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Synthesis and Properties of Poly(10-Octylphenothiazine-*CO*-2′,3′,6′,7′-Tertrakis-Octyloxy-9-Spirobifluorene) for OLEDs

Ji-Soung Kang
Jong-Wook Park
Department of Chemistry/Display Research Center, The Catholic University of Korea, Puchon, Kyonggi, Korea

Ji-Hoon Lee
Department of Polymer Engineering/Chung-Ju National University, Chung-Ju, Chungbuk, Korea

Se-Young Oh
Department of Chemical Engineering, Sogang University, Mapo, Seoul, Korea

Many attempts have been focused on polymer light-emitting diodes (PLEDs) for large area display application. We report synthesis and properties of new phenothiazyl polymer derivatives, Poly(10-octyl-10H-phenothiazine-3,7-diyl) (POP), Poly(2′,3′,6′,7′-tertrakis-octyloxy-9-spirobifluorene-2,7-diyl) (PTOSF), and their random copolymers, Poly(10-octylphenothiazine-co-2′,3′,6′,7′-tertrakis-octyloxy-9-spirobifluorene) (POTOSF), which were polymerized by Yamamoto reaction. The obtained compound was identified by ^{1}H-NMR, UV-Visible spectroscopy and GPC data. Weight average molecular number (Mn) of the polymers ranged from 17,000 to 300,000 g/mol with polydispersity indices of 1.6 ~ 6.5. Maximum UV-Visible absorption of the polymers was distributed from 285 to 403 nm. PL emission of POP, PTOSF and POTOSF copolymer were found to be 480, 434 and 484 nm, respectively. EL emission peak of double-layer EL device of POTOSF was at 494 nm (bluish green).

Keywords: electroluminescence; phenothiazine; polymer light-emitting diodes (PLEDs); Yamamoto reaction

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Address correspondence to Jong-Wook Park, Department of Polymer Science/Display Research Center, Catholic University of Korea, Puchon, Kyonggido, Korea. E-mail: hahapark@catholic.ac.kr

INTRODUCTION

Polymer light-emitting diodes (PLEDs) have attracted much attention from academia and industry because of their applications in large area flat-panel displays [1,2]. In particular, interest in PLEDs fabricated from conjugated Polymers [3,4] has augmented because such PLEDs have properties that are well-suited to flat panel displays: good processability, low operating voltages, fast response times, and facile color tunability over the full visible range.

On the other hand, a number of issues, such as low electroluminescent (EL) efficiencies and luminescent stability, which need to be resolved, currently spoil their commercial applications, although many light-emitting polymers have been synthesized and investigated, and the performance of PLEDs has been improved greatly in recent years. Therefore, investigation for new π-conjugated polymers with higher luminescent performance remains one of the major challenges in the area. Among the many kinds of conjugated polymers, PPV and its derivatives are the most extensively investigated polymers employed as emitting layers in PLEDs [5,6]. Recently, dendrimer-type Ir complexes, having large molecular weight, have been investigated so that the thin film of these materials can be fabricated by the solution process [7]. Phenothiazine is a well-known heterocyclic compound with electron-rich sulfur and nitrogen heteroatoms. Molecules and polymers [8,10,11] containing phenothiazine moieties have recently attracted much research interest because of their unique electro-optical properties and their resulting potential in diverse applications such as light-emitting diodes [9,11]. It has been suggested that inclusion of phenothiazine into a polyfluorene should improve the hole-transporting properties of the polyfluorene and thus improve the EL device efficiency. recently synthesized an alternating copolymer of phenothiazine and fluorene by the Suzuki coupling reaction and characterized its properties [11].

In this paper, we have synthesized phenothiazine homopolymer and spriofluorene copolymer. Poly(10-octyl-10H-phenothiazine-3,7-diyl) (POP), Poly(2′,3′,6′,7′-tertrakis-octyloxy-9-spirobifluorene-2,7-diyl) (PTOSF), and their random copolymers, Poly(10-octylphenothiazine-*co*-2′,3′,6′,7′-tertrakis-octyloxy-9-spirobifluorene) (POTOSF), were synthesized through Yamamoto polymerization. Optical properties of these polymers were characterized by UV-visible and photoluminescence (PL) spectra. Moreover, double-layer EL device was fabricated using POTOSF as emitting materials.

