

# Synthesis of an Amphiphilic $\pi$ -Conjugated Triblock Copolymer of Poly(9,9-didodecylfluorene-2,7-diyl) and Poly(hydroxyl ethyl methacrylate)

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**Abstract:** A novel amphiphilic, symmetric rod-coil, triblock copolymer (denoted as PHEMA-*b*-PF-*b*-PHEMA) of poly(9,9-didodecylfluorene-2,7-diyl) (PF) and poly(hydroxyl ethyl methacrylate) (PHEMA) was synthesized. A  $\pi$ -conjugated poly(9,9-didodecylfluorene-2,7-diyl) (PF) was used as a rodlike midblock segment and connected with hydrophilic end blocks of poly(hydroxyl ethyl methacrylate) (PHEMA) by using an ATRP technique. The chemical structure of PHEMA-*b*-PF-*b*-PHEMA was confirmed by <sup>1</sup>H-NMR and GPC, and its PL properties were investigated in selected solvents. Due to the dissimilarities in molecular conformation and solubility between PHEMA and PF blocks, both block segments were segregated to display a phase-separated morphology on a Si wafer.

**Keywords:** rod-coil triblock copolymer, polyfluorene, phase-separated morphology.

## Introduction

Poly(*p*-phenylene), poly(*p*-phenylene vinylene), polyfluorene and their derivatives are of special interest due to their excellent optical and optoelectrical properties both in the solid state and in selective solvents.<sup>1,2</sup> The molecular backbones of these materials have delocalized,  $\pi$ -conjugated electronic structures which result in electronic band gaps with light emitting capability.<sup>3</sup> The polymer chains of the  $\pi$ -conjugated systems are rigid and tend to aggregate by strong interchain interactions between rigid polymer backbones with aromatic or heteroaromatic rings, which have restricted the areas of practical applications.<sup>4,5</sup> One attractive approach to tune interchain interactions between  $\pi$ -conjugated molecules is to combine heterogeneous polymer segments to the conjugated polymer backbones through block copolymerization.<sup>6</sup> The spatial confinement of the conjugated blocks in nanometer domains reduces the dimensions of the molecular clusters, resulting in the decrease in intermolecular aggregation between the luminescent, conjugated molecules.<sup>7</sup> Highly ordered, nanoscale domain structures of  $\pi$ -conjugated block copolymers are also promising in view of applications in display electronic devices by solution processing.<sup>4,8</sup> The conjugated block segments are rigid and block copolymerization of these rod-like moieties with coil-like polymers leads to self-assembling nanostructures with unique morphologies such as self-assembling layers, tubules, honeycomb or mushroom-like nanostructures depending on the

volume ratio of each segment and the interaction between blocky segments.<sup>9,11</sup> The combination of hydrophobic,  $\pi$ -conjugated rod blocks with hydrophilic coil blocks in a polymer chain, exhibiting a great variety of phase-separated morphologies both in the solid state and in selective solvents allows better processibility and extends the area of optoelectronic application to other fields.<sup>7,10,11</sup> Several amphiphilic diblock and triblock block copolymers with a  $\pi$ -conjugated polyfluorene block segment have been reported.<sup>4,11,12</sup> Due to the rigid, planar aromatic moiety of fluorene, these polymers exhibit almost the same electroluminescence (EL) and photoluminescence (PL) properties as those seen in a polyfluorene homopolymer.<sup>13</sup>

In this study, we synthesized a novel amphiphilic, symmetric rod-coil triblock copolymer, PHEMA-*b*-PF-*b*-PHEMA, containing the conjugated midblock. Poly(9,9-didodecylfluorene-2,7-diyl) (PF), used as a rodlike midblock segment, was connected with the hydrophilic end blocks of poly(hydroxyethyl methacrylate) (PHEMA) by using an ATRP technique.<sup>11,14</sup> The PL properties of PHEMA-*b*-PF-*b*-PHEMA were investigated in selective solvents. Due to the dissimilarities in molecular conformation and hydrophilicity between PHEMA and PF blocks, both block segments are expected to be strongly segregated to display a highly ordered, phase-separated morphology.

