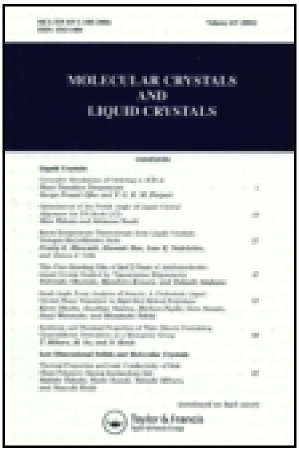

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Electrical and Optical Properties of Poly[2,5-bis(Trimethylsilyl)- 1,4-Phenylenevinylene] and PPV Copolymers

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ELECTRICAL AND OPTICAL PROPERTIES OF POLY[2,5-BIS(TRIMETHYLSILYL)-1,4-PHENYLENEVINYLENE] AND PPV COPOLYMERS

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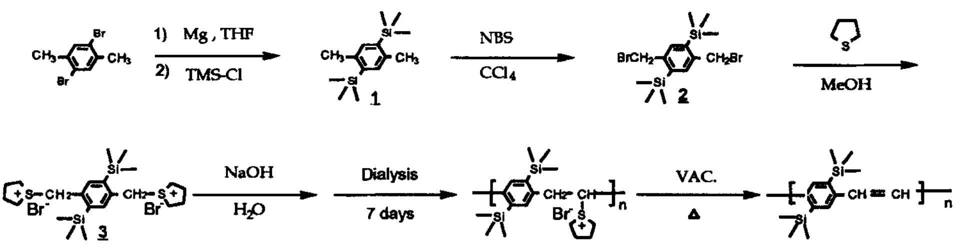
Abstract Novel silicon substituted PPV derivatives, poly[2,5-bis(trimethylsilyl)-1,4-pheylenevinylene] (BTMS-PPV) and PPV copolymers, were synthesized through water-soluble precursor route, and their electrical and third-order nonlinear optical properties were studied. The BTMS-PPV films could not be doped with I_2 but doped with $FeCl_3$ to show the electrical conductivity of 5.0×10^{-4} S/cm. The conductivities of $FeCl_3$-doped copolymer films ranged from 5.0×10^{-1} to 25 S/cm depending on their copolymer compositions and draw ratios. The third-order nonlinear optical susceptibility, $\chi^{(3)}(-\omega;\omega,\omega,-\omega)$, was also investigated by the degenerate four-wave mixing (DFWM) measurement technique at 602 nm. The calculated $\chi^{(3)}$ value of BTMS-PPV was 5.8×10^{-10} esu. The photoluminescence spectrum of BTMS-PPV was observed and it showed its emission in pure green region.

INTRODUCTION

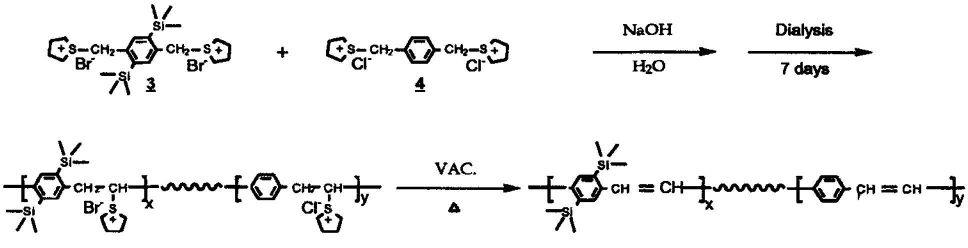
The field of organic conjugated polymers such as polyacetylene, polyaromatics, polyheteroaromatics, poly(p-phenylenevinylene) and polyaniline, etc. has emerged as one of the most exciting and interdisciplinary areas in last a few decades because they show not only high electrical conductivity after doping but also optical nonlinearity, piezoelectricity, pyroelectricity, photoconductivity and luminescent properties.[1,2] The attractions of polymers to the industries include their low cost and easy preparation and fabrications and their mechanical properties as compared to semi-conductors and metals, but the infusibility and insolubility of the most conjugated polymers have prevented from their being processed. These preventions put great emphasis on precursor routes where a soluble polymer can be processed to a film or fiber and then converted thermally to conjugated polymer.[3] Poly(1,4-phenylenevinylene) (PPV) is one of the well-known precursor route conjugated polymers. Interests in PPV and its derivatives have been spawned in recent years by the recognition that these polymers show high electrical conductivities after doping,[4] third-order optical nonlinearity[5] and high film quality, in addition to good processibility from a water-soluble precursor polymer. Also the photoluminescence (PL) and electroluminescence (EL) of these polymers have been extensively studied for realization of light emitting devices and large area multicolor display.[6,7] High molecular weight films of PPV can be prepared through a water-soluble precursor route. Substitution on the phenylene ring of the 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 the other physical properties of the resulting polymers.[8,9,10]