EXPERIMENT

Instrument

^{1}H-NMR spectra was recorded on a Brucker DPX-300 MHz spectrometer at room temperature. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) analysis using a Waters high pressure GPC assembly Model M410. The optical absorption spectra were measured by a Hewlett Packard 8453 Spectrometer. Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photo- and EL spectroscopy. For EL devices, polymer film was prepared by spin coating a solution containing 0.7 wt% of the polymer in toluene. Smooth and pinhole free film with a thickness around 70 nm was easily obtained from the polymer solutions. For double layered device, a modified water dispersion of PEDOT [poly(3,4-ethylenedioxy-thiophene)] doped with poly(styrene sulfonate) (PSS) (Bayer AG, Germany) was used as the hole-injection/trantransport layer. Cathode (LiF/Al) was deposited with 10^{-6} torr give an emitting area of 9 mm^2. Current-Voltage (I-V) characteristic of the film was measured using Keithley 2400 electrometer. Light intensity was obtained by Minolta CS-1000.

Synthesis

10-octyl-10H-phenothiazine (1)

Phenothiazine of 10 g (50 mmol) and potassium hydroxide of 8 g (147 mmol) were dissolved in dimethyl sulfoxide of 300 ml under nitrogen. After stirring for 1 hour, 1-bromo-octane of 9.5 ml (54 mmol) was added. The mixture was refluxed for 24 hours. After reaction mixture was worked up by silica gel chromatography to have colorless liquid of 11 g (72% reaction yield).

^{1}H NMR: δ: 7.12(m, 4H), 6.88(d, 4H), 3.80(t, 2H), 1.81(m, 2H), 1.40 (m, 2H), 1.26(m, 8H), 0.86(t, 3H)

3,7-dibromo-10-octyl-10H-phenothiazine (2)

10-Octyl-10H-phenothiazine of 11 g (35 mmol) was dissolved in chlorform of 200 ml under nitrogen and cooled to 5–10°C with ice-water bath. After N-bromosuccinimide (NBS) of 14 g (80 mmol) was added slowly. The mixture stirred for 2 hours at room temperature. The crude product was purified by column chromatography using a cosolvent (hexane/ethyl acetate = 10:1) as the eluent., yellow liquid of 9 g (65% yield).

^{1}H NMR: δ: 7.34(m, 4H), 6.95(d, 2H), 3.81(t, 2H), 1.62(m, 2H), 1.31 (m, 2H), 1.19(m, 8H), 0.81(t, 3H).

1,2-bis(octyloxy)benzene (3)

Pyrocatechol of 15 g (130 mmol), K_2CO_3 of 47 g (340 mmol) and KI of 2.1 g (13 mmol) were dissolved in acetonitrile of 300 ml under nitrogen. After stirring for 1 hour, 1-bromo-otane of 62 ml (320 mmol) was added. The mixture was refluxed for 40 hours. After the reaction mixture was worked up by silica gel chromatography to have colorless liquid of 43 g (95% yield).

^{1}H NMR: δ: 6.78(m, 2H), 6.70(m, 2H), 3.77(t, 4H), 1.54(m, 4H), 1.13(m, 20H), 0.73(t, 6H).

4-bromo-1,2-bis(octyloxy)benzene (4)

The redish liquid product was obtained by reacting 1,2-bis(octyloxy)benzene of 43 g (120 mmol) with NBS of 23 g (130 mmol) with 94% yield (50 g).

^{1}H NMR: δ: 6.95(s, 1H), 6.87(d, 1H), 6.73(d, 1H), 3.80(m, 4H), 1.54 (m, 4H), 1.11(m, 20H), 0.72(t, 6H).

2-(3,4-bis(octyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5)

4-Bromo-1,2-bis(octyloxy)benzene of 20 g (48 mmol) was dissolved in anhydrous THF of 300 ml and cooled to –78°C and then n-BuLi of 38 ml (62 mmol) was added. After 2 hours, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-diozaborolane of 12 ml (62 mmol) was added slowly to reaction mixture. The product was obtained reddish liquid of 20 g (90% yield).

^{1}H NMR: δ: 7.03(d, 1H), 6.93(m, 2H), 4.01(m, 4H), 1.77(m, 4H), 1.37(m, 32H), 0.87(t, 6H).

