Synthesis, electrical and optical properties of multifunctional poly[2-(2-ethyl-hexyloxy)-1,4-phenylenevinylene]

Min-Sik Jang, Hong-Ku Shim*

Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1 Kusong-Dong, Yusong-Gu, Taejon, 305-701, Korea

Summary

Branched monoalkoxy-substituted poly[2-(2-ethylhexyloxy)-1,4-phenylene-vinylene] (EH-PPV) was prepared in thin films via the water-soluble precursor technique and solution elimination method. These precursor polymer films could be stretched up to 8 times, and the drawn films of the EH-PPV could be doped with I_2 and $FeCl_3$ to give conductivities of 5.28×10^{-3} and 0.56 S/cm, respectively. The third-order nonlinear optical susceptibility of the polymer was determined by using third harmonic generation (THG) method at 1907 nm, fundamental wavelength. Measured $\chi^{(3)}(-3\omega; \omega,\omega,\omega)$ value was 3.8×10^{-12} esu. The maximum emission wavelength of EH-PPV film in photoluminescence spectrum was 560 nm, corresponding to the yellowish red color.

Introduction

Many types of conjugated polymers are now very actively researched. Among them, the interests in poly(1,4-phenylenevinylene) (PPV) and its derivatives have been increased in recent decades because of their possible application to the electronic and photonic devices. Especially, for Light Emitting Device materials, PPV derivatives were extensively studied in these days.[1-3] It was caused by good processibility, high efficiency of radiative decay process and easy tuning of emitting color than inorganic materials.[3]

In 1991, Heeger et al. reported fabrication of light emitting device using poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) for emitting layer[2]. This polymer offers the advantage of being soluble in organic solvent in the conjugated form. So, It makes simplified device fabrication because of direct casting of the semiconducting polymer from solution without high temperature thermal treatment. MEH-PPV film emitted red color light. Recently, we reported that mono-methoxy substituted PPV, poly(2-methoxy-1,4-phenylenevinylene) (PMPV), emits yellow color.[4,5]

In this study, we synthesized branched monoalkoxy-substituted poly[2-(2-ethylhexyloxy)-1,4-phenylenevinylene] via the water-soluble precursor

---

* Corresponding author

polymer route and organic-soluble precursor polymer route, and their electrical, nonlinear optical and luminescence properties were characterized.

Synthetic scheme

(1)

(2)

(3)

(P-1)

(P-2)

