Macromolecular Research, Vol. 11, No. 3, pp 194-197 (2003)

Synthesis and Characteristics of New Poly(*p*-phenylenevinylene) with Bulky *t*-Octylphenoxy Group

Yun-Hi Kim, Hyun-Ouk Lee, Sung-Ouk Jung, and Soon-Ki Kwon*

Department of Polymer Science & Engineering and Engineering Research Institute, Gyeongsang National University, Chinju 660-701, Korea

Received Apr. 14, 2003; Revised May 22, 2003

Abstract: A new 2,5-di(*t*-octylphenoxy) group substituted poly(*p*-phenylenevinylene) derivative was synthesized by Gilch polymerization. The obtained polymer was characterized by NMR, FT-IR, and chemical analysis and completely soluble in common organic solvents. The polymer showed good thermal stability with T_g of 105 °C. The polymer dissolved in chloroform showed maximum emission at 514 nm with a shoulder peak at around 560 nm. The EL spectrum of the ITO/PEDOT/TOP-PPV/Al device was observed maximum emission at 545 nm with a shoulder peak at around 585 nm.

Keywords: poly(*p*-phenylenevinylene), Gilch polymerization, electroluminescence.

Introduction

Since the first report of polymeric light-emitting diodes (PLEDs) based on poly(*p*-phenylenevinylene) (PPV) by the Cambridge group,[1] great progress has been made in the study of PLEDs due to their promising application in the field of patterned light source and flat panel display. Many works have been done to develop novel luminescent polymeric materials with good processability, environmental stability, and intense luminance as well as to optimize the device structures to improve the efficiencies.[2-7]

PLEDs based on PPV and its derivatives offer several advantages associated with their intrinsic characteristics of thermal stability, solution processability and simple device architectures. These characteristics which offer the potential for cheaper manufacturing routes. Although noticeable improvements have been made in many areas in LED application, there still remain drawbacks such as impurity, short lifetime and low device quantum efficiency.[8]

A wide variety of PPV derivatives had been synthesized and applied in LED applications, very few are attractive for commercial exploitation because very few have high PL efficiencies in solid states.[9-16] The major reason is that conjugated backbones tend to stack with each other due to the favorable interchain interactions, which lead to a self-quenching process of excitons.[17,18] Introducing appropriate substituents such as 3,7-dimethyloctyl,[12] dimethyloctylsilyl,[19] to the PPV backbone to prevent its close packing should therefore increase its PL efficiency. However, the PPV derivatives containing the longer flexible alkyl or alkoxy substituents have low T_g or low morphological stability. Therefore, the introduction of proper bulky rigid arylalkoxy substituents makes excellent PPVs having a high quantum efficiency due to the inhibition of interchain interaction, good solubility, high T_g and morphological stability.[20]

In this study, we report a new soluble PPV derivative containing *t*-octylphenoxy group in the 2,5-position of PPV ring. The bulky *t*-octylphenoxy group is expected that polymer has enhanced the thermal stability with high T_g and solubility, and minimized intermolecular interaction and a self-quenching process of excitons.

Experimental

2,5-Di(*t*-octylphenoxy)-*p*-xylene. 223.5 g (1.8 mol) of 4-*t*-octylphenol and 101 g (1.8 mol) of KOH in benzene solvent were refluxed for getting off water by using Dean-Stark trap. After reaction, benzene was removed, and 318.7 g (1.65 mmol) of 2,5-dibromo-*p*-xylene and 1.5 g of Cu in NMP solvent were refluxed for 48 h. Then, the reaction mixture was stirred with 2N KOH, and extracted with ether. The crude product was purified by column chromatography. The product yield was 406.2 g (70%); mp 144 °C. FT-IR (KBr pellet, cm^{-1}): 3030, 2890, 1250. ^{1}H-NMR ($CDCl_3$): δ 6.8 -7.3 (m, 10H, aromatic C-H), 2.1(s, 6H), 1.7(s, 4H). 1.4(s, 12H), 0.8(s, 18H).