3,4,3′4′-tetrakis-octyloxy-biphenyl (6)

$Pd(OAC)_2$ of 0.97 g (4.3 mmol) and $(tri\text{-}O\text{-}tolyl)_3$ phosphine of 1.3 g (4.3 mmol) were dissolved in dimethylether of 150 ml and H_2O of 100 ml under nitrogen. After 4-bromo-1,2-bis(octyloxy)benzene of 21 g (51 mmol) and 2-(3,4-bis(octyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane of 20 g (43 mmol) were injected, and then K_2CO_3 of 15 g (100 mmol) and H_2O (100 ml) added. The mixture was refluxed for 3 hours. The product was obtained by recrystallization with ethyl acetate/ethanol (white solid of 17 g, 60%yield).

^{1}H NMR: δ: 7.17(s, 2H), 7.11(d, 2H), 6.99(d, 2H), 4.06(m, 8H), 1.77(m, 8H), 1.51(m, 8H), 1.48(m, 32H), 0.89(m, 12H).

2-bromo-4,5,3′,4′-tetrakis-octyloxy-biphenyl (7)

The product was obtained by bromination of 3,4,3′,4′-tetrakis-octyloxy-biphenyl of 17 g (26 mmol) with NBS of 5 g (28 mmol). It was obtained by recrystallization with methylene chloride/ethanol (white solid of 16 g, 60%yield).

^{1}H NMR: δ: 7.18(s, 1H), 6.98(s, 2H), 6.89(s, 1H), 6.87(d, 1H), 4.06 (m, 8H), 1.77(m, 8H), 1.51 (m, 8H), 1.48(m, 32H), 0.89 (m, 12H).

2,7-dibromo-9-(4,5,3′,4′-tertrakis-octyloxy-biphenyl-2-yl)-9H-fluoren-9-ol (8)

2-Bromo-4,5,3′,4′-tetrakis-octyloxy-biphenyl of 16 g (22 mmol) was dissolved in anhydrous THF of 300 ml under nitrogen and cooled to −78°C, and then t-BuLi of 31 ml (53 mmol) was added. After 1 hour, 2,7-dibromo-9H-fluoren-9-one of 9 g (26 mmol) was added slowly to reaction mixture. The product was purified by column chromatography using a cosolvent (hexane/EA = 50:1) as the eluent to have yellowish viscous liquid of 9 g (40% yield).

^{1}H NMR: δ: 7.17(d, 2H), 7.12(m, 4H), 6.98(m, 5H), 4.06(m, 8H), 1.83(m, 9H), 1.34(m, 40H), 0.87(m, 12H).

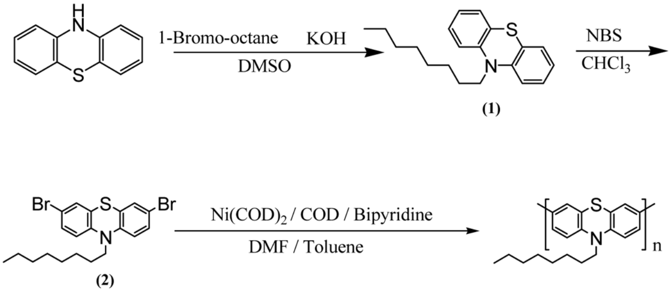
2,7-dibromo-2′,3′,6′,7′-tertrakis-octyloxy-9-spirobifluoren (9)

3,6-dibromo-9-(4,5,3′,4′-tertrakis-octyloxy-biphenyl-2-yl)-9H-fluoren-9-ol of 9 g (8.8 mmol) was dissolved in acetic acid of 200 ml under cooled to 0–5°C. And then HCl of 10 ml was added slowly. The product was purified by column chromatography using a cosolvent (hexane/ethyl acetate = 50:1) as the eluent to have white solid of 5 g (60% yield).

^{1}H NMR: δ: 7.64(d, 2H), 7.46(m, 2H), 7.19(s, 2H), 6.84(s, 2H), 6.13 (s, 2H), 4.10(t, 4H), 3.71(t, 4H), 1.84(m, 4H), 1.34(m, 44H), 0.87(m, 12H).

