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Synthesis and electro-optical properties of polythiophene derivatives for electroluminescence display

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Abstract

A new series of light emitting polymers composed of thiophene repeating units were synthesized and characterized by oxidative polymerization. Introduction of alkyloxyphenyl substitutent into the 3-position of the thiophene unit not only influences solubility but also controls the emission colors and electro-optical properties. Chemical structures of the resulting polymers were confirmed by UV–visible, ¹H- and ¹³C-NMR spectra. The resulting polymers were soluble in common organic solvents and could be spin-cast onto ITO glass substrate to obtain optical thin films without defects. The turn-on voltage of the polymers were about 4.5–6.5 V and emitted a red color on forward bias. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The primary recent development in the fields of flat panel display has been the discovery of polymer light-emitting displays (LEDs). It is fluorescent polymers that emit light when excited by the injection of an electronic current. Conjugated polymers have attracted considerable attention as a novel class of organic semiconductors in the past decade because of their promising electronic and optical applications. Polymer LEDs, which consists of conjugated polymers, have much of the interest as conducting materials by Friend and coworkers [1].

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To establish the correlation between structure and property of the polymeric emitting materials, many researches of PPV [2], polyfluorene [3], polythiophene [4] and their derivatives have been achieved and progressing now. Conjugated polymers are organic semiconductors, the semiconducting behavior being related with the π -molecular orbital delocalized along the polymer main chain. The tuning of the emission colors of emitting materials is necessary for full color LED. Various techniques have been proposed to tune the emitting colors by modification of molecular structure, doping and blending methods [5–7]. Recently, we have synthesized the various types of novel electroluminescence (EL) polymers and blending systems to improve the device efficiency and to control the emission colors of the polymers [8,9].

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In this article, we present the control of effective mean conjugation length along the polymer backbone by adding substitutents on the different position of π -conjugated polymer backbone. Large substitutents lead to a large dihedral angle between the rings and to give a short conjugation length along the polymer backbone.

2. Experimental

2.1. Synthesis of 3-[4-(3,8-dimethyloctyloxy)phenyl]thiophene (para-DOTh)

The synthetic scheme of monomer, para-DOTh and polymerization of para-DOTh are shown in Scheme 1. In the first step, the hydroxyl group of **1** was substituted with Br using phosphorus tribromide in dichloromethane. The 1-bromo-3,7-dimethyloctane was obtained with a good yield. The resulting material, 2 was reacted with reagent of 4bromophenol in the presence of KOH in methanol solution. To the preparation of the Grignard reagent, magnesium was added in synthesized material, 3 in THF. Dibromoethane used in this step as an initiator. A solution of this product and 3bromothiophene was coupled in THF by Grignard reaction to give the desired monomer para-DOTh. And [1,3-bis(diphenylphosphino)propane]dichloro nickel(II) used in this synthetic step as a catalyst. With different synthetic process, 4-bromoanisole and 3-bromothiophene was used. In the first step, the Grignard reagent was prepared with 4-bromoanisole and magnesium in THF. A solution of this



Scheme 1.

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product and 3-bromothiophene was coupled in THF by Grignard coupling reaction. 3-(4-Methoxyphenyl) thiophene was synthesized in this step. The resulting material, 4 was used to synthesize the demethylation product, 5 using AlCl₃, dimethyl sulfide and NH₄Cl in dichloromethane. Monomer, para-DOTh was synthesized by Williamson ether synthesis with 1-bromo-3,7-dimethyloctane and hyodroxylphenyl thiophene, 5. ortho-DOTh was synthesized in a similar method for para-DOTh. Poly[3-(4'-(3,7-dimethyloctyloxy)phenyl)thiophene], poly(para-DOTh) was prepared by chemical oxidative coupling using FeCl₃ via the dehydrogenation condensation of monomer in the presence of metal halogenide (FeCl₃, AlCl₃, etc.) in an appropriate medium such as chloroform solution (or suspension). Under inert conditions, the polymerization was carried out by stirring a chloroform solution containing 2 g (6.32 mmol) of the pure monomer and 4.1 g (25.38 mmol) of FeCl₃ as both the oxidant and reagent at 35 °C for 24 h. The reaction mixture was poured into methanol and a precipitate was formed. The resulting polymer was filtered off and washed with methanol. The resulting polymer was then completely dedoped by stirring the polymer in chloroform and concentrated ammonia, while the mixture was being boiled for 30 min. The water phase was separated and fresh ammonia was added. This procedure was repeated four times and then the chloroform solution was washed twice with ethylenediaminetetraacetic acid (EDTA) dissolved in water (0.05 M). The chloroform solution was finally washed with water and then filtrated. The amount of chloroform was reduced and then the residue was poured into methanol and the polymer precipitated. The low molecular weight and irregular part of the polymer were removed by soxhlet extraction with methanol. The yield of poly(para-DOTh) was 34%, and the molecular weight was determined to be $M_{\rm n} = 3400$ and $M_{\rm w} = 5300$ by gel permeation chromatography using polystyrene standards.