1,4-Bis(bromomethyl)-2,5-di(*t*-octyl phenoxy)benzene. After 5 g (9.7 mmol) of 2,5-di(*t*-octyl phenoxy)-*p*-xylene was

*e-mail : skwon@nongae.gsnu.ac.kr

dissolved in benzene, 3.45 g (19.4 mmol) of *N*-bromosuccinimide and catalytic amount of BPO was added and refluxed for 6 h. After reaction, crude product was purified by column chromatography. The product yield was 3.3 g (52%); mp 140°C. FT-IR (KBr pellet, cm^{-1}): 3030, 2890, 1250, 650. ^{1}H-NMR ($CDCl_3$): δ 6.8 -7.3 (m, 10H, aromatic C-H), 4.3 (s, 4H), 1.7 (s, 4H). 1.4 (s, 12H), 0.8 (s, 18H)

Poly[2,5-di(*t*-octyl phenoxy)-1,4-phenylenevinylene]. After *t*-BuOK (0.4 g, 3.6 mmol) in THF (3 mL) was added to a solution containing 1,4-bis(bromomethyl)-2,5-di(*t*-octyl phenoxy)benzene (0.8 g, 1.2 mmol) in 20 mL of THF, the solution was refluxed for 5 h. After cooling, the 0.05 g of sodium methoxide was added and refluxed 2 h. The polymer was obtained from precipitation in methanol. The yield of polymer after complete work up was 0.39 g (60%). FT-IR (KBr pellet, cm^{-1}): 3000, 2890, 1500, 1250, 960, 800. ^{1}H-NMR ($CDCl_3$): δ 6.6-7.5 (m, 12H, aromatic and vinylic C-H), 1.7 (s, 4H, $-CH_2-$). 1.4 (s, 12H, $-CH_3$), 0.8 (s, 18H, *t*-butyl). Anal. Cacld for $C_{36}H_{46}O_2$: C, 84.7%; H, 9.02%; O, 6.28%. Found: C, 84.53%, H, 8.97%, O, 6.5%.

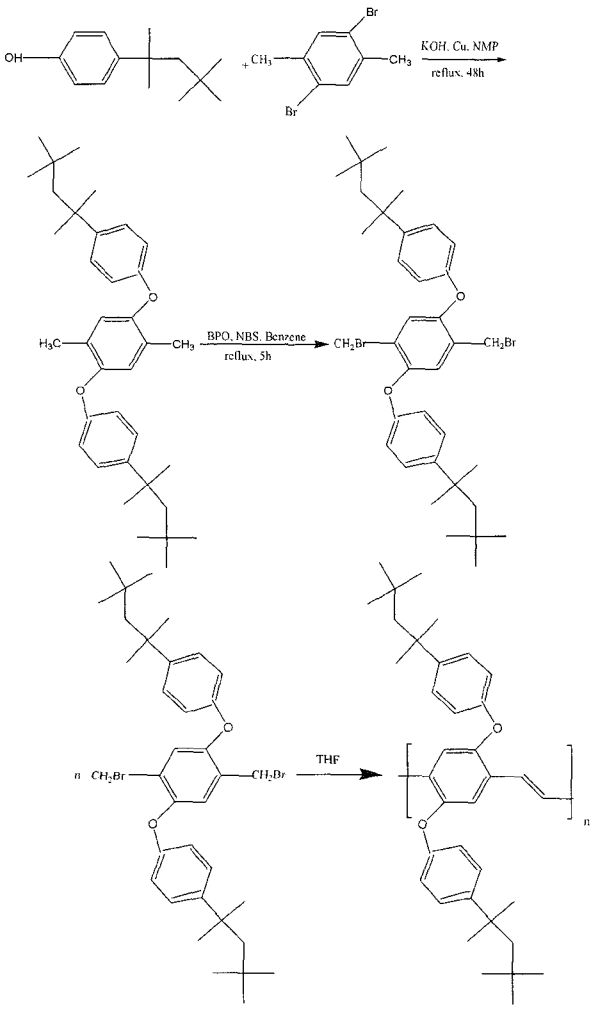
Characterization

^{1}H-NMR spectra data were expressed in ppm relative to the internal standard and were obtained on a DRX 500 MHz NMR spectrometer. FT-IR spectra were obtained with a Bomem Michelson series FT-IR spectrometer, and the UV-vis absorption spectra obtained in chloroform on a Shimadzu UV 3100 spectrometer. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (Waters high pressure GPC assembly model M590 pump ì-styragel columns of 105, 104, 103, 500, and 100 Å, refractive index detectors, solvent THF). Elemental analysis was performed by Leco Co. CHNS-932. TGA measurements were performed on a Perkin-Elmer series 7 analysis system under N_2 at a heating rate 10°C/min. The photoluminescence spectra were recorded on a Perkin-Elmer LS-50 fluoremeter utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. For the measurements of device characteristics current-voltage (I-V) changes were measured using a current/voltage source (Keithly238) and optical power meter (Newport 818-SL).

