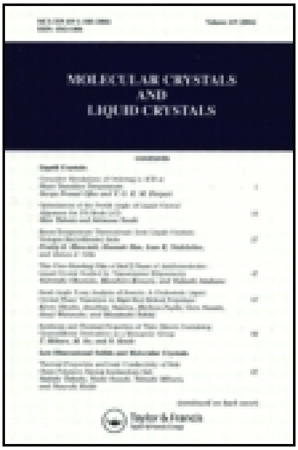

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Synthesis and Characterization of Poly (2-Methoxy-5-Ethylhexylthio-1,4-Phenylenevinylene)

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SYNTHESIS AND CHARACTERIZATION OF POLY (2-METHOXY-5-ETHYLHEXYLTHIO-1,4-PHENYLENEVINYLENE)

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Abstract. New alkylthio group substituted PPV derivative, poly (2-methoxy-5-ethylhexylthio-1,4-phenylenevinylene) (PMEHTPV) was synthesized and characterized with electrical conductivity, UV-VIS, IR and photoluminescence spectrum. The effects of substitution on the electronic and optical properties are discussed in this study.

INTRODUCTION

Extensive researches about conjugated polymers have been studied in recent years.[1] These polymers are applicable in light emitting diodes (LED) and nonlinear optical areas such as optical switches and waveguides, and they have advantages in light tuning, good processibility, and so on.[2] Among these conjugated polymers, the most efficient polymeric systems are poly (1,4-phenylenevinylene) (PPV) derivatives, which emit basically green light. Many color-tuning PPV derivatives by changing substituents on the phenylene ring were synthesized and characterized.

So far, poly (2-methoxy-5-ethylhexyloxy-1,4-phenylenevinylene) (MEH-PPV)[3] was discovered as soluble PPV derivatives and it showed yellowish-red light emission. In this study, poly (2-methoxy-5-ethylhexylthio-1,4-phenylenevinylene) (PMEHTPV) was synthesized through the similar way with MEH-PPV. This polymer is expected to show blue-shifted emission compared with yellowish-red emission of MEH-PPV due to weaker donating effect of alkylthio group than alkoxy group[4]. In addition, this polymer should be expected to show different properties compared to other dialkoxy-substituted PPV derivatives because of the nonbonding electron of sulfur atom. Figure 1 shows the synthetic scheme of PMEHTPV.