3. Results and discussion

Scheme 1 shows the synthetic scheme of the monomers and corresponding polymers by oxi-

dative polymerization. In order to improve the processibility and color tuning of the resulting polymers, bulky alkyloxy substitutent, 3,7-dimethyloctyloxy group is introduced into the orthoand para-positions of the phenyl side group by Williamson ether synthesis reaction. The introduction of bulky substitutent groups into the 3-position of the thiophene backbone not only influence solubility and processibility but also control and modify other physical, electronic and electro-optical properties of polythiophene derivatives. Polythiophene derivatives with different position of the 3,7-dimethyloctyloxy group into the phenyl ring were synthesized by FeCl₃ in dry CHCl₃. The resulting polymers were soluble in organic solvents and could be spin-cast onto the indium-tin-oxide (ITO) coated glass substrate. The weight average molecular weights (M_w) of the poly(ortho-DOTh) and poly(para-DOTh) were in the range of 5300-8700 g/mole with polystyrene standards. Polymerization results of the poly-(ortho-DOTh) and poly(para-DOTh) are summarized in Table 1.

TGA thermogram of the polymers revealed that an onset temperature of 5% weigh loss was about 380 °C. As shown in Fig. 1, optical absorption maxima of the polymer thin films with 3,7-dimethyloctyloxy group into the ortho- and para-position of phenyl ring showed red-shifted from 400 to 440 nm. As the shifting the substitutents from para- to ortho-position in the phenyl side ring along the π -conjugated polymer backbone, the effective mean conjugation length is shortening than that of para-position. The absorption maximum band of the poly(ortho-DOTh) was more blue-shifted compared to that of poly(para-DOTh). This means that the π -electron delocalization of the polymer main chain is interrupted by

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Polymerization	results of	f ortho-DOTh	and	para-DOTh

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Polymer	Yield (%)	M _n	$M_{ m w}$	$M_{ m w}/M_{ m n}$
Poly(ortho-DOTh)	20	3100	8700	2.8
Poly(para-DOTh)	34	3400	5300	1.6

 $M_{\rm n}$, $M_{\rm w}$ and PDI of the polymers were determined by gel permeation chromatography.



Fig. 1. UV–visible absorption spectra of poly(ortho-DOTh) and poly(para-DOTh) in thin film.

ortho and meta linkage, yielding a reduction of the π -conjugation length. We compared the optical property of poly[3-(4-octylphenyl)thiophene] with present two polymers. The absorption spectrum of poly[3-(4-octylphenyl)thiophene] showed at 467 nm. The red-shift of the absorption maximum compared to present polymers is attributed to the enhanced regioregularity and therefore higher structural order in π -conjugated polymer backbone. The photoluminescence (PL) spectra of the polymers were obtained under excitation at the absorption maximum wavelength of the each sample. Fig. 2 shows the PL spectra of the



Fig. 2. PL spectra of poly(ortho-DOTh) and poly(para-DOTh) in chloroform solution.



Fig. 3. Current-voltage characteristics of ITO/PEDOT/polymer/Al devices.

poly(ortho-DOTh) and poly(para-DOTh) in chloroform solution. The PL spectra of poly(para-DOTh) showed that the emission maximum is 534 nm in a solution state. The emission maximum of the poly(ortho-DOTh) was blue-shifted about 9 nm compared to that of poly(para-DOTh). However, the PL spectra of the poly(ortho-DOTh) and poly(para-DOTh) in solid state were broadened and the maximum emission peaks were red-shifted compared to the solution PL spectra, which was attributed to the new conformation of the polymer chain or intermolecular aggregation between the polymer chains in the solid film. Fig. 3 shows the current-voltage characteristics of ITO/PEDOT/ polymer/Al devices. In order to decrease the operating voltage and increase film forming properties of the emitting polymers, we first spin-coated PEDOT (25 nm) doped with PSS on the ITO substrate and dried for 30 min at 110 °C to remove the residual solvent. The resulting emitting polymers (100 nm) were successively spun on the top of the PEDOT film and then aluminum (150 nm) was thermally evaporated at 10^{-6} Torr, to give an active area of about 4 mm². The turn-on voltage of the poly(ortho-DOTh) is about 4.5 V, which is considerable lower compared with the poly(para-DOTh) (6.5 V) as shown in Fig. 3. Fig. 4 shows the EL spectra with an ITO/PEDOT/polymer/Al devices. The EL spectra were almost identical to the solid state PL spectra, indicating that the emission mechanisms are the same excited processes. The poly(ortho-DOTh) film showed maximum EL



Fig. 4. Electroluminescence spectra of an ITO/PEDOT/polymer/Al devices.

emission at 600 nm, corresponding to the red emission color. The EL spectra of poly(para-DOTh) exhibited at 607 nm with more red-shifted about 7 nm compared to poly(ortho-DOTh).

4. Conclusions

We have synthesized and characterized a new class of light emitting polymers composed of alternating thiophene repeating units on the polymer backbone. The synthetic strategy for the present polymers with alkyloxyphenyl substituents into the thiophene unit provides a relatively red shift of absorption maxima and high band gap. The polymer with ortho-position of alkyloxyphenyl in thiophene provides molecular weights, $M_w = 8700$ ($M_w/M_n = 2.8$), $\lambda_{max} = 400$ nm. Chemical structures of the polymers were confirmed by UV–visible and ¹H-, ¹³C-NMR spectra. The resulting polymers were soluble in organic solvent such as chloroform and could be spin-cast onto ITO glass

substrate to obtain optical quality and fine free thin film. Light emitting diodes could be fabricated and they showed red light emission on forward bias voltage of 4.5 V for poly(ortho-DOTh) and 6.5 V for poly(para-DOTh), respectively. The maximum EL emission of poly(ortho-DOTh) and poly(para-DOTh) showed at 600 nm and 607 nm, respectively.

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