Macromolecules **2009**, *42*, 887−891

Notes

Reduced Excimer Formation in Polyfluorenes by Introducing Coil-like Poly[penta(ethylene glycol) methyl ether methacrylate] Block Segments

Yong Ku Kwon,* Hyun Seok Kim, Hyun Jung Kim, Ju Hyun Oh, Han Sun Park, Yoon Soo Ko, Kyu Bo Kim, and Min Sung Kim

Department of Polymer Science and Engineering, Inha University, Incheon 402-751, Korea

Received August 7, 2008
Revised Manuscript Received November 3, 2008

Introduction

Conjugated polymers are of special interest due to their excellent optical and optoelectrical properties both in the solid state and in selective solvents.[1,2] They have delocalized, conjugated electronic structures in their main chains, which results in unique material characteristics such as photoluminescence (PL),[3] electroluminescence (EL),[4] conductivity, and oxidative stability.[5] Typical examples include the oligomers and polymers of thiophene,[6] *p*-phenylene,[7] phenylenevinylene,[8,9] phenylquinoline,[10] and fluorene,[11,12] which have been extensively used in molecular electronics and electronic devices.[13,14] The molecular chains of these polymers tend to aggregate by strong interchain interactions between neighboring aromatic moieties, which causes an undesirable red-shift fluorescence and reduced emission intensity upon thermal annealing or with the passage of current.[15−17] In addition, because of the strong, interchain interactions between the highly anisotropic, rigid polymer backbones, most of these compounds are insoluble or infusible.

Recent attempts have been made to enhance the performance of conjugated compounds by controlling their strong interchain interactions through introducing structural irregularities within the polymer backbone or copolymerizing with conjugated or nonconjugated comonomers.[18−30] One attractive approach is to combine heterogeneous polymer segments to the conjugated polymer backbones in the forms of block copolymers.[22−30] Interesting results have been reported on the incorporation of conjugated, rod-like block segments such as polythiophene,[23] poly(*p*-phenylene),[24] poly(phenylenevinylene),[25,26] phenylquinoline, vinylenic biphenyls,[27] and polyfluorene[11,12] into a heterogeneous polymer chain. Amphiphilic rod−coil diblock and triblock copolymers consisting of poly(phenylenevinylene) or polyfluorenic block were also synthesized to form self-assembling nanostructures in selective solvents.[11,26,28−30] In the case where rod−coil block copolymers are used, coil-like blocks tend to be segregated from rod-like blocks due to a conformational dissymmetry between component blocks to generate a series of supramolecular nanostructures.[31] These block copolymers exhibit almost the same EL and PL properties as those observed for the corresponding conjugated homopolymers. The spatial confinement of the conjugated blocks in the geometrically well-defined nanoscopic structures may reduce the dimensions of the molecular clusters and decrease the intermolecular aggregation between the luminescent, conjugated molecules.

Polyfluorene and its derivatives are one of promising materials for light-emitting diodes because of its high PL quantum efficiencies and thermal stability.[18,32−35] However, rigid-rod-like polyfluorene chains tend to stack cofacially with each other due to the favorable interchain $\pi-\pi$ interactions between aromatic moieties, which is considered to be troublesome in light-emitting devices because it may enhance nonradiative decay both in solution and in the solid state.[15−17] Here, we attempt to synthesize a novel, amphiphilic symmetric triblock copolymer containing a conjugated rod-like midblock of poly(9,9-didodecylfluorene-2,7-diyl) (PF) and coil-like endblocks of poly[penta(ethylene glycol) methyl ether methacrylate]s (PEGMA) by using the atom transfer radical polymerization (ATRP) technique and demonstrate the effect of the coil-like PEGMA endblocks on the aggregation and excimer formation of the conjugated PF segments during annealing at high temperature. PEGMA was chosen as a hydrophilic, coil-like endblock due to its excellent solubility in both hydrophobic and hydrophilic media. Because of the dissimilarities in the molecular conformation and hydrophilicity between the rod-like, conjugated PF and coil-like PEGMA blocks, they are expected to be phase-separated to display a self-assembled nanostructure.