EH-PPV
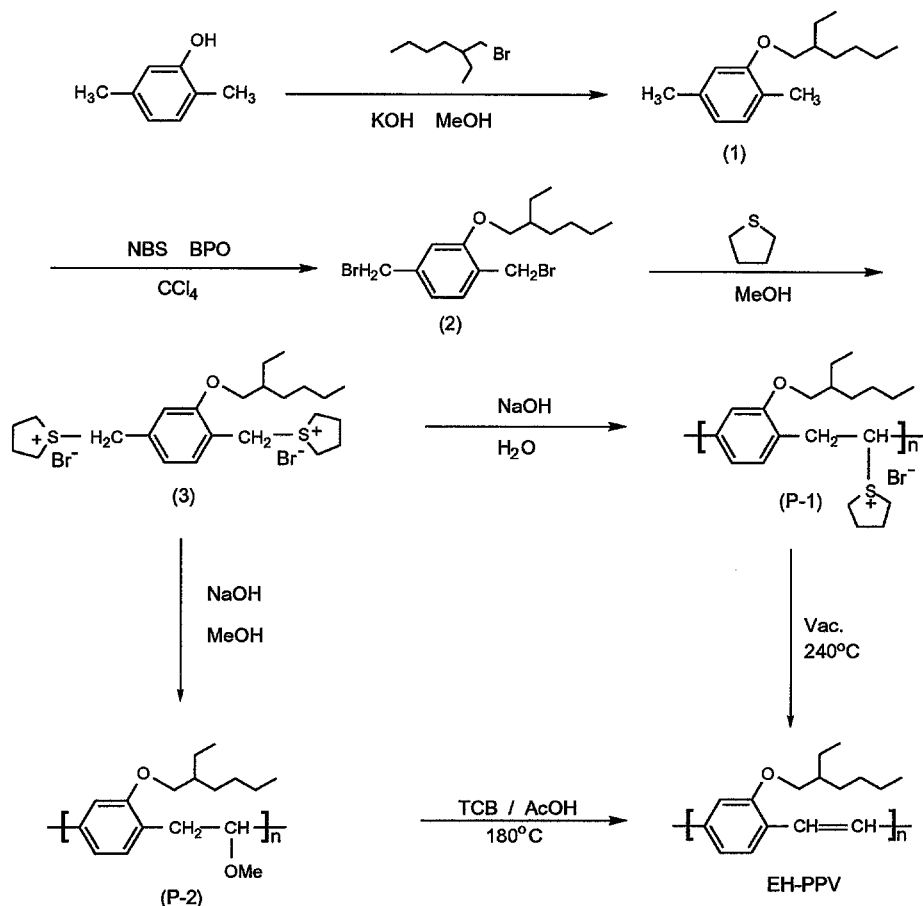
Experimental

Monomer synthesis

2-(2-Ethylhexyloxy)-1,4-dimethylbenzene (1) was prepared by reacting 2,5-dimethylphenol (82 mmol, 10 g) with 2-ethylhexylbromide(98.4 mmol, 18.42 ml). The contents were refluxed at 110 °C for 48 hrs in KOH-methanol solution. Colorless liquid was obtained and the yield was 69 % (13.2 g, 56.5 mmol). ^{1}H-NMR (CDCl$_3$, ppm) ; 7.10-6.70 (m, 3H), 3.90 (d, 2H), 2.38 (s, 3H), 2.25 (s, 3H), 1.80-1.30 (m, 8H), 1.00 (m, 6H) and 7.24 (CHCl$_3$ from solvent)

1,4-Bisbromomethyl-2-(2-ethylhexyloxy)benzene (2) was synthesized by reacting (1) (56.5 mmol, 13.2 g) with the N-bromosuccinimide (119 mmol, 21.3 g) and catalytic amount of benzoyl peroxide (0.5 g) for 3 hrs in carbontetrachloride at 85 °C. The yield was 40 % (22.6 mmol, 8.9 g). ^{1}H-NMR (CDCl$_3$, ppm) ; 7.30-6.80 (m, 3H), 4.51 (s, 2H), 4.44 (s, 2H), 3.92 (d, 2H), 1.80-1.30 (m, 8H), 0.90 (m, 6H), 7.24 (CHCl$_3$ from solvent)

The compound (2) (22.6 mmol, 8.9 g) and excess tetrahydrothiophene were reacted at 50°C in 20 ml of methanol for 20 hrs. The reaction solution was concentrated by distilling out a part of the solvent and unreacted terahydrothiophene. The concentrated solution was poured into cold acetone and then, the precipitate was washed with acetone and dried. The yield of 2-(2-ethylhexyloxy)-1,4-phenylene-dimethylenebis(tetrahydrothiophenium bromide) (3) was 80 % (18.1 mmol, 10.2 g). ^{1}H-NMR (D$_2$O, ppm) ; 7.40-6.90 (m, 3H), 4.37 (s, 2H), 4.35 (s, 2H), 3.91 (d, 2H), 3.40-3.20 (m, 8H), 2.30-2.00 (m, 8H), 1.60-1.10 (m, 8H), 0.70 (m, 6H) and 4.60 (DOH from solvent).

Polymerization

Water-soluble precursor route

The sulfonium salt monomer (3) was dissolved in distilled water resulting in 1.0M solution. Equimolar standard 1.0 N NaOH aqueous solution was added to monomer solution under N$_2$ atmosphere at 0 °C. As white viscous gel was formed, a small amount of methanol was gradually added to the solution until the viscous gel was completely dissolved. The polymerization reaction was quenched by neutralization with 0.5 N aqueous HCl. To remove low molecular weight oligomers and unreacted monomers, the neutralized polyelectrolyte precursor solution was dialyzed against deionized water for 3 days using dialysis tube with a molecular weigh cut-off at 12,000. The precursor polymer film (P-1) was obtained by casting from this solution. For THG measurement, it was spin-coated on the BK-7 glass with 1200 rpm. Then, these films were subjected to the thermal elimination in vacuo at 240 °C for 12 hrs to transform into the final polyconjugated polymer film. If desired, the precursor polymer films were uniaxially drawn at 120 °C using a zone-heating apparatus.

Organic-soluble precursor route

The sulfonium salt monomer (3) was dissolved in methanol resulting in 1.0 M solution. Equimolar 1.0 N NaOH methanol solution was added to the monomer solution under N$_2$ atmosphere at 0 °C. And, the precursor polymer was precipitated and washed with methanol. The precursor polymer (P-2) was soluble in dichloromethane, chloroform, xylene and trichlorobenzene, etc. The polyconjugated EH-PPV was obtained by solution elimination technique in trichlorobenzene using acetic acid as a catalyst, which is similar to reported method by Wudl et al.[7] The obtained polyconjugated polymer was soluble in dichloromethane, chloroform, xylene and trichlorobenzene, etc.