In this article, we synthesized new PPV derivatives containing silicon atoms. The influences of silicon atom on electrical, nonlinear optical and luminescent properties are very interesting in many respects. Poly[2,5-bis(trimethylsilyl)-1,4-phenylenevinylene] (BTMS-PPV) and a series of PPV copolymers were synthesized through a water-soluble precursor route, and their electrical, 3rd-order nonlinear optical and luminescent properties were studied. Synthetic schemes and the polymer structures are shown below;

Scheme 1



Scheme 2



EXPERIMENT

Synthesis of monomers. 2,5-Bis(trimethylsilyl)-1,4-phenylenedimethylene bis(tetrahydrothiophenium) bromide, **3**,[11] and 1,4-phenylenedimethylene bis(tetrahydrothiphenium) chloride, **4**,[4] were synthesized by the reported methods.

Polymerization. Synthetic methods for the homopolymer and copolymers were the same as reported by us and others.[12,13] The monomer sulfonium salt solution was polymerized in a 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. If desired, the precursor polymer films were uniaxially stretched in the temperature range of 110-120 °C using a zone heating apparatus.

Characterization. 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 nitrogen atmosphere at a heating rate of 10 °C/min with 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 index was measured by prism coupling method. Electrical conductivities of the doped polymer films were measured by the four-in-line probe method at room temperature. The photoluminescence spectrum was observed at room temperature utilizing a lock-in amplifier system with chopping frequency of 150 Hz and an Ar ion laser (457.9 nm) as an excitation light source.

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

Table 1 summarizes the data for monomer conversions to precursor polymers, polymer yields, and the compositions of the 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 (45-85 %) and polymer yields (30-60 %) to precursor polymers are comparable to those of the reported other similar polymerization systems.[8,10] The contents of BTMSPV units incorprated into the copolymers are slightly smaller than those in the feed monomer mixture solutions, suggesting that the reactivity of BTMSPV monomer is slightly smaller than that of PV monomer.

The FT-IR spectrum of BTMS-PPV film was compared with that of the precursor polymer film, though not given in this article. The precursor polymer film exhibits a broad absorption peak at 3100-3600 cm^{-1} due to the absorbed water which disappears in the spectrum of the final polyconjugated film. A strong absorption peak appears at 960 cm^{-1} after elimination which corresponds to the out-of-plane bending mode of the trans-vinylene group, suggesting that the generated double bonds after elimination are exclusively trans configuration.

Figure 1 shows the UV-visible spectrum of the eliminated BTMS-PPV film. The absorption maximum and band edge are slightly blue-shifted than those of the PPV film. The two bulky trimethylsilyl (TMS) groups slightly break the coplanarity of the conjugated polymer backbone, so BTMS-PPV can not have completely coplanar structure like PPV, thus shows blue-shifted absorption property.