## Experimental

**Materials and Characterization.** 2,7-Dibromo-9,9-di-*n*-dodecylfluorene (97%), toluene (anhydrous, 99.8%), *N,N*-

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dimethylformamide anhydrous (99.8%), hydrazine, bis(1,5-cyclooctadiene)nickel(0) ( $\text{Ni}(\text{COD})_2$ ), bipyridine (99+%), 1,5-cyclooctadiene (COD, 99+%), 4-bromobenzyl alcohol (99%), 2-hydroxyethyl methacrylate (HEMA, 98%), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA, 99%), copper(I) bromide (CuBr, 98%) (all from Aldrich) were all used as received. 2-Bromoisobutyryl bromide (BIB) and triethylamine (all from TCI) were also used as received. HEMA was passed through a column of alumina to remove inhibitor. CuBr was purified by stirring with glacial acetic acid, followed by filtration and washing the solid three times with ethanol and twice with diethyl ether.

$^1\text{H-NMR}$  spectra were recorded on a Bruker AC 250 spectrometer at 250 and 63 MHz, respectively, and were referenced to TMS. Molecular weights and molecular weight distributions were determined using a GPC equipped with a Waters Associates 410 RI detector, 510 HPLC pump, and *i*-Styragel columns with pore sizes of 102, 500, 103, and 104 Å. The eluant was THF, and the molecular weights were calibrated with polystyrene standards.

**Synthesis of Hydroxyl End-Functionalized Polyfluorene (2).**  $\text{Ni}(\text{COD})_2$ , COD, bipyridine, and anhydrous DMF were mixed with stirring at 70 °C for 30 min under dry  $\text{N}_2$  gas. In this dark blue solution, 2,7-dibromo-9,9'-didodecylfluorene **1** and 4-bromobenzyl alcohol in anhydrous toluene were added *via* a syringe. Then, the reaction continued with stirring at slightly-elevated temperature, 85 °C in the absence of light for additional 2 days. After the reaction, the mixture was then cooled to room temperature and diluted with THF and aqueous hydrazine solution. The mixture solution was stirred overnight. The organic layer of the mixture solution where the product was assumed to be dissolved was separated, filtered, concentrated, and poured into methanol. The precipitated powder product was purified by extraction with methanol, and reprecipitated into methanol.

**Synthesis of Polyfluorene Macroinitiator (3).** Compound **2**, triethylamine, anhydrous methylene chloride, purified with  $\text{CaCl}_2$ , were added in a round-bottom flask and then the mixture was cooled at 0 °C. BIB was added dropwise in the cooled mixture, *via* a syringe under dry  $\text{N}_2$  gas. The solution was stirred overnight at 20 °C. The resulting solution was extracted with water, dried with sodium sulfate, concentrated and precipitated into methanol. The obtained, tint yellow polymer powder was filtered, rinsed with methanol and passed silica short column (toluene eluant) for purification.

**Synthesis of PHEMA-*b*-PF-*b*-PHEMA (4).** Compound **3**, HEMA, PMDETA, and DMF were added to a 25 mL flask and degassed by three vacuum-nitrogen cycles. After stirring the mixture at room temperature for 1 hr, CuBr was added to initiate the reaction and the mixture was transferred to an oil bath at 90 °C. After stirring for 24 hrs, the reaction was finally stopped by opening the flask and exposing the catalyst to air. The reacted mixture was diluted

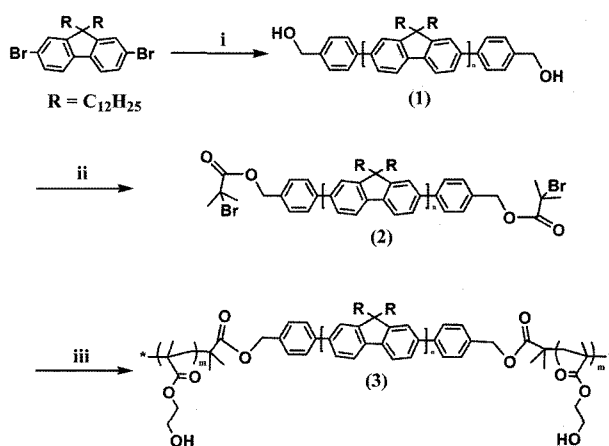
with methylene chloride and passed through the alumina column to remove the catalyst. The unreacted monomers were removed by precipitation with diethyl ether for several days and the resulting product was dried under vacuum at 40 °C.