Polymerization

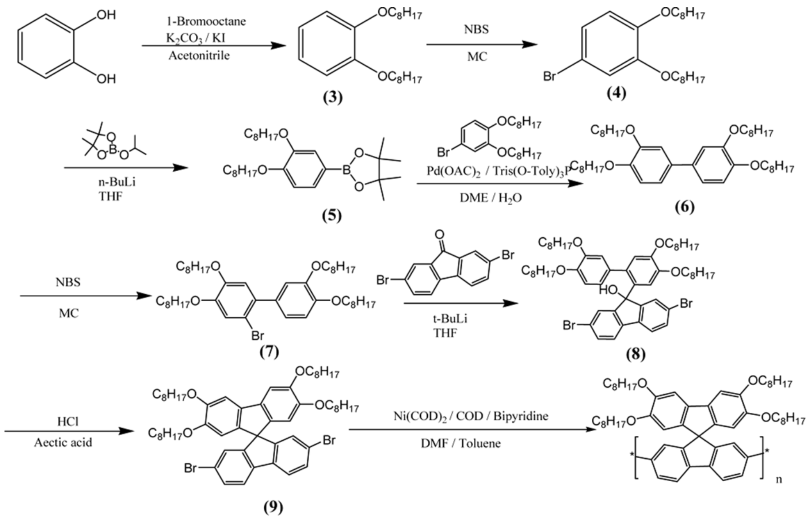
POP, PTOSF and POTOSF, which were polymerized by Yamamoto reaction. Each Schlenk tube containing 5 ml of DMF, bis(1,5-cyclooctadienyl)nickel(0), 2,2-dipyridyl and 1,5-cyclooctadiene (the last three in a molar ratio of 1:1:1) was kept under nitrogen at 80°C for 30 min. 5 ml of anhydrous toluene was then added to the monomer. Polymerization was maintained at 80°C for 48 hours, and then bromopentafluorobenzene (0.1 mol% of monomer) was dissolved in toluene and added to the reaction mixture for end-capping. When the reaction had finished, each polymer was precipitated from an equivolume mixture of concentrated HCl, methanol, and acetone. The isolated polymers were dissolved in toluene and precipitated in methanol. Finally, the resulting polymers were purified by soxhlet extraction by using acetone and then dried in a vacuum. All polymer yields ranged from 10 to 75% after purification [12].



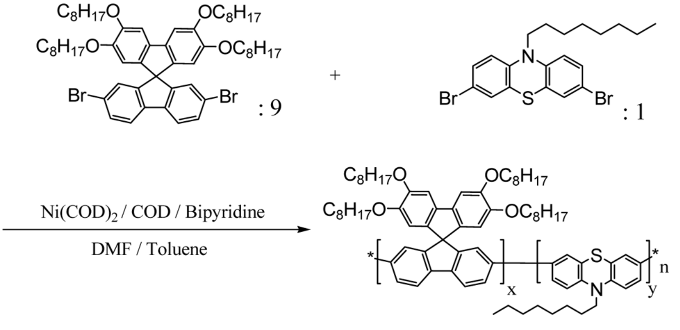
SCHEME 1 Synthetic route of POP.

RESULTS AND DISCUSSION

Synthesized polymer structures are shown in Scheme 1–3. The number average molecular weights (Mn) of POP, PTOSF and POTOSF copolymer were determined by gel-permeation chromatography (GPC) using a polystyrene standard with THF solvent and found to be range from 17,000 to 300,000 g/mol with polydispersity indices of 1.6 ~ 6.5. Although molecular weights of synthesized polymers were high, their polydispersity was wide. These results are summarized in Table 1.



SCHEME 2 Synthetic route of PTOSF.



SCHEME 3 Synthetic route of POTOSF.

POP homopolymer showed low molecular weight with good polydispersity value. POTOSF copolymer exhibited high molecular weight of 300,000 (Mn) and 1,440,000 (Mw) g/mol. The reason why phenothiazine moiety of 10% was introduced into spirofluorene moiety is that phenothiazine could be working as charge carrier moiety to emitter of spirofluorene group.

UV-visible absorption spectra of thin films of POP, PTOSF and POTOSF copolymer are depicted in Figure 1. Each spectrum was normalized to the peak maximum for more accurate comparison of wavelength. The maximum UV-visible absorption and absorption onset of POP, PTOSF and POTOSF copolymer exhibited at around 370, 391, 403 nm and 466, 434, 436 nm, respectively, which are originated from π-π^* transition of conjugated polymer backbone. The optical band gaps of the polymers were determined from the analysis of absorption edge with a plot of (hv) vs. $(\alpha hv)^2$, where α, h, and v are absorbance, Plank's constant, and the frequency of light. The optical band gap of POP, PTOSF and POTOSF copolymer were found to be 2.76, 2.91 and 2.90 eV.