Figure 2 shows the TGA thermograms of the precursor polymers of BTMS-PPV and copolymers. There are two regions in these thermograms, i.e, linear weight loss below 120°C and steep weight loss above 120°C. The weight loss in the temperature region below 120°C corresponds to the loss of the absorbed water and the higher temperature one corresponds to the elimination of tetrahydrothiophene and HCl or HBr.

Table 1. Monomer conversions and polymer yields of BTMS-PPV and copolymers

Polymer [a]	Feed ratio	Actual ratio (PV [b]:BTMSPV [c])	Monomer conversion(%)	Polymer yield(%)
BTMS-PPV	0 : 100	0 : 100	85	60
47-poly(PV-co-BTMSPV)	50 : 50	53 : 47	70	38
8-poly(PV-co-BTMSPV)	91 : 9	92 : 8	45	30

[a] The numerical values stand for mol-% of BTMSPV units in the final copolymers, and these values were calculated from the results of the elemental analyses (C. H.)

[b] PV : 1,4-phenylenevinylene unit

[c] BTMSPV : 2,5-bis(trimethylsilyl)-1,4-phenylenevinylene unit

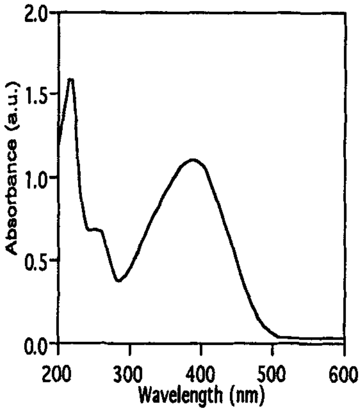


Figure 1. UV-visilble spectrum of the BTMS-PPV film

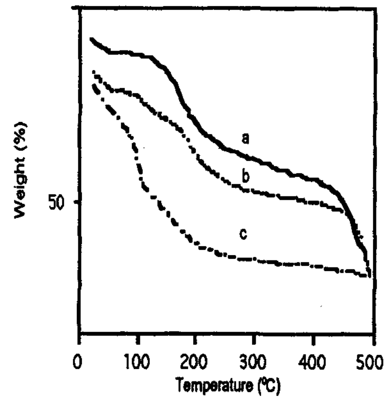


Figure 2. TGA thermograms of the precursor polymers of (a) BTMS-PPV, (b) 47-poly(PV-co-BTMSPV) and (c) 8-poly(PV-co-BTMSPV)

Electrical conductivities of polymers. Table 2 shows the draw ratios and the maximum conductivity values of the $FeCl_3$-doped BTMS-PPV and copolymer films. Substitution on the phenylene ring of PPV with different types of electron donating or withdrawing groups significantly influences on the electronic structures and morphologies of the resulting polymers. For example, the PPV films are hardly doped with weak oxidizing dopant like I_2. In contrast, poly(2,5-dimethoxy-1,4-phenylenevinylene) (PDMPV) can be easily doped with I_2 and $FeCl_3$ to give electrical conductivities of 10^1-10^3 S/cm.[14] These high conductivities of the PDMPV can be attributed to the electron donating effect of two methoxy groups. By the way, the precursor polymers of PDMPV cannot be stretched any extent, whereas the precursor polymer of PPV can be well stretched. The BTMS-PPV films could not be doped with I_2 but could be doped with $FeCl_3$. The electrical conductivity of the $FeCl_3$-doped BTMS-PPV film was 5.0×10^{-4} S/cm. This conductivity value is somewhat low one on considering the fact that BTMS-PPV have