Results and Discussion

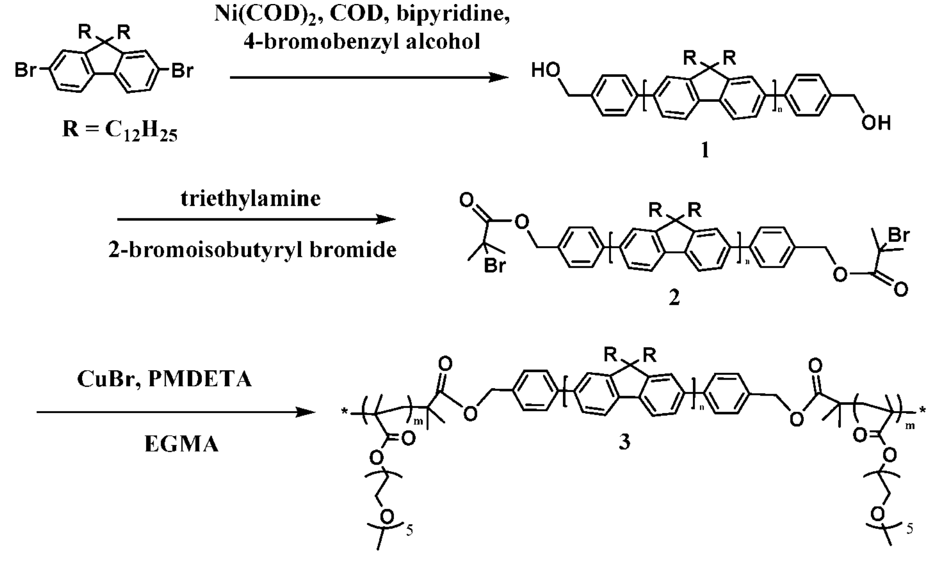
A novel conjugated triblock copolymer containing the rod-like PF midblock and coil-like PEGMA endblocks was synthesized by ATRP of the bromo-ended polyfluorene macroinitiator. It is well-known that the alkyl substituents at the C_9 positions of PF do not alter its optical and electronic properties in either the solid state or selective solvents.[36] The substituted fluorene containing a didodecyl unit at the C_9 position was used as a monomeric unit because introducing such long alkyl substituents would enhance the solubility of PF during the reaction. The PF blocks with hydroxyl ends **1** was prepared by the Yamamoto-type coupling of 2,7-dibromo-9,9-didodecylfluorene using a bis(1,5-cyclooctadiene)nickel(0) [Ni(COD)$_2$] catalyst in order to serve as a reductive transition metal−base coupling agent. The monofunctional comonomer of bromobenzyl alcohol was also used as an end-capper to functionalize each end of **1** into hydroxyl ends. The ^{1}H NMR data of compound **1** confirmed the successful end-capping of the hydroxyl units on the 2,7-positions of 9,9-didodecylfluorene. The reaction was carried out in the dark in order to prevent the formation of fluorenone defects, which are known to reduce the PL properties of fluorenic compounds.[37,38] The symmetric triblock copolymer of PEGMA-*b*-PF-*b*-PEGMA (**3**) was successfully synthesized by the ATRP of the bromo-ended polyfluorene macroinitiator **2**. In order to prepare a α-haloester-type macroinitiator **2**, the

---

* Corresponding author: tel +82-32-860-7482; fax +82-32-865-5178; e-mail ykkwon@inha.ac.kr.