Characterization

^{1}H and ^{13}C -NMR were recorded on a Brucker 200AM spectrometer. FT-IR spectra of the polymers were obtained with Bomem Michelson series FT-IR spectrophotometer. UV-visible analyses of the precursor polymers were performed by Shimadzu UV-3100S. The photoluminescence spectra of polymers were obtained with Perkin-Elmer LS-50 Luminescence Spectrometer at room temperature. 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 electrical conductivities of the polymer films were measured by using a four-in-line probe configuration on which resistance measurements were performed using a Keithley 197 digital multimeter at the room temperature. Thicknesses of spin coated polymer films were measured by using Alpha step 200.

$\chi^{(3)}$ measurement

Third harmonic generation (THG) was performed to measure $\chi^{(3)}$ value of polymers. Q-switched Nd:YAG laser which generates 1064 nm was used as a light source. The pulse duration and repetition rate were 8 ns and 10 Hz, respectively. The beam of 1064 nm was converted into 1907 nm using H_2 Raman cell to perform this measurement in transparent region which corresponds to the nonresonent 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 detected by PM tube and Boxcar integrator

Results and Discussion

Major problem of the conventional PPV derivatives is insoluble and infusible because of their polyconjugated structures. Our EH-PPV is easily soluble in organic solvents such as chloroform, xylene and trichlorobenzene compared with MEH-PPV. So EH-PPV has a good processibility in high quality film forming without any film defects.

Thermal analyses of the elimination reaction of the precursor polymer (P-1) by TGA and DSC (Figure 1) with heating rate of 10 °C/min indicate that major weight losses occur at about 100 °C and 170 °C. The lower temperature endotherm corresponds to the loss of the absorbed water and the higher temperature one to the elimination of HBr and tetrahydrothiophene.

The IR spectrum of the precursor polymer film, 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. The IR spectra of the polymers are not shown in this article because the characteristic peaks are very similar with those of other PPV derivatives which can find elsewhere.[4,6]
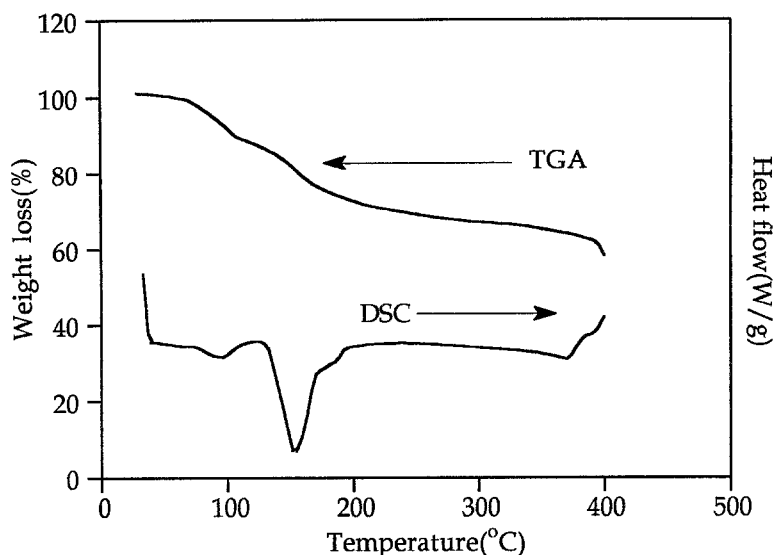
Figure 1. DSC and TGA thermograms of EH-PPV precursor polymer

