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Electrical and third-order nonlinear optical properties of poly(2-fluoro-1,4-phenylenevinylene) and its copolymers

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Summary

Poly(2-fluoro-1,4-phenylenevinylene), PFPV, and its copolymers have been synthesized via water soluble precursor route and their electrical and optical propreties were measured. It seems that electron-withdrawing fluorine substituent on phenylene ring increases the band-gap of PFPV and it affects electrical and optical properties. The conductivity values of $FeCl_3$-doped drawn polymer films ranged from 10^{-1} to 10^{1} Scm^{-1} depending on their composition, and were 10 times larger than those of undrawn ones. The $\chi^{(3)}$ value for undrawn PFPV, using THG technique at 1907nm fundamental wavelength, was 4.76×10^{-12} esu.

Introduction

Conjugated conducting polymers are a fascinating candidate of semi-conducting parts, because of their high mechanical properties, such as tensile strength, specific density, etc. They have a quasi one-demensional electronic structure, which on addition of charge, causes a lattice defects such as polarons or bipolarons[1]. Conductance in conjugated backbone polymers is due to these mobile charge carriers. Generally, conjugated conducting polymers are infusible and insoluble and, as a result, nonprocessible. But poly(1,4-phenylenevinylene), PPV and its derivatives can be easily prepared in high molecular weight and in film form from water-soluble precursor polymers[2,3]. Especially, the PPV derivatives have high conductivity value[4] and third order optical nonlinearities[5] because of the conjugated nature of poymers. Substitution on the phenylene ring of PPV with different types of electron-donating[6] or electron-withdrawing groups[7] has a significant influence on the electronic

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structure of the resulting polymer and thus affects the electrical and nonlinear optical properties. It is important to examine the effect of electron-withdrawing substituent on the electrical and nonlinear optical properties for asymmetrically ring-substituted PPV. In this paper, poly(2-fluoro-1,4-phenylenevinylene), PFPV and its copolymers were synthesized via water soluble precursor route and their electrical and nonlinear optical properties were characterized. The electrical effect of substituted fluorine atom were discussed.

Experimental

Monomer synthesis

2-Fluoro-p-xylene(1) was prepared by the Schiemann reaction of 2,5-dimethylaniline (colorless liquid). ^{1}H-NMR ($CDCl_3$, ppm) ; δ = 7.2-6.9 (m; 3H), 2.4 (d; 6H) and 7.24 ($CHCl_3$ from solvent). ^{19}F-NMR (CF_3COOH, ppm) ; δ = -41.09 (s; vinyl fluorine). By reacting of this product with N-bromosuccinimide (NBS) in CCl_4, bisbromomethyl compound(2) was obtained. ^{1}H-NMR ($CDCl_3$, ppm) ; δ = 7.3-7.1 (m; 3H), 4.4 (d; 4H) and 7.24 ($CHCl_3$ from solvent). This product was melt over 99-101 °C. The sulfonium salt monomer(3) was obtained by reacting bisbromomethyl compound with excess tetrahydrothiophene in methanol at 50 °C for 24hrs. The reaction mixtures were concentrated and precipitated in cool acetone. The sulfonium salt was purified by recrystallization in acetone and dried under reduced presure. The 2-fluoro-1,4-phenylenedimethylene bis (tetrahydrothiophenium bromide) was white powder and very hygroscopic.^{1}H-NMR (D_2O, ppm) ; δ = 7.3 (m; 3H), 4.4 (d; 4H), 3.3 (m; 8H), 2.3 (m; 8H) and 4.8 (HDO from solvent). The synthetic route and the structures of PFPV and its copolymers prepared and characterized in this study are shown below.