10.1021/ma801806m CCC: $40.75

Scheme 1



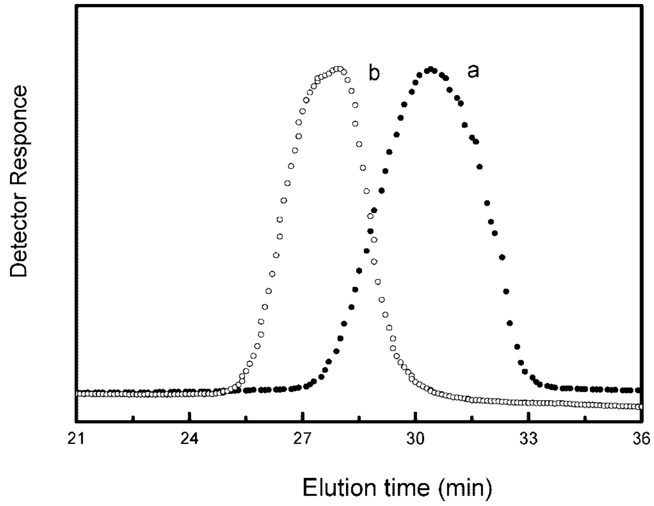


Figure 1. GPC traces of (a) PF macroinitiator **2** (closed circles) and (b) PEGMA-*b*-PF-*b*-PEGMA triblock copolymer **3** (open circles).

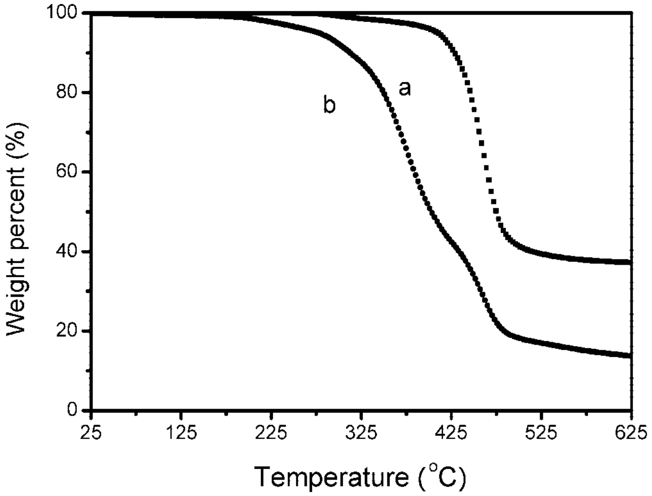


Figure 2. TGA data of (a) PF macroinitiator **2** and (b) PEGMA-*b*-PF-*b*-PEGMA (**3**).

hydroxyl end-capped **1** was reacted with 2-bromoisobutyryl bromide (BIB), and the completion of the reaction was confirmed by ^{1}H NMR data. The absence of fluorenone defects was confirmed by the ^{13}C NMR data of the compound **2**, indicating that the formation of the fluorenone defects was prevented during the reaction. ^{1}H NMR data also confirmed the successful synthesis of PEGMA-*b*-PF-*b*-PEGMA (**3**) by ATRP, which was carried out for 24 h at 70 °C. The schematic representation of the synthetic procedure of hydroxyl end-functionalized, substituted polyfluorene **1**, polyfluorene macroinitiator **2**, and PHEMA-*b*-PF-*b*-PHEMA (**3**) is illustrated in Scheme 1.

The M_n values of **2** and **3** measured from GPC, as shown in Figure 1, were measured as 5900 and 24 500 g/mol, and their corresponding polydispersity indices (PDI) were given as 1.51 and 1.36, respectively. The PDI of **2** was relatively high as a result of the intermolecular coupling reaction between **1**'s, which also increased the PDI of **3**. Parts a and b of Figure 2 show the TGA data of **2** and **3**, respectively, measured during heating from room temperature to 700 °C at a heating rate of 1 °C/min. Like other polyfluorene derivatives, **2** also exhibits a high thermal stability, showing less than 10% weight loss at higher than 400 °C. The onset temperature of the major weight loss of **2** was at about 380 °C. The thermal decomposition of **3** involves two steps. The first and second steps start from near 200 and 375 °C, respectively. It has been reported that the onset of the thermal decomposition of the PEGMA segments of PEGMA-grafted polymeric systems occurs at about 200−250 °C in air.[39] Therefore, the first weight loss may be assigned as the thermal decomposition of the PEGMA endblocks. The second major weight loss, starting from near 375 °C, can be assigned as the thermal decomposition of the aromatic oligofluorenic moieties. The stepwise thermal decomposition of **3** confirms the synthesis of a triblock copolymer **3** by ATRP.