Figure 2. shows UV-visible spectra of EH-PPV, its water-soluble precursor polymer film and EH-PPV film through solution elimination method. The uneliminiated polymer film displayed a maximum absorption peak around at 270 nm, which corresponds to partially formed stilbene and other units
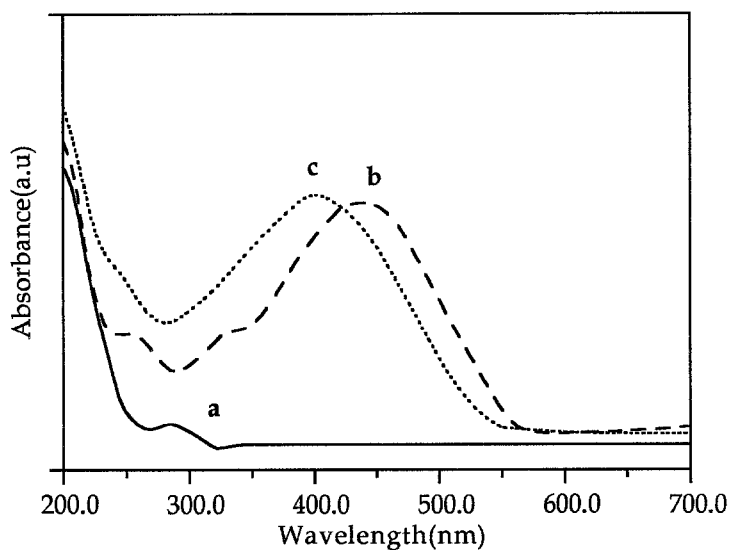

Figure 2. UV-visible spectra of thin film of a) EH-PPV precursor polymer
b) EH-PPV(thermal elimination) and c) EH-PPV (solution elimination)

containing delocalized π-electron.

When the film was thermally eliminated, the absorption maximum for π–π* transition and absorption edge were red shifted to 445 nm and 555 nm, respectively. The EH-PPV film through solution elimination pathway has the absorption maximum of 400 nm and absoption edge of 550 nm. We expect that solution-eliminated EH-PPV was not fully eliminated, so, this polymer has partially nonconjugated parts. In the UV-vis spectra, there is no absoption at 600-700 nm. This indicates that this polymer film is nonresonant at 636 nm wavelength used in third harmonic generation experiment.

Figure 3 shows photoluminescence spectra of EH-PPV films via thermal elimination of water-soluble precursor polymer and solution elimination of organic-soluble precursor polymer. Both of the films show the same emission maxima at 560 nm. This result shows that solution elimination method is a convenient and good elimination method for organic-soluble EH-PPV because thermal elimination process is needless, so can avoid thermal defects such as thermal crosslinking, pin hol formation and other undesired side reactions during the high temperature treatment. Therefore, finally organic-soluble EH-PPV can be a good material for electroluminescence device because of direct and convenient casting of light emitting layer on the ITO plate (anode). We can expect that the color of light emitted by light emitting device using EH-PPV will be yellowish-red. The fabrication of electroluminescence device and characterization are in progress.
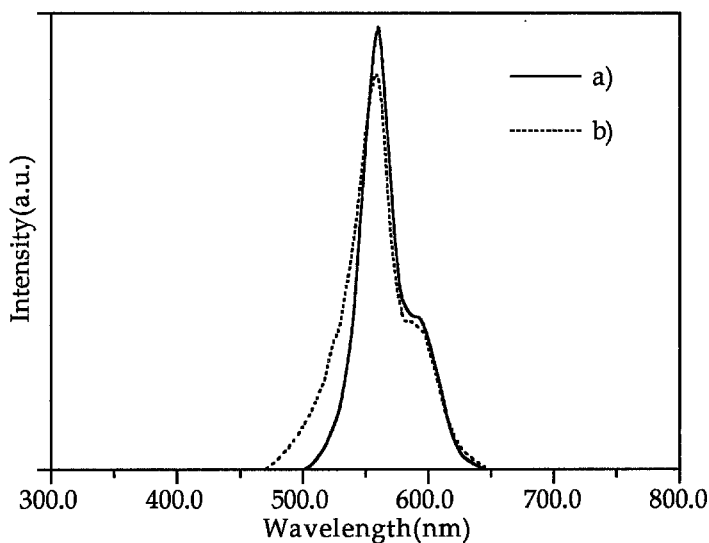

Figure 3. Photoluminescence spectra of thin film
EH-PPV a) via thermal elimination b) via solution elimination

The electrical conductivities of the EH-PPV were measured by four-probe method at room temperature. The conductivities of undrawn and drawn (L/L_0=8) films of EH-PPV when doped with I_2 were 1.0×10^{-3} and 2.6×10^{-3} S/cm, respectively and those for undrawn and drawn (L/L_0=8) $FeCl_3$-doped films were 5.28×10^{-3} and 0.56 S/cm respectively. The conductivity values of EH-PPV are slightly lower than those of poly(2-methoxy-1,4-phenylenevinylene) (PMPV).[4] This difference of conductivity values is resulted from that more bulky side chain, 2-ethylhexyloxy, may decrease the packing ability between polymer chains.