Table 2. Maximum conductivities of $FeCl_3$-doped BTMS-PPV and copolymers

Polymer	Draw ratio	Conductivity (S/cm)
BTMS-PPV	1	5.0×10^{-4}
47-poly(PV-co-BTMSPV)	1	5.0×10^{-1}
	2.5	1.0
8-poly(PV-co-BTMSPV)	1	2.0
	10	25

two weakly electron donating TMS groups. We suppose that this small conductivity value was caused by steric effect of the bulky TMS groups. Symmetrically di-substituted highly bulky TMS groups hinder the dopants to penetrate and oxidize the conjugated polymer backbone and thus the doping reaction ocurrs only surface of the polymer film. The precursor polymer film of BTMS-PPV could not be stretched any extent like PDMPV. On the contrary, the precursor polymer films of 47-poly(PV-co-BTMSPV) and 8-poly(PV-co-BTMSPV) could be strectched up to the draw ratios of 2.5 and 10, respectively. The drawn copolymer films of 8-poly(PV-co-BTMSPV), when doped with $FeCl_3$, showed a maximum conductivity value of 25 S/cm. This value is 10^4 times higher than that of BTMS-PPV. On the other hand, as the content of BTMSPV unit in the copolymer increases further, the electrical conductivity decreases as shown in Table 2. The unsubstituted PPV films showed relatively low electrical conductivities of 10^{-3}-10^{-4} S/cm after $FeCl_3$-doping.[15] Nevertheless, the copolymer films containing small amount of bulky BTMSPV units show significantly high conductivity values. This result can be explained by morphological effect of the polymer. A small amount of a comonomer units effectively break the dense packing structure of PPV backbone and thus it makes easier the dopants to approach and oxidize the polymer chain. We believe that the doped PV unit largely contribute to the net conductivities of the copolymers.

Third-order nonlinear optical susceptibility, $\chi^{(3)}$ $(-\omega;\omega,\omega,-\omega)$, using DFWM. The third-order nonlinear optical susceptibility, $\chi^{(3)}$ $(-\omega;\omega,\omega,-\omega)$, value of the thin film of BTMS-PPV 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;

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

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 $\chi^{(3)} = 3.7\times10^{-14}$ esu was used as the reference value for THF. The subpicosecond response of the BTMS-PPV film sample is shown in Figure 3. The calculated $\chi^{(3)}$ value of BTMS-PPV was 5.8×10^{-10} esu. This value is slightly higher than that of unsubstituted PPV, 4.0×10^{-10} esu at 602 nm reported by Singh et al.[5]

Figure 4 shows the photoluminescence spectrum of the BTMS-PPV film excited at 457.9 nm at room temperature. This spectrum is similar to that of PPV and three well-defined equally spaced phonon sidebands appear at 500 nm, 540 nm and 580 nm, respectively, consistent with a stretching vibration of the carbon-carbon backbone.[16]

The photoluminescence spectrum of the BTMS-PPV film showed its emission in pure green region. The detailed luminescent properties are in progress.

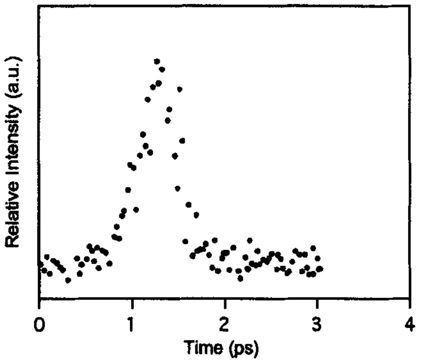


Figure 3. Observed DFWM signal of the BTMS-PPV film

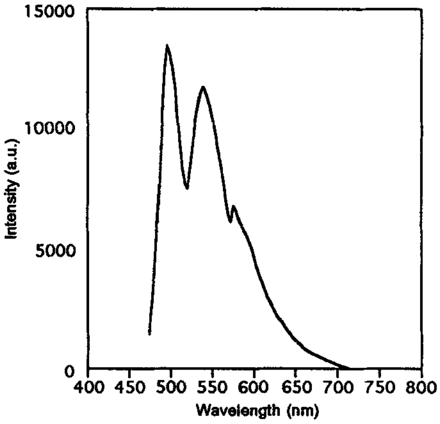


Figure 4. Photoluminescence spectrum of the BTMS-PPV film

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