150 Hz and Xenon lamp as an excitation light source.

Measurement of third-order nonlinear optical susceptibility, $\chi^{(3)}$

The experimental set-up used for degenerate four wave mixing (DFWM) utilized a laser system in which the I.R. 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

Figure 1 shows the UV-visible spectra of PFEMPV and copolymer films. The PFEMPV shows strong absorption at about 330 nm by π-π^* transition of the stilbene moiety, and also shows distinct absorption band due to the conjugated main chain about 400 nm. By decreasing the FEMPV unit in copolymers, the maximum absorption peak about 330 nm by stilbene moiety gradually decreases and the maximum position is slightly moved to the longer wavelength region.

Figure 2 shows the TGA thermogram of the precursor polymer of 32-poly(PV-co-FEMPV), which contains 32 mole % of FEMPV unit in copolymer. In this thermogram, the elimination reaction is completed below 200 °C and the eliminated polymer film shows a good thermal stability up to 350 °C.

Table 1 shows draw ratios and the maximum conductivity values of $FeCl_3$-doped PFEMPV and copolymer films. The PFEMPV film couldn't be doped with I_2 but doped with $FeCl_3$ and the electrical conductivity of the PFEMPV film was 5.0 x 10^{-4} S/cm. In copolymers, as the content of FEMPV unit in the copolymer decreases further, the electrical conductivity steadily increases as shown in Table 1. The precursor polymer films of PFEMPV and copolymers containing high contents of the FEMPV unit couldn't be stretched to any extent, but the precursor polymer films containing low contents of

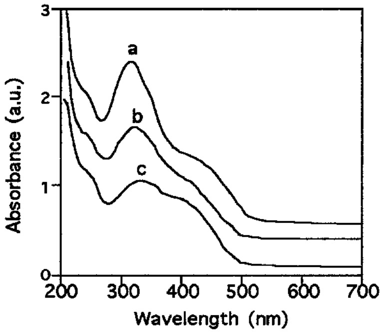


Figure 1. UV-visible spectra of (a) PFEMPV, (b) 32 and (c) 8-poly(PV-co-FEMPV)

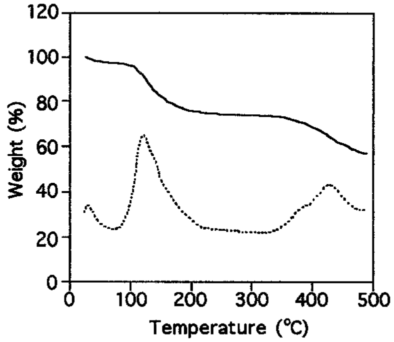


Figure 2. TGA thermogrm of 32-poly(PV-co-FEMPV)

Table 1. Maximum conductivities of $FeCl_3$-doped PFEMPV and poly(PV-co-FEMPV)s

Polymer[a]	Draw ratio (ℓ/ℓ_o)	Conductivity (S/cm)
PFEMPV	1	5.0×10^{-4}
41-poly(PV-co-FEMPV)	1	2.0×10^{-3}
32-poly(PV-co-FEMPV)	1	1.5×10^{-2}
22-poly(PV-co-FEMPV)	1	1.5×10^{-1}
	5	5.0×10^{-1}
8-poly(PV-co-FEMPV)	1	4.0×10^{-1}
	6	2.0

[a] The numerical values stand for mole % of FEMPV unit in the final copolymers, and these numbers were calculated by determining the amount of carbon and fluorine in copolymers from the results of the ESCA data

FEMPV unit could be stretched up to the draw ratio of 6. The drawn copolymer film of 8-poly (PV-co-FEMPV), when doped with $FeCl_3$, showed a maximum conductivity value of 2.0 S/cm. It is originally expected that the presence of the strong electron-withdrawing trifluoromethyl group raises the oxidation potential of the polymer chain resulting in reduced dopability. Therefore, the conductivity values of FEMPV rich polymers are not so high. We suppose that a small amount of FEMPV unit effectively breaks the dense packing structure of PPV backbone and thus this makes it easier for the dopants to approach and oxidize the PPV polymer chain. It is well known that PPV could hardly be doped with I_2 and $FeCl_3$. We believe that the doped PV units largely contribute to the net conductivities of the copolymers.

Third-order nonlinear optical susceptibility of PFEMPV. The $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$ values of the thin films of PFEMPV was 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;

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

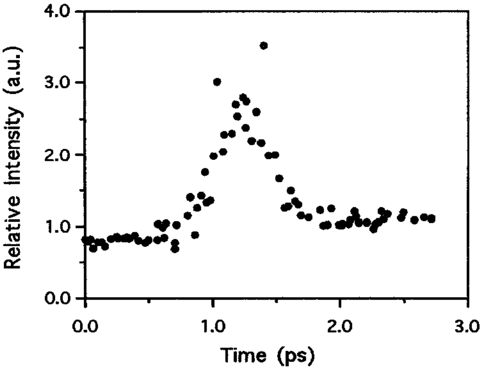


Figure 3. DFWM signal observed for PFEMPV as a function of the forward beam delay (wavelength 602 nm, 400 fs pulses)

where n is the refractive index, ℓ the interaction length, α the linear absorption coefficient of 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.[14,15] The subpicosecond response of the PFEMPV film is shown in Figure 3. The measured $\chi^{(3)}$ value for PFEMPV was 6.9×10^{-11} esu. This value is smaller than that of PPV, 4.0×10^{-10} esu at 602 nm reported by Singh et al.[15] Though the conjugation length of PFEMPV is more extended than that of PPV by the introduction of the stilbene moiety, the strong electron-withdrawing trifluoromethyl group decreases the π-electron density and also disturbs the delocalization of the π-electrons in the conjugated polymer chain. Therefore we can conclude that the $\chi^{(3)}$ value of PFEMPV is more affected by the strong electron-withdrawing nature of trifluoromethyl group than the extended conjugation length by the stilbene moiety.

The light-emitting properties of PPV and its derivatives have been extensively studied in these days for their attractive application to the large area multicolor display. Figure 4 shows the photoluminescence spectrum of PFEMPV excited at 360 nm. The PFEMPV shows its emission maximum at about 550 nm, which corresponds to yellow color region. Generally photoluminescence is very close to the electroluminescence spectrum, so we expect that the PFEMPV film will show a yellow electroluminescence. The detailed light-emitting properties of PFEMPV are under investigation. The PFEMPV film which has a good processibility from the soluble precursor polymer and yellow light-emitting properties may be a good candidate for application to the polymer LEDs.

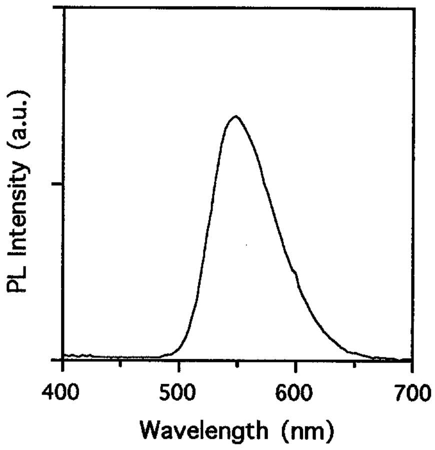


Figure 4. Photoluminescence spectrum of PFEMPV film.

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