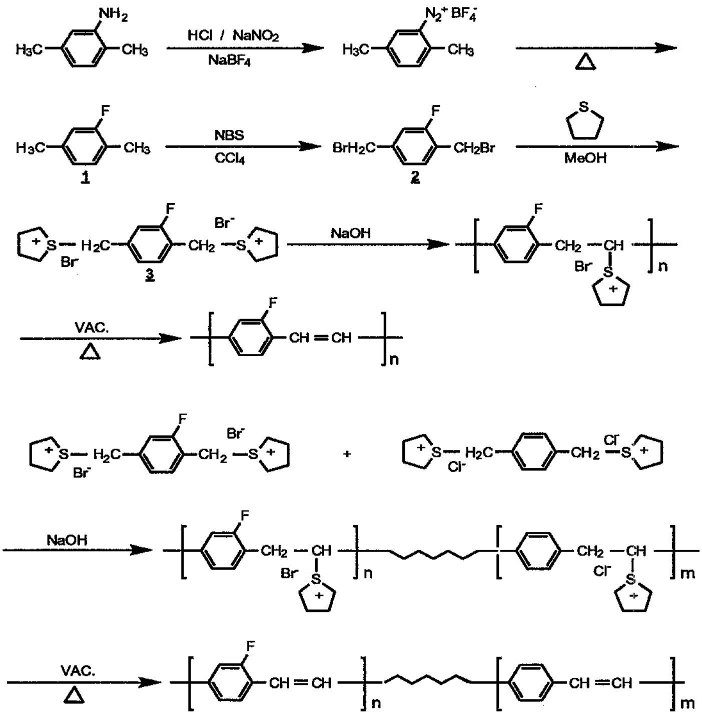
Polymerization

The sulfonium salt monomer(3) was dissolved in distillated water resulting in 1.0M solution. Equimolar prestandardized 1.0N NaOH solution was add to monomer solution under N_2 atomsphere at 0°C. As white viscous gel was formed, MeOH added in small amount, until the viscous gel was completely dissolved. The polymerization reaction was quenched by standard HCl solution. To remove low molecular weight oligomers and unreacted monomers, the neutralized polyelectrolyte precursor solution was dialyzed aganist deionized water for 3 days using dialysis tube with a molecular cut-off at 12,000.

Characterization

^{1}H and ^{19}F-NMR were recorded on a Brucker 200AM and a Varion FT-80A spectrometer, respectively. Melting point was determined using an Electrochemical Model 1307 digital analyzer. FT-IR spectra of polymers were obtained with Bomem Michelson series FT-IR spectrophotometer. UV-VIS analyses of precursor polymers and final polymers were perfomed by Shimadzu UV-3100S. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed under N_2 atmosphere at a heating rate of 10 °C/min with Dupont 9900 analyzer. The actual compositions of copolymers were analyzed by ESCA. The electrical conductivities of polymer films were measured by using four-in-line probe method at the room temperature. Thicknesses of spin-coated polymer films were measured by using Alpha step 200.

Synthetic scheme.



$\chi^{(3)}$ *measurement*

Third harmonic generation (THG)was performed to determine $\chi^{(3)}$ value of polymers. Q-switched Nd: Yag laser which generates 1064nm was used as a light source. The pluse duration and repetition rate were 8ns and·10Hz, respectively. The beam of 1064 was converted into 1907nm using H_2 Raman cell to perform this measurement in transparent region which corresponds to the nonresonant region of three-photon resonance. The undrawn film sample was mounted on a rotational stage and rotated around an axis perpendicular to the laser beam polarization. Third harmonic intensities were measured using PM tube and Boxcar integrator.

Results and discussion

Table 1 summarizes the data for the monomer conversions to the precursor polymers, the polymer yields and the actual compositions of copolymers. Data for conversions were obtained by titration of the precursor polymer solution with 0.337N HCl solution. Polymer yields were estimated gravimetrically from the weight of dialized casting films. The actual compositions of copolymers were calculated by the difference of the intensities of the carbon versus fluorine 1s-orbital peaks from the ESCA spectra. The degree of monomer conversions to precursor polymers are very high but polymer yields are slightly lower than values reported for similar polymerization system[8].

Table 1. Monomer conversions, polymer yields and actual compositions of copolymers.

Polymers [a]	Feed ratios (PV : FPV)	Conversion (%)	Polymer yields (%)
63-poly (PV-co-FPV)	17 : 83	92.0	23.0
29-poly (PV-co-FPV)	50 : 50	89.7	22.0
7-poly (PV-co-FPV)	91 : 9	90.3	24.0
4-poly (PV-co-FPV)	95 : 5	91.2	22.5
PFPV	0 : 100	93.2	21.4
PPV	100 : 0	91.8	23.1

[a] The numerical values stand for mole % of FPV units in final copolymers.

As shown in Table 1, FPV monomeric units are less reactive than PV monomeric units. This suggests that the electron-withdrawing substituent (F) retards chain propagation or reduces the reactivity of the bis-sulfonium monomer. Thermal analyses of elimination reaction of the precursor polymers by the TGA and DSC indicate that major weight losses occur at about 100 °C and 170 °C, as shown in Figure 1. The lower temperature endotherm corresponds to the loss of water and the higher temperature one to the elimination of HBr and tetrahydrothiophene.

The IR spectrum of precursor polymer film, as shown in Figure 2, exhibits strong absorption at 3100-3600 cm^{-1} due to the absorption of water, which disappears in final polymer film after thermal elimination. The film of the final polymer exhibits sharp and strong IR absorption at 960 cm^{-1} indicating the vinyl C=C bonds were entirely the trans configuration. This means that polymer main chains are transformed into polyconjugated trans-structures.