The nanoscopic, self-assembled structure of **3** was investigated by SAXS. An overview of a typical SAXS data, measured from the as-received powders of **3** at room temperature, is given in Figure 3. In this scan, a broad peak was only found at a Q of about 0.35 nm^{-1}, corresponding to a d-spacing of ~18 nm. The broadness of the peak appeared to be due to a short-range order in the form of small cluster or aggregate of **3**, composed of the repulsive PF and PEGMA block segments with different hydrophilicities. Because long alkyl substituents of 9,9-didodecyl units are attached to the C_9 position of rod-like 9,9-didodecylfluorene-2,7-diyl moieties, they are asymmetric in molecular geometry and may create only roughly defined interfaces which

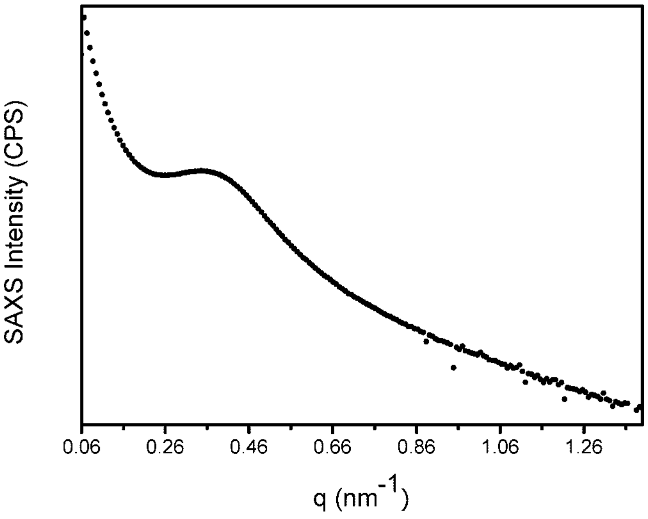


Figure 3. SAXS data of the as-received specimen of PEGMA-*b*-PF-*b*-PEGMA, measured at room temperature.

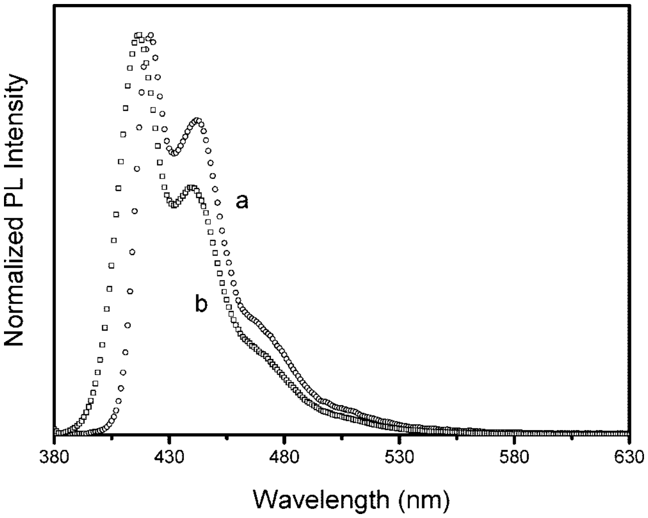


Figure 4. Fluorescence spectra of (a) PF macroinitiator **2** and (b) PEGMA-*b*-PF-*b*-PEGMA (**3**).

reduces the structural perfection of the self-assembled domain structure. In addition, the relatively large polydispersity of the PF rod segment also causes a broadening in the phase-separated nanostructure.