Figure 4 shows the Maker-fringe patterns for EH-PPV film sample and reference BK-7 glass as a function of incident angles. The $\chi^{(3)}$ value of the EH-PPV was calculated by comparing the measured THG peak intensity of the film and that of the substrate using the equation reported else where[8], assuming the film thickness to be much thinner than the coherence length of the film. And, it also regarded that the effect of the refractive index difference between the EH-PPV and the substrate for $\chi^{(3)}$ calculation is negligible.[9] The measured $\chi^{(3)}$ value and film thickness of EH-PPV were 3.8×10^{-12} esu and 0.22 μm, respectively. The reported $\chi^{(3)}$ value of PMPV is 1.20×10^{-11} esu.[4] The $\chi^{(3)}$ value of EH-PPV is smaller than that of PMPV. It is well known that $\chi^{(3)}$ value is inversely proportional to 6th power of band gap energy.[10] Recently we reported that the band gap energy is increased with increasing of the alkoxy side chain length.[11] The other is the effect of non-linear optical (NLO) chromophore density. As the side chain length is increased, the NLO chromophore density is decreased because of the increased volume fraction and the poor chain packing ability.
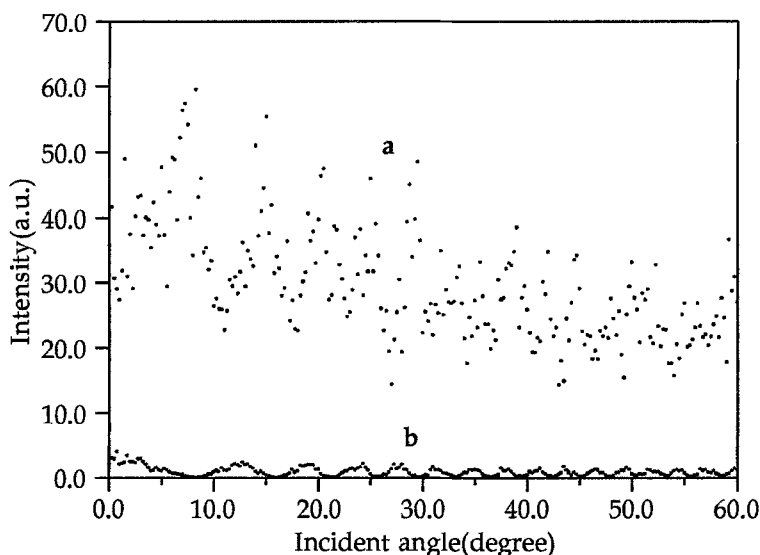

Figure 4. Maker-fringe patterns of a) EH-PPV and b) BK-7 glass

Acknowledgment

<u>Reference</u>

1. J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Markes, K. Mackey, R.H. Friend, P.L. Burns & A.B. Holmes, (1990) Nature 347 : 11.

2. D. Braun, A.J. Heeger , (1991) Appl. Phys. Lett. 58 : 6

3. A.B. Holmes, D.D.C. Bradley, A.R. Brown, P.L. Burn, J.H. Burroughes, R.H. Friend, N.C. Greenham, R.W. Gymer, D.A. Halliday, R.W. Jackson, A.Kraft, J.H.F. Martens, K.Pichler, I.D.W. Samuel, (1993) Synth. Met., 55-57: 4031

4. Hong-Ku Shim, Do-Hoon Hwang, Kwang-Sup Lee, (1993) Macromol. Chem., 194 : 1115-1124

5. T. Zyung, J.J. Kim, W.Y. Hwang, D.H. Hwang, H.K. Shim, these Proceedings, Synth. Met., submitted for publication

6. D.D.C. Bradley, (1987) J.Phys. D: Appl. Phys. 20 : 1389

7. F. Wudl, P.M. Allemand, G. Srdanov, Z. Ni, D. McBranch, (1991) ACS Sym. ser., 455 (Mater. Nonlinear Opt.) : 683

8. B. Buchalter, G. R. Meredith (1982) Appied Optics 17 : 3221

9. Ken'ichi Kubodera (1991) Nonlinear Optics 1 : 71

10. C. Sauteret, J.-P. Hermann, R. Frey, F. Pradere, J. Ducuing. R.H Baughman and R.R. Chance (1976) Phys. Rev. Lett. 36 : 956

11. Jeong-Ik Lee, Do-Hoon Hwang, Hong-Ku Shim, MinYung Lee, Sung-Kyu Yu, Geon-joon Lee, (1994) Mol. Cryst. Liq. Cryst. 247 : 121