Figure 3 shows UV-VIS spectra of the fully eliminated polymers. The maximum absorptions and absorption edges due to π–π^* transition of the polyconjugated systems are 400-420 nm and 520-540 nm, respectively. As the content of FPV units increases, the position of maximum absorption gradually shifts to the shorter

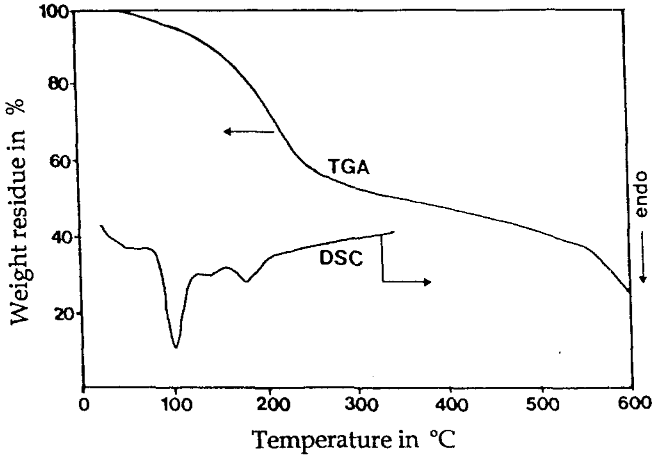


Figure 1. TGA and DSC theromograms of the precursor polymer of PFPV

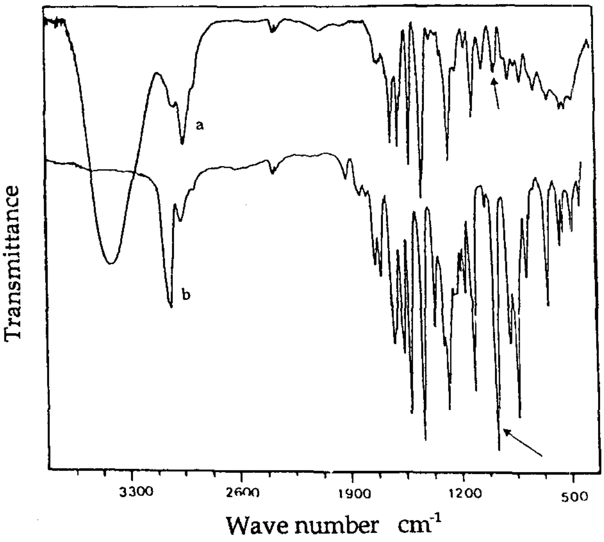


Figure 2. FT-IR spectra of precursor(a) and final PFPV(b)

wavelength region. This indicates that the fluorine substituent causes a hypsochromic shift. As shown in UV-VIS spectra of the polymer films, there are no absorptions at 600-800nm. This indicates that these polymer films are nonresonant at 636nm wavelength used in third harmonic generation experiment.

Electrical conductivities of the polymer films were measured by using a four-in-line probe DC technique. Table 2 shows the doping ratios and the maximum

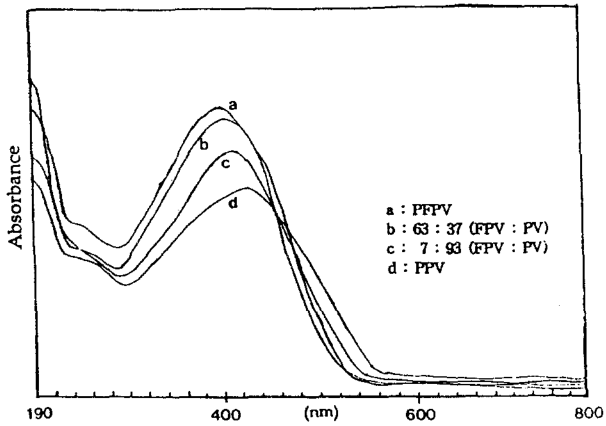


Figure 3. UV-VIS spectra of final polymers

Table 2. Electrical conductivities and doping ratios of polymers.

Polymers	Draw Ratio L / L_o	Conductivity (S /cm) $FeCl_3$ doped	Doping Ratio ($FeCl_4^-$ / RU [a])
63-poly (PV-co-FPV)	1	6.1×10^{-3}	0.20
	10	0.14	
29-poly (PV-co-FPV)	1	0.75	0.24
	10	2.81	
7-poly (PV-co-FPV)	1	1.90	0.53
	10	13.4	
4-poly (PV-co-FPV)	1	8.1×10^{-3}	0.23
	10	2.40	
PFPV	1	1.2×10^{-3}	0.20
	6	0.14	
PPV	1	8.3×10^{-3}	0.19
	10	1.50	

[a] RU stands for average repeating unit.

conductivity values obtained for drawn and undrawn polymer films. The conductivities of the drawn polymer films are larger than those of undrawn ones, since carrier transport along polymer chain and carrier hopping between polymer chains become easier in the drawn film than in the undrawn film. According to the Table 2, the conductivity values and doping ratios of the polymer films, compared with those of homopolymers,slightly increase upto 7-poy(PV-co-FPV) copolymer. The degrees of doping and the maximum conductivity values are closely parallel. This indicates that improvement of dopability guarantees high conductivity of doped polymers. The copolymer film containing 7 mole% of FPV units, 7-poly(PV-co-FPV), when doped with $FeCl_3$, showed maximum values of conductivity of 1.9 Scm^{-1} and 13.4 Scm^{-1} for undrawn and drawn films, respectively.