The PL property of compounds **2** and **3** was investigated in chloroform. Parts a and b of Figure 4 show the photoluminescence spectra of compounds **2** and **3**, respectively, measured in chloroform. In Figure 4a, we found a fluorescence maximum at 422 nm (blue) and two vibronic bands at $\lambda = 442$ and 475 nm, which appeared to be due to the photoemission of the PF blocks. In Figure 4b, the fluorescence maximum of **3** was slightly blue-shifted to 417 nm compared to one measured from **2**, which was mainly due to the better solubility of **3** in chloroform. PEGMA blocks, composed of methacrylate backbone with hydrophilic side groups of ethylene glycol, are more soluble in chloroform than the aromatic PF blocks are, and their addition as endblocks reduces the aggregation of the conjugated PF moieties and makes the effective conjugation length of the PF moiety become shorter. Note that the equation describing the emission of the conjugated polymers, $\sigma(\lambda) = \alpha(\lambda)/N$ ($\sigma(\lambda)$ is the molecular absorption cross section, $\alpha(\lambda)$ is the absorption coefficient, and N is the number of molecular entities contained within a unit volume of the absorbing medium along the light path) shows that the emission is inversely proportional to the effective molecular length of the conjugated chains.[40]

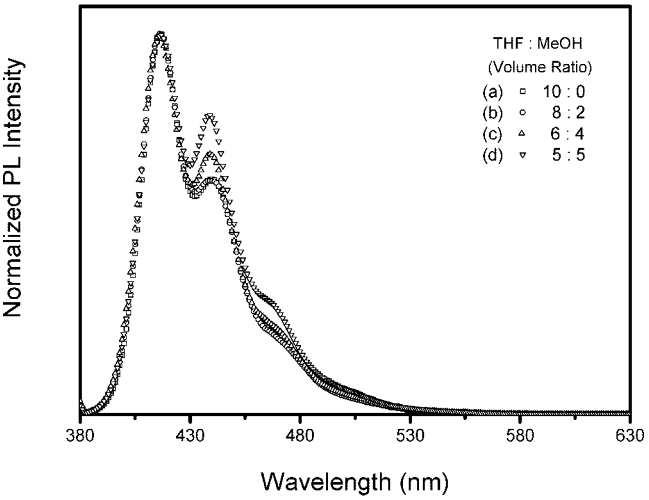


Figure 5. Fluorescence spectra of PEGMA-*b*-PF-*b*-PEGMA in a mixed solvent of THF and methanol with a THF:methanol volume ratio of (a) 10:0, (b) 8:2, (c) 6:4, and (d) 5:5.

The aggregation behavior of **3** can be demonstrated by the continuous addition of methanol in its THF solution. Since THF is a common solvent for both PF and PEGMA blocks, whereas methanol is a poor solvent for the PF block, adding methanol in the THF solution of **3** causes the aggregation of **3**. Figure 5a–d shows the PL spectra of **3** in mixed solvents of THF and methanol with a THF:methanol volume ratio of (a) 10:0, (b) 8:2, (c) 6:4, and (d) 5:5. The PL intensities of the peaks at $\lambda =$ 440 and 475 nm (vibronic bands) were slightly increased due to the aggregation of **3**. The result indicates that the 0–1 and 0–2 radiation transitions were enhanced by the aggregation of **3** due to $\pi-\pi$ interactions between the neighboring aromatic PF moieties.