Fabrication of the LED: Poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT) for a conducting polymer hole-injection layer was coated on an indium-tin oxide coated glass substrate which had been washed with water, acetone, and isopropyl alcohol sequantially. A tin polymer film was spin coated (3000 rpm, 50 s) from a filtered (0.2 m filter) 1.0 wt% polymer solution in chlorobenzene on a PEDCT layer. An aluminium electrode was deposited on top of the device at a high vacuum (below 1×10^{-5} Torr). Wires were attached to the respective electrodes with a conductive epoxy adhesive. All fabrication steps were performed in clean room conditions. Measurements were done at room temperature in air.

Results and Discussion

The method for preparing the monomer and polymer is outlined in Scheme I. The monomer was prepared via bromination of 2,5-di(*t*-octylphenoxy)-*p*-xylene which is obtained from Williamson reaction of 2.5-dibromo-*p*-xylene with of 4-*t*-octylphenol. The polymer, poly[2,5-di(*t*-octylphenoxy)-1,4-phenylenevinylene] (TOP-PPV), was obtained through the typical Gilch method. ^{1}H-NMR and FT-IR spectra agree with the proposed structures of various compounds and polymer showing no evidence of defects. In the ^{1}H-NMR spectrum of the polymer, the aromatic and vinyl protons appeared in the range 7.8-6.6 ppm, and *t*-octyl protons appeared at around 1.7-0.8 ppm, respectively (Figure 1). It is reported that PPVs contained head-to-head (H-H) (or tail to tail, T-T) couplings as the result of a side reaction. They assigned the CH_2-CH_2 groups resulting from H-H couplings



Scheme I

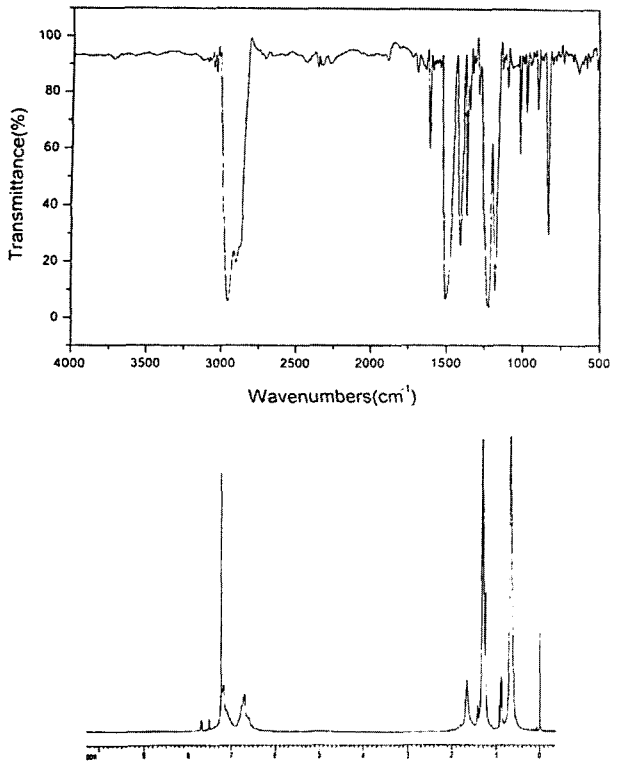


Figure 1. ^{1}H-NMR and IR spectra of poly(TOP-PPV).

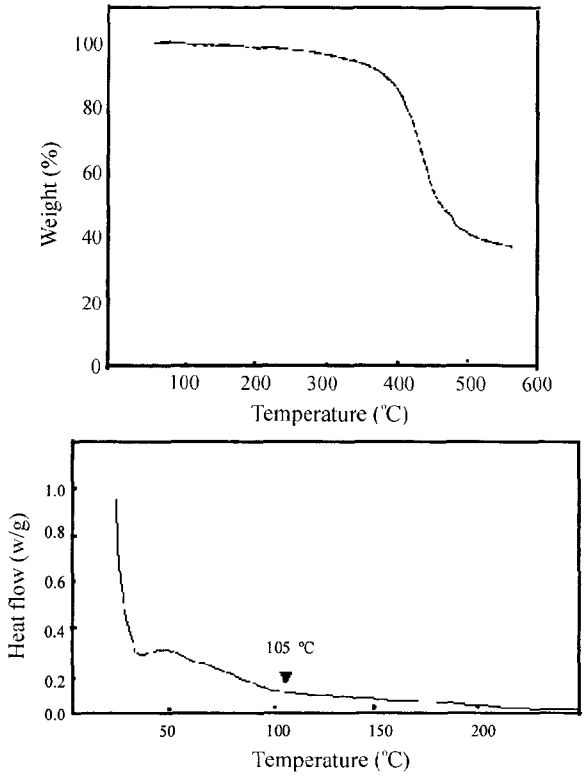


Figure 2. TGA and DSC thermograms of poly(TOP-PPV).

to peak around 2.7-2.9 ppm. As shown in the ^{1}H-NMR spectrum of TOP-PPV, it is clear that this side reaction could not be detected with ^{1}H-NMR measurements. In the IR-spectrum, the stretching absorption bands for C-Br in the monomer at 650 cm^{-1} disappeared after polymerization, while a new band with strong intensity occurred at 960 cm^{-1}, which is due to the vinylic out of plane deformation. This result suggests that the vinylene group formed through Gilch route is in the trans configuration.