## Results and Discussion

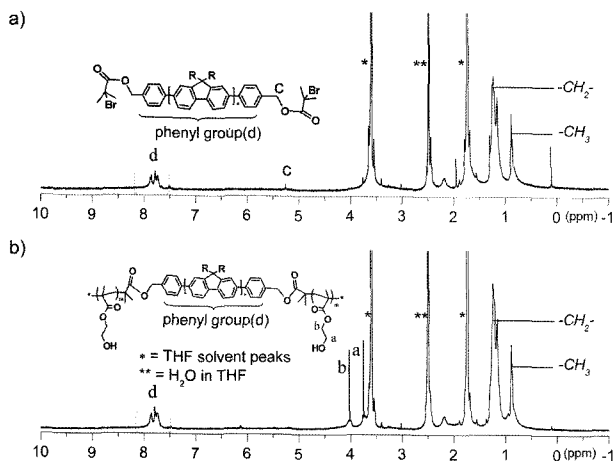
Scheme I describes the synthetic procedure of hydroxyl end-functionalized, substituted polyfluorene (**1**), polyfluorene macroinitiator (**2**) and PHEMA-*b*-PF-*b*-PHEMA (**3**). The oligofluorene with hydroxyl ends **1** was prepared by the Yamamoto-type coupling of 2,7-dibromo-9,9'-didodecylfluorene using a  $\text{Ni}(\text{COD})_2$  catalyst as a reductive transition metal-base coupling agent.<sup>14</sup> The reaction was carried out in the dark to block the formation of fluorenone defects,<sup>15</sup> which tend to reduce the PL properties of fluorenic compounds.

Esterification of the hydroxyl-endcapped polyfluorene with BIB afforded macroinitiator. 2-Bromoisobutyrate derivatives have proven versatile for ATRP of many vinyl monomers. The chemical structure of PF macroinitiator, **2** was confirmed by  $^1\text{H NMR}$  data shown in Figure 1.

**3** was synthesized by ATRP of the bromo-ended polyfluorene macroinitiator.<sup>14</sup> The chemical structure of **3** was confirmed by  $^1\text{H NMR}$  data shown in Figure 1. ATRP was carried out at 90 °C for 24 hrs, in order to achieve the complete conversion of the monomer, without increasing the polydispersity (PDI) of the final polymer. The  $M_n$ s of **2** and **3** were determined by GPC and measured as 7,290 and 11,358 g/mol and their polydispersity indices (PDIs) were 3.2 and 2.8, respectively. The PDI of **2** was high, as a result of the intermolecular coupling reaction between **1**s, which also led to **2** having a high PDI. The slightly lower PDI of **3**, as compared with that of **2**, resulted from the increase in the



**Scheme I.** (i)  $\text{Ni}(\text{COD})_2$ , COD, bipyridine, DMF, 70 °C/2,7-dibromo-9,9'-didodecylfluorene, 4-bromobenzyl alcohol, 85, 48 hrs, dark; (ii) **1**, triethylamine, methylene chloride, 0 °C/BIB, RT, 12 hrs; (iii) **2**, CuBr, PMDETA/ HEMA monomer, DMF, 90, 24 hrs.