The effect of the PEGMA endblocks on the aggregation behavior and spectral stability of thin films of **2** and **3** in their solid states was investigated during annealing at high temperature. The thin films of **2** and **3** were prepared by spin-coating from their THF solutions. Prior to the PL measurements, thermal behavior of both compounds was measured to select an adequate temperature for annealing and monitor the chemical degradation during heat treatment at high temperature. We measured the first and subsequent cooling and second heating scans of the as-prepared films of **2** and **3** by using differential scanning calorimetry (DSC). The data show that double endothermic peaks in the temperature range near 40–45 and 58–60 °C in the first heating DSC scans of the samples of **2** and **3** which corresponded to the melting of melting of the didodecyl substituents attached to the C_9 sites of the fluorene units and substituted fluorene moieties in the midblocks, which were successfully decoupled from the flexible coil-like PEGMA endblocks. However, in the first cooling and second heating DSC scans, the exothermic and/or endothermic peaks were also absent, again indicating that no recrystallization of the didodecyl substituents and the fluorene moieties of both **2** and **3** occurred during the cooling and reheating scans performed at a rate of 10 °C min^{-1}. This implies that the reorganization of the 9,9-didodecylfluorene units proceeded slowly in the experimental temperature range. Since the thin films of **2** and **3** are mobile in the isotropic phase and the molecular reorganization by chain aggregation through the $\pi-\pi$ interactions between aromatic moieties can be facilitated by the increased thermal motion of

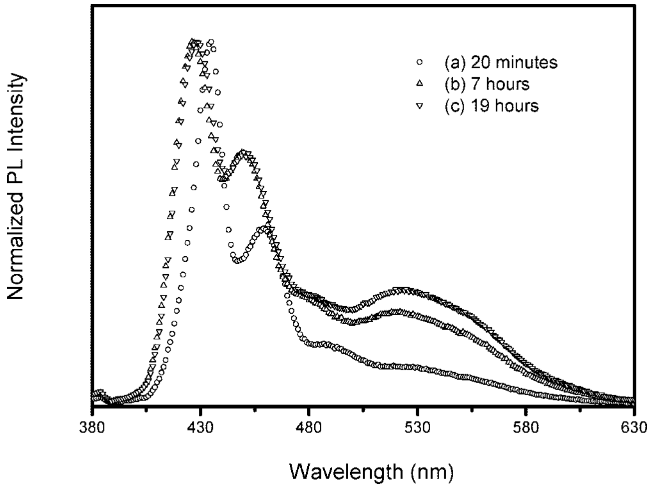


Figure 6. Fluorescence data of the thin film of PF macroinitiator **2**, annealed at 100 °C for (a) 20 min, (b) 7 h, and (c) 19 h.

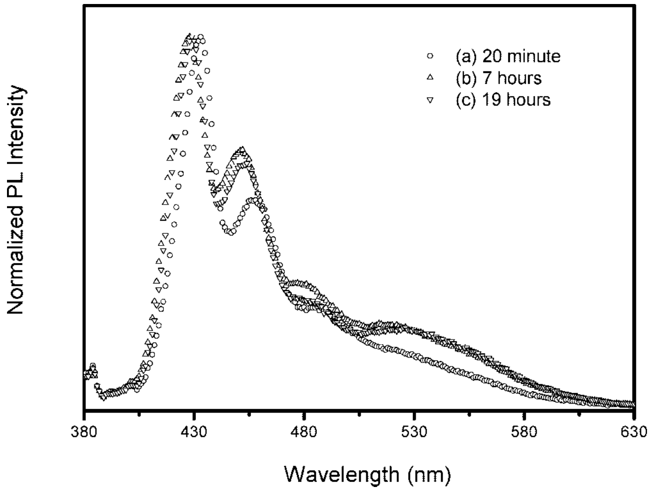


Figure 7. Fluorescence data of the thin film of PEGMA-*b*-PF-*b*-PEGMA **3**, annealed at 100 °C for (a) 20 min, (b) 7 h, and (c) 19 h.

the polymer chains, both samples were heat-treated in their isotropic state, e.g. 100 °C. Based on the TGA data described earlier, there was no substantial chemical degradation or change that occurs during and after heating at 100 °C with a heating rate of 1 °C/min. The PL emission spectra of the thin films of **2** and **3** annealed at 100 °C during various annealing times are shown in Figures 6 and 7, respectively. The thin films of the PF macroinitiator and PEGMA-*b*-PF-*b*- PEGMA were prepared by spin-coating and annealing at 100 °C in a convection oven during various times from 20 min to 19 h prior to the PL measurements. Both samples were heat-treated at the same experimental conditions. These figures clearly demonstrated that the emission maximum at 525 nm was reduced for **3**, as compared with one measured from **2**. The enhanced spectral stability of **3** ascribed due to the presence of the PEGMA endblocks, attached to the PF midblocks, which may suppress the excimer formation of the PF blocks during annealing at high temperature.