The polymer was readily dissolved in common organic solvents such as chloroform, THF, toluene, chlorobenzene. The good solubility of polymer may be originated from bulky *t*-octylphenoxy substituents.

The number average molecular weight ($\overline{M_n}$) and the weight average molecular weight ($\overline{M_w}$) of the polymer were determined to be 43,000 and 95,000 (with the polydispersity index of 2.1), respectively, by gel permeation chromatography (GPC) using polystyrene as a standard.

The thermal stability of the polymer was evaluated by thermogravimetric analysis (TGA) under a nitrogen atmosphere. Figure 2 shows that the polymer exhibits good thermal stability. The polymer has onset degradation temperature above 300 °C, and no weight loss was observed at lower temperatures. The glass transition temperatures (T_g) of the polymer was determined by differential scanning calorimetry (DSC) in a nitrogen atmosphere at a heating rate of 10 °C/min. As shown DSC thermogram, the polymer with bulky *t*-octylphenoxy has T_g of 105 °C, which is 30-40 °C higher than that of the soluble polymer MEH-PPV (65 °C) with alkoxy substituents. It has been known that materials with a high glass transition temperature as the active emissive can provide device longevity.

The UV-vis absorption and photoluminescence spectra of the polymer in chloroform are shown in Figure 3. The absorption maximum (λ_{max}) and emission maximum of the polymer showed at 456 and 514 nm, respectively. The optical energy band gap of the polymer was 2.4 eV calculated from the threshold of the optical absorption.

A light emitting diode (LED) was constructed to have the configuration of ITO/PEDOT/TOP-PPV/Al by spin coating of the two polymer layers consecutively onto an indium-tin oxide (ITO) coated glass followed by vacuum deposition of Al. Here, PEDOT stands for poly(2,3-ethylenedioxythiophene) doped with sulfonated polystyrene, which was utilized in order to enhance hole injection and transport from the ITO anode and also to improve interface contact. Figure 4 shows the PL spectrum as film and EL spectrum of the ITO/PEDOT/TOP-PPV/Al device. The solid PL spectrum is similar to solution PL spectrum. It means that intermolecular interaction is inhibited by bulky arylalkoxy substituent. The EL spectrum of the ITO/PEDOT/TOP-PPV/Al device is very similar to the solid PL spectrum of the polymer. It can be explained that both EL and PL originate from the same radiative decay process of the singlet exciton. From

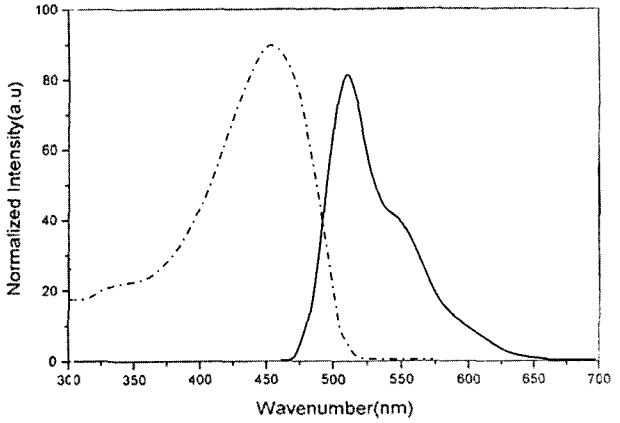


Figure 3. UV-absorption and photoluminescence spectra of poly(TOP-PPV).

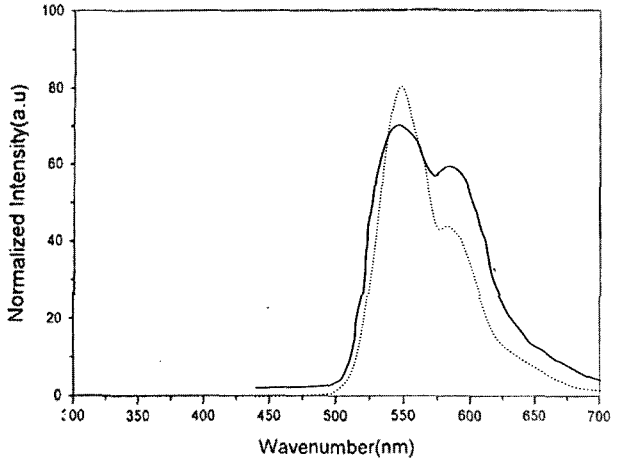


Figure 4. Solid photoluminescence and electroluminescence spectra of ITO/PEDOT/TOP-PPV/Al device.