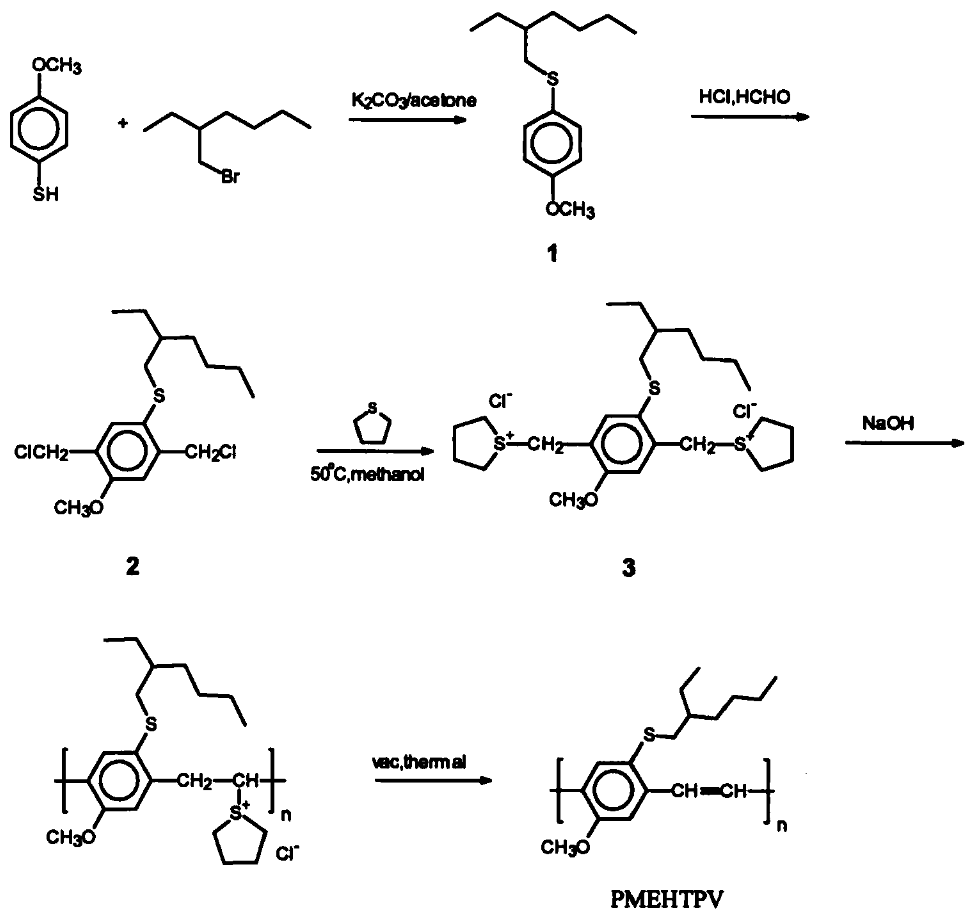

FIGURE 1. Synthetic Scheme of PMEHTPV

EXPERIMENTAL

Polymerization

The polymerization method are same as the Wessling's method in the literature.[5] The monomer sulfonium salt solution (1.0 M) in a mixed solvent of H_2O and methanol was polymerized in NaOH solution (1.0M) under nitrogen atmosphere at 0°C. A few hours later, greenish viscous solution was obtained. The reaction was quenched by neutralization with 0.5 N aqueous HCl, and the neutralized polyelectrolyte precursor solutions were dialyzed against deionized water for 1 days to remove unreacted monomers and low molecular weight oligomers using a dialysis tube with a molecular weight cut off at 12,000. The coated precursor polymer films were subjected to thermal treatment in vacuum at 200°C for 4hrs to transform into the final polyconjugated polymer.

Characterization

^{1}H-NMR spectra were recorded on a Brucker AM 200 spectrometer. FT-IR spectra were obtained with Bomem Michelson series FT-IR spectrophotometer and UV-VIS spectra were measured by Shimadzu UV-3100S. Electrical conductivities were measured by using a four-in-line probe configuration on which resistance measurements were performed using a Keithley 197 digital multimeter. Photoluminescence was obtained with Perkin-Elmer LS-50 Luminescence Spectrometer.

DISCUSSION

Poly (1,4-phenylenevinylene) derivatives through precursor pathway are identified by several methods. Though these polymers are insoluble after casting or elimination, UV-VIS and IR spectra are convenient tool for the identification of elimination reaction. PMEHTPV shows similar spectral trends with early results.[5] Figure 2 shows the UV-VIS spectra of PMEHTPV and its precursor polymer. After elimination, new band appeared at longer wavelength region (π-π^* transition) and gave absorption maximum at 430nm. This maximum wavelength is comparable to poly (2-methoxy-1,4-phenylenevinylene) (PMPV)[6] but lower about 60nm than that of MEH-PPV, indicating that alkylthio group of phenylene ring hardly affects the electronic property of PPV backbone as an electrodonating group. In FT-IR spectra of PMEHTPV precursor and final eliminated polymer, The precursor one exhibited a broad absorption at 3300cm~3600cm^{-1} due to the absorbed water, which disappears in the spectrum of the eliminated one. IR spectrum of fully eliminated PMEHTPV shows a sharp peak at 960cm^{-1} verifying the formation of trans-vinylene double bond.