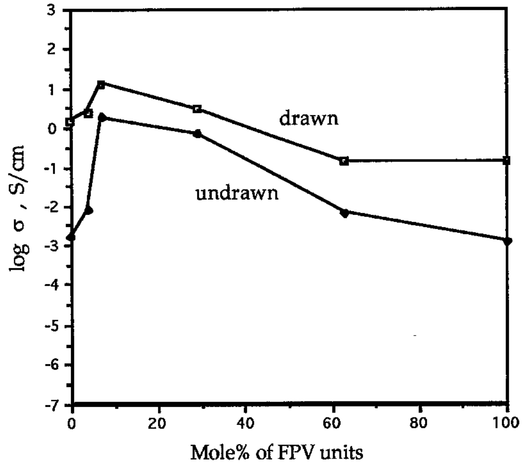


Figure 4. Conductivity curves of drawn and undrawn polymer films.

This suggests that the presence of fluorine substituents on the phenylene ring make it easier for the dopng species to approach and oxidize the polymer chain. On the other hand, as the content of FPV unit in the copolymer increased futher, the electrical conductivity steadily decreased as presented in Figure 4. In both case of drawn and undrawn, the conductivity values of PPV homopolymer are about 10 times higher than those of PFPV homopolymer. This can be explained that the electronic effect of the fluorine substituent predominates and the dopability as well as conductivity of doped materials diminishes.

Figure 5 shows the TH intensity patterns for PFPV film sample and reference quartz as a function of incident angle θ. $\chi^{(3)}$ value for film sample can be determined by comparing the TH intensity with the standard sample according to the following equation.

$$\chi^{(3)} = (2/\pi)\, \chi_s^{(3)} \{(I_{3w})^{1/2}\, l_{c,s}\} \,/\, \{(I_{3w,quartz})^{1/2}\, l\,\} \qquad \text{for } l \ll l_c$$

where I_{3w} and $I_{3w,quartz}$ are TH peak intensities for film and standard sample (fused quartz), respectively (extrapolated maximum value of the envelope function at $\theta = 0$ in the case of Maker fringe), l and $l_{c,s}$ are the film thickness and the coherence length of quartz, respectively. As the polymer was coated on substrate, it is necessary to calibrate the interference and superposition of TH waves from the film and substrate.

$$I_{3w,film} = (I_{max} + I_{min}) / 2 - I_{3w,sub} / 2$$

I_{max} and I_{min} are the extrapolated values of two envelope function at $\theta = 0$ in the observed TH pattern. The value of $\chi^{(3)} = 2.76 \times 10^{-14}$ esu and $l_{c,s} = 18.4$ μm were used

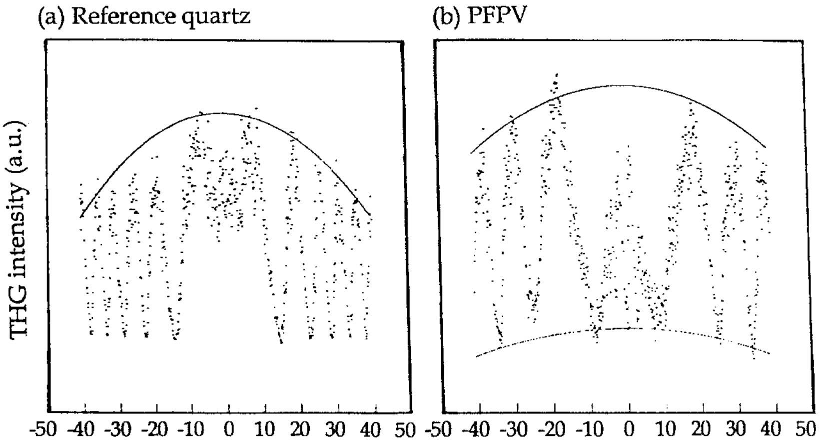


Figure 5. Maker fringe patterns of reference quartz(a) and PFPV(b)

as the reference values for fused quartz. The calculated $\chi^{(3)}$ value for PFPV was 4.76 x 10^{-12} esu.

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