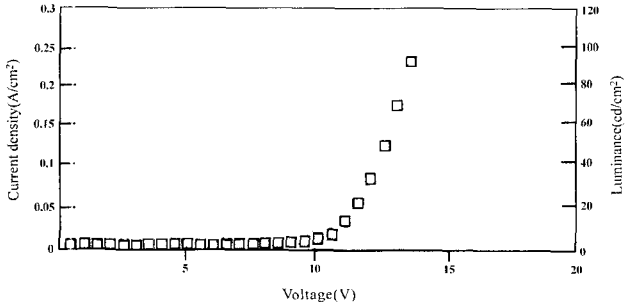


Figure 5. I-V-L characteristics of ITO/PEDOT/TOP-PPV/Al device.

the current-voltage-brightness characteristic of the device, the turn-on voltage of the device was observed at 10 V and the maximum brightness of the device showed 100 cd/m^2 (Figure 5). To achieve a higher EL performance, optimization of the device structure will be necessary.

Acknowledgements. This work was supported by Korea Research Foundation Grant (KRF-2000-005-E00005) and KOSEF (R03-2000-000-00016-0).

References

(1) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. MacKay, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature*, **347**, 539 (1990).
(2) G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, and A. J. Heeger, *Nature*, **357**, 477 (1992).
(3) N. C. Greenham, S. C. Moratti, D. D. C. Bradley, R. H. Friend, P. L. Burn, and A. B. Holmes, *Nature*, **365**, 628 (1993).
(4) P. L. Burn, A. B. Holmes, A. Kraft, D. D. C. Bradley, A. R. Brown, R. H. Friend, and R. W. Gymer, *Nature*, **356**, 47 (1992).
(5) J. Bettenhausen and P. Strohriegl, *Adv. Mater.*, **8**, 507 (1996).
(6) B. K. An, Y. H. Kim, D. C. Shin, S. Y. Park, H. S. Yu, and S. K. Kwon, *Macromolecules*, **34**, 3993 (2001).
(7) M. Yoshida, A. Fujii, Y. Ohmori, and K. Yoshino, *Jpn. J. Appl. Phys.*, **35**, L397 (1996).
(8) R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Lögdlund, and W. R. Salaneck, *Nature*, **397**, 121 (1999).
(9) N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. Kessener, S. C. Moratti, A. B. Holmes, and R. H. Friend, *Chem. Phys. Lett.*, **269**, 376 (1995).
(10) B. Winkler, L. Dai, and A. W. H. Mau, *Chem. Mater.*, **11**, 704 (1999).
(11) I. D. W. Samuel, G. Rumbles, C. J. Colison, B. Crystall, S. C. Moratti, and A. B. Holems, *Synth. Met.*, **76**, 15 (1996).
(12) D. H. Hwang, S. T. Kim, X. C. Li, B. S. Chuah, J. C. Demello, R. H. Friend, S. C. Moratti, and A. B. Holmes, *Polym. Prepr.*, **38**, 319 (1997).
(13) Z. Pheng, J. Zhang, and B. Xu, *Macromolecules*, **32**, 5162 (1999).
(14) B. R. Hsieh, Y. Yu, E. W. Forsythe, G. M. Schaaf, and W. A. Feld, *J. Am. Chem. Soc.*, **120**, 231 (1998).
(15) D. C. Shin, Y. H. Kim, H. You, and S. K. Kwon, *Macromolecules*, in press (2003).
(16) D. C. Shin, Y. H. Kim, H. You, and S. K. Kwon, *Macromolecules*, submitted.
(17) L. J. Rothberg, M. Yan, E. W. Kwock, T. M. Miller, ME. Galvin, S. Son, and F. Papadimitrakopoulos, *IEEE Trans. Electron Decices*, **44**, 1258 (1997).
(18) S. A. Jenekhe and J. A. Osaheni, *Science*, **265**, 765 (1994).
(19) D. H. Hwang, H. K. Shim, and J. I. Lee, *J. Chem. Soc. Chem. Commun.*, **23**, 453 (1994).
(20) N. P. H. Nam, V. Parasad, S. W. Cha, D. W. Lee, and J. -I. Jin, *Bull. Korean Chem. Soc.*, **23**, 1470 (2002).