Conclusions

An amphiphilic triblock copolymer of PEGMA-*b*-PF-*b*-PEGMA was successfully synthesized by ATRP utilizing the PF macroinitiator. Because of the conformational dissymmetry between the coil-like PEGMA blocks and rod-like PG blocks, they create the short-range ordered self-assembled domain structure at room temperature. The fluorescence maximum for PEGMA-*b*-PF-*b*-PEGMA was blue-shifted as compared with that observed from the PF macroinitiator, mainly due to the decrease in the effective length of the conjugated PF blocks in solution. The PL emission spectra of the thin films, annealed at 100 °C for various times, clearly indicated that the PEGMA endblocks attached to the PF midblocks may suppress the excimer formation of the PF blocks during annealing at high temperature.

Table 1. GPC Data of the PF Macroinitiator and PEGMA-*b*-PF-*b*-PEGMA Triblock Copolymer

samples	yield (%)	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)
PF macroinitiator (**2**)	84	5900	8900	1.51
PEGMA-*b*-PF-*b*-PEGMA (**3**)	72	24500	33300	1.36

Acknowledgment. This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2007-D00141).

Supporting Information Available: Experimental procedures for the syntheses of **1**, **2**, and **3** and their ^{1}H NMR data; ^{13}C NMR data of **2**; the first and second DSC heating scans of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Mena-Osteritz, E.; Meyer, A.; Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Meijer, E. W.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 2679.
(2) (a) Child, A. D.; Reynolds, J. R. *Macromolecules* **1994**, *27*, 1975. (b) Balanda, P. B.; Ramey, M. B.; Reynolds, J. R. *Macromolecules* **1999**, *32*, 3970. (c) Widawski, G.; Rawiso, M.; François, B. *Nature (London)* **1994**, *369*, 387. (d) François, B.; Pitois, O.; François, J. *Adv. Mater.* **1995**, *7*, 1041.
(3) Valeur, B. *Molecular Fluorescence: Principles and Applications*; Wiley-VCH: Paris, 2002.
(4) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Logdlund, M.; Salaneck, W. R. *Nature (London)* **1999**, *397*, 121.
(5) Lee, J. I.; Klaerner, G.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1083.
(6) Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 329.
(7) Zhang, C.; Schlaad, H.; Schlüter, A. D. *J. Polym. Sci., Polym. Chem.* **2003**, *41*, 2879.
(8) Li, W.; Wang, H.; Yu, L. *Macromolecules* **1999**, *32*, 3034.
(9) Wang, H.; Wang, H. H.; Urban, V. S.; Littrell, K. C.; Thiyagarajan, P.; Yu, L. *J. Am. Chem. Soc.* **2000**, *122*, 6855.
(10) Jenekhe, S. A.; Chen, X. L. *Science* **1998**, *279*, 1903.
(11) Surin, M.; Marsitzky, D.; Grimsdale, A. C.; Müllen, K.; Lazzaroni, R.; Leclère, P. *Adv. Funct. Mater.* **2004**, *14*, 708.
(12) Tsolakis, P. K.; Kallitsis, J. K. *Chem.— Eur. J.* **2003**, *9*, 936.
(13) Braun, D. M. *Today* **2002**, *5*, 32.
(14) Hadziioannou, G., van Hutten, P. F., Eds.; *Semiconducting Polymers: Chemistry, Physics and Engineering*; Wiley-VCH: Weinheim, Germany, 2000.
(15) Kreyenschmidt, M.; Klaerner, G.; Fuhrer, T.; Ashenhurst, J.; Karg, S.; Chen, W. D.; Lee, V. Y.; Scott, J. C.; Miller, R. D. *Macromolecules* **1998**, *31*, 1099.
(16) Klaerner, G.; Davey, M. H.; Chen, W. D.; Scott, J. C.; Miller, R. D. *Adv. Mater.* **1998**, *10*, 993.
(17) Klaerner, G.; Miller, R. D. *Macromolecules* **1998**, *31*, 2007.
(18) Klarner, G.; Lee, J.-I.; Lee, V. Y.; Chan, E.; Chen, J.-P.; Nelson, A.; Markiewicz, D.; Siemens, R.; Scott, J. C.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1800.
(19) Donat-Bouillud, A.; Levesque, I.; Tao, Y.; D'Iorio, M.; Beaupre, S.; Blondin, P.; Ranger, M.; Bouchard, J.; Leclerc, M. *Chem. Mater.* **2000**, *12*, 1931.
(20) Blondin, P.; Bouchard, J.; Beaupre, S.; Belletete, M.; Durocher, G.; Leclerc, M. *Macromolecules* **2000**, *33*, 5874.
(21) Xia, C.; Advincula, R. C. *Macromolecules* **2001**, *34*, 5854.
(22) Liang, Y. Y.; Wang, H. B.; Yuan, S. W.; Lee, Y. G.; Yu, L. P. *J. Mater. Chem.* **2007**, *17*, 2183.
(23) Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 329.