TABLE 1 Average Molecular Weight and Polydispersity Indices of Synthesized Polymer

	Feed mole ratio of spirofluorene unit (%)	Feed mole ratio of phenothiazine unit (%)	Mn	Mw	Polydispersity
POP	–	100	17,000	28,000	1.63
PTOSF	100	–	71,000	460,000	6.48
POTOSF	90	10	300,000	1,440,000	4.78

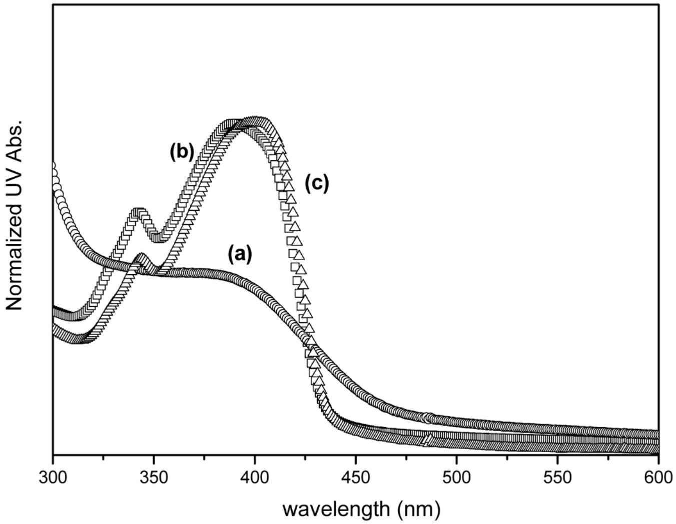


FIGURE 1 UV-visible spectra of POP (a, circle), PTOSF (b, square), and POTOSF (c, triangle) copolymer films on glass.

Figure 2 shows the PL emission spectra of polymer thin films. Two homopolymer of POP and PTOSF showed its own characteristic PL maximum value as 480 nm and 434 nm including 454 nm shoulder

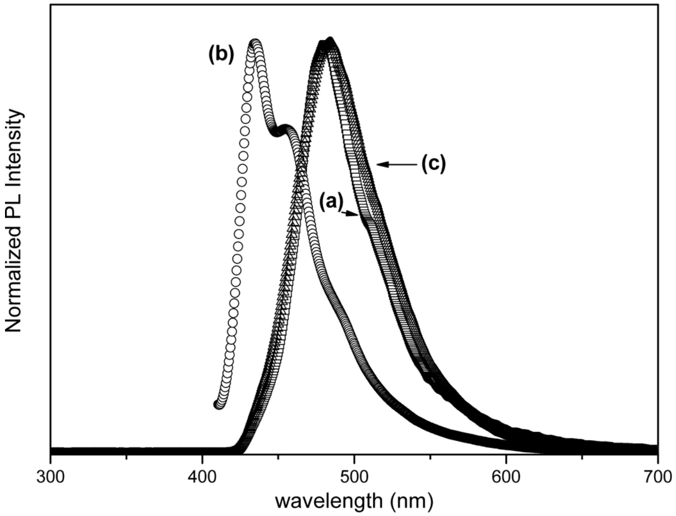


FIGURE 2 PL spectra of POP (a, square), PTOSF (b, circle), and POTOSF (c, triangle) copolymer films on glass.

TABLE 2 Electronic Levels of POP, PTOSF and POTOSF Copolymer

	HOMO	LUMO	Optical band gap
POP	5.26	2.50	2.76
PTOSF	5.63	2.72	2.91
POTOSF	5.64	2.74	2.90

peak. Copolymer POTOSF which contained POP (10%) and PTOSF (90%) exhibited PL maximum value of 484 nm, which means that the exciton energy of PTOSF unit in POTOSF might be transferred to POP unit. As shown in Scheme III, the feed ratio of POP moiety and PTOSF moiety in synthesis of POTOSF was 9:1 and polymerization yield was always more than 50%. It means that POTOSF contains PTOSF moiety and POP moiety together. Therefore the reason why Figure 2(c) of POTOSF is similar to Figure 2(a) of POP is that exciton energy in copolymer can be transferred from PTOSF moiety having relatively wide band gap energy to POP moiety.