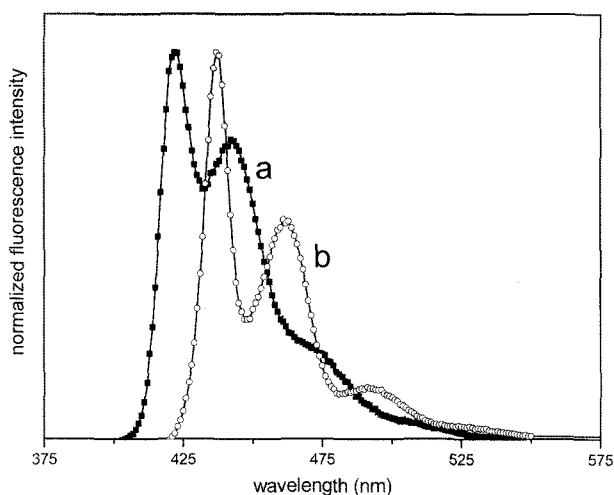
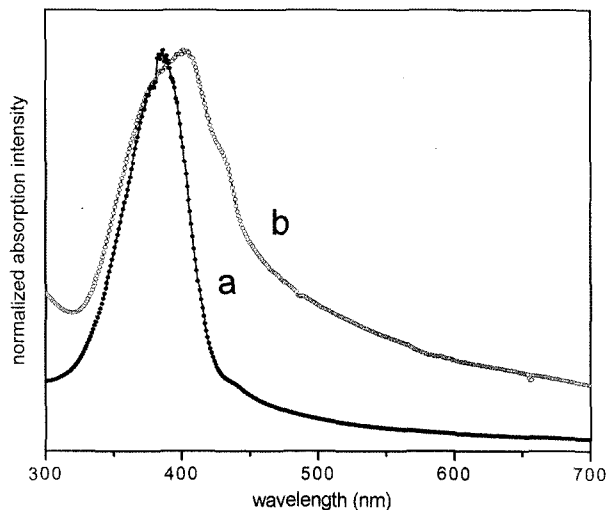


**Figure 1.** <sup>1</sup>H NMR spectra of macroinitiator (2) and PHEMA-*b*-PF-*b*-PHEMA (3) in deuterated THF (\*: deuterated THF).

molecular weight of the final polymer. The relative mole fraction of each block, estimated from the <sup>1</sup>H NMR data shown in Figure 1 was similar to that measured from the GPC data.

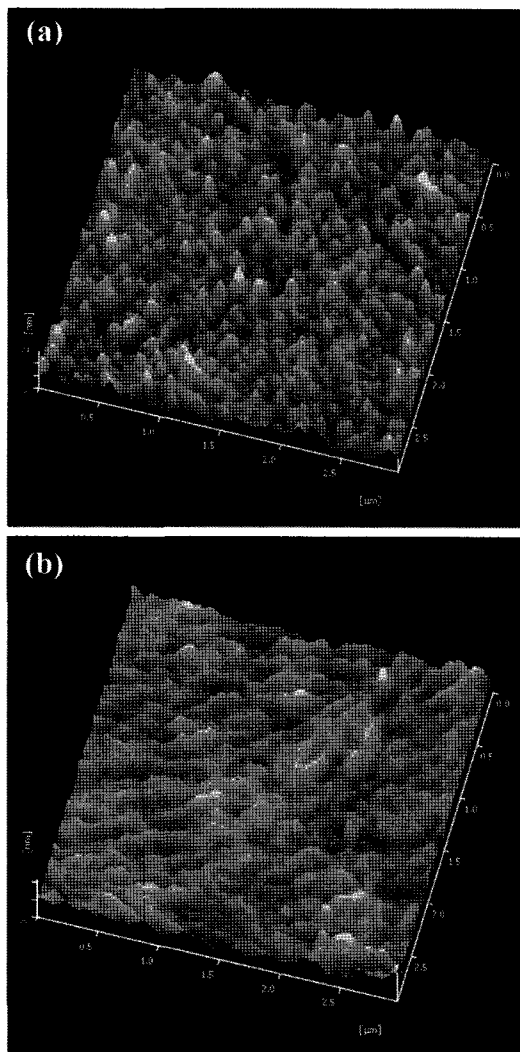
The PL property of compound 3 highly depends on the self-assembly behavior in selective solvents. Figure 2 shows