(24) Zhang, C.; Schlaad, H.; Schlüter, A. D. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2879.

(25) Li, W.; Wang, H.; Yu, L. *Macromolecules* **1999**, *32*, 3034.

(26) Wang, H.; Wang, H. H.; Urban, V. S.; Littrell, K. C.; Thiyagarajan, P.; Yu, L. *J. Am. Chem. Soc.* **2000**, *122*, 6855.

(27) Lee, M.; Kim, J. W.; Hwang, I. W.; Kim, Y. R.; Oh, N. K.; Zin, W. C. *Adv. Mater.* **2001**, *13*, 1363.

(28) Lu, S.; Fan, Q. L.; Chua, S. J. *Macromolecules* **2003**, *36*, 304.

(29) Lu, S.; Fan, Q. L.; Liu, S.-Y.; Chua, S. J. *Macromolecules* **2002**, *35*, 9875.

(30) Marsitzky, D.; Klapper, M.; Mullen, K. *Macromolecules* **1999**, *32*, 8685.

(31) Gunther, J.; Stupp, S. I. *Langmuir* **2001**, *17*, 6530.

(32) Fukuda, M.; Sawada, K.; Yoshino, K. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2465.

(33) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.

(34) Ranger, M.; Rondeau, D.; Leclerc, M. *Macromolecules* **1997**, *30*, 7686.

(35) Leclerc, M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2867.

(36) Byun, H. Y.; Chung, I. J.; Shim, H.-K.; Kim, C. Y. *Chem. Phys. Lett.* **2004**, *393*, 197.

(37) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477.

(38) Romaner, L.; Pogantsch, A.; Scandiucci de Freitas, P.; Scherf, U.; Gaal, M.; Zojer, E.; List, E. J. W. *Adv. Funct. Mater.* **2003**, *13*, 597.

(39) Chen, Y. W.; Wang, W. C.; Yu, W. H.; Kang, E. T.; Neoh, K. G.; Vora, R. H.; Ong, C. K.; Chen, L. F. *J. Mater. Chem.* **2004**, *14*, 1406.

(40) (a) Schenk, R.; Ehrenfreund, M.; Huber, W.; Müllen, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1673. (b) Kohler, B. K. *Springer Ser. Solid State. Sci.* **1985**, *63*, 101. (c) Tolbert, L. M. *Acc. Chem. Res.* **1992**, *25*, 561.

MA801806M