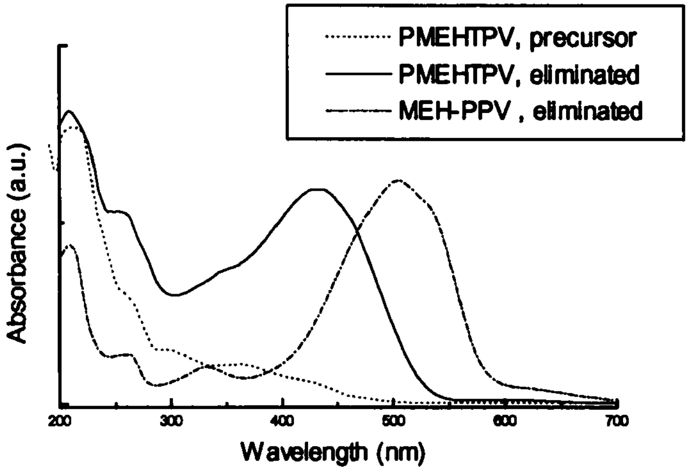

FIGURE 2. UV-VIS spectrum of PMEHTPV

Electrical conductivities of the polymers were measured using a four-in-line technique. On doping with $FeCl_3$ solution, the polymer films became brown and highly electroconducting. The conductivities of undrawn and drawn ($L/L_0=10$) films of PMEHTPV, when doped with $FeCl_3$, were 1.2×10^{-2} Scm^{-1} and 1.3×10^{-1} Scm^{-1} respectively. These conductivity values are lower than those of MEH-PPV, which showed conductivity values of 22.3 Scm^{-1} for stretched film and 1.13 Scm^{-1} for unstretched one.[7] This result indicates that alkylthio group of PMEHTPV does not act as an electron-donating group in the phenylene ring.

Many polymers were studied as an active layer of light emitting diodes. Fully conjugated polymers such as MEH-PPV emit at yellowish-red light region.[6] Since photoluminescence and electroluminescence have same intermediate state[8] and similar spectral shapes, photoluminescence is used as an indirect method for identification of electroluminescent property. Figure 3 shows the photoluminescence spectrum of PMEHTPV. The spectrum shows emission maximum at 550 nm, which is blue-shifted about 50nm compared with that of MEH-PPV. Especially the emission maximum wavelength is strongly dependent on the bandgap of PPV backbone, so greatly influenced by substituents of phenylene ring. Hammet constant ($\sigma_p=0.0$) of alkylthio group is well consistent with our results. So, we can conclude that the light emission process may not be affected by nonbonding electron of sulfur atom, but significantly blue-shifted by electronic effect of ethylhexylthio group.

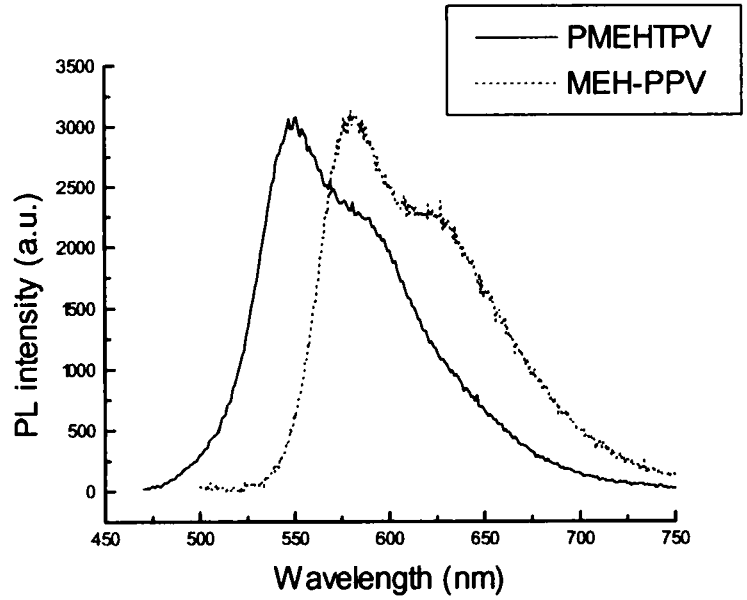

FIGURE 3 Photoluminescence spectra of PMEHTPV when excited at 438nm

CONCLUSION

Akylthio substituted poly (2-methoxy-5-ethylhexylthio-1,4-phenylenevinylene) was synthesized and characterized. This polymer film was easily stretched about 10 times and showed very flexible property. It showed electrical conductivity up to 0.13 Scm^{-1} when doped with $FeCl_3$, and exhibited lower absorption and emission wavelength than MEH-PPV. The alkylthio group of phenylene ring hardly affects the electronic property of PPV backbone.

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