The electrochemical characteristics of the polymers were investigated by using cyclic voltammetric analysis. The first oxidation potential was used to determine the HOMO energy level. Ferrocene was used as an internal standard for calibrating the potential. This data accounts that we could get HOMO level. Based on UV-visible data

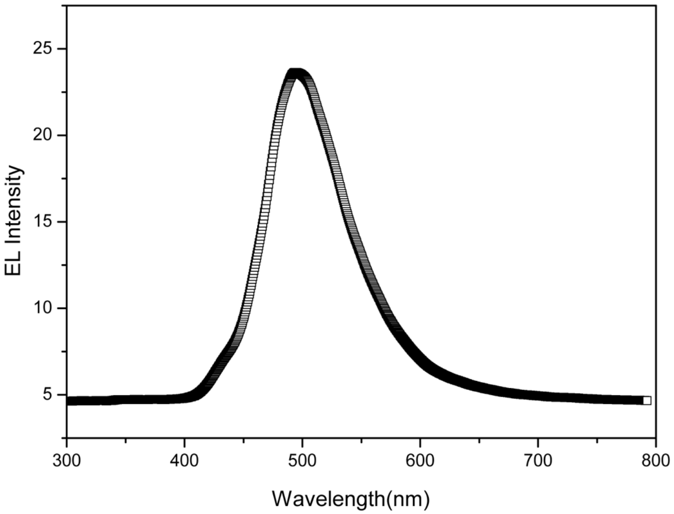


FIGURE 3 EL spectrum of ITO/PEDOT:PSS(50 nm)/POTOSF(70 nm)/LiF(1 nm)/Al(200 nm) device at 20 mA/cm^2.

and CV data, all electronic levels of HOMO, LUMO and band gaps are summarized in Table 2.

Even though POP has smaller band gap than PTOSF and POTOSF, it shows higher LUMO level of 2.5 eV. We believe that there is energy barrier to inject electron from cathode compared to PTOSF and POTOSF in device. Also PTOSF and POTOSF showed similar band gap value and HOMO and LUMO level values, but they showed quite different PL spectrum because of energy transfer as shown in Figure 2.

Double-layer EL device was fabricated using POTOSF copolymer such as ITO/PEDOT:PSS (50 nm)/POTOSF (70 nm)/LiF (1 nm)/Al (200 nm) device. EL spectrum of POTOSF device is shown in Figure 3. Emission peak of copolymer POTOSF device exhibited EL maximum value of 494 nm, which matched with its PL emission peak of 484 nm.

Further studies of synthetic compounds devices optimization are under way. We will report the EL efficiency and life time data in other paper.

REFERENCES

[1] Tang, C. W. & Vanslyke, S. A. (1987). *Appl. Phys. Lett.*, *54*, 913.

[2] Friend, R. H., Gymer, R. W., Holmes, A. B., Burroghes, J. H., Marks, R. N., Taliani, C., Bradley, D. D. C., Dos Santos, D. A., Bredas, J. L., Logdlund, M., & Salaneck, W. R. (1999). *Nature (London)*, *397*, 121.

[3] Burn, P. L., Holmes, A. B., Kraft, A., Bradley, D. D. C., Brown, A. R., Friend, R. H., & Gymer, R. W. (1992). *Nature*, *356*, 47.

[4] Kraft, A., Grimsdale, A. C., & Holmes, A. B. (1998). *Angew. Chem., Int. Ed.*, *37*, 402.

[5] Spreitzer, H., Becker, H., Kluge, E., Kreuder, W., Schenk, H., Demandt, R., & Schoo, H. (1998). *Adv. Mater.*, *10*, 1340.

[6] Chen, Z. K., Lee, N. H. S., Huang, W., Xu, Y. S., & Cao, Y. (2003). *Macromolecules*, *36*, 1009.

[7] Markham, J. P. J., Lo, S. C., Magennis, S. W., Burn, P. L., & Samuel, I. D. W. (2002). *Appl. Phys. Lett.*, *80*, 2645.

[8] Jenekhe, S. A., Lu, L., & Alam, M. M. (2001). *Macromolecules*, *34*, 7315.

[9] Kim, S. K., Lee, C. J., Lee, J. H., Kang, I. N., & Park, J. W. *Thin Solid Films*, *509*, 132.

[10] Park, J. W., Lee, S. E., Park, H. C., Chung, T. G., & Seo, H. J. (2004). *Materials Science and Engineering*, *24*, 103.

[11] Kong, X., Kulkarni, A. P., & Jenekhe, S. A. (2003). *Macromolecules*, *36*, 8992.

[12] Hwang, D. H., Kim, S. K., Park, M. J., Lee, J. H., Koo, B. W., Kang, I. N., Kim, S. H., & Zyung, T. (2004). *Chem. Mater.*, *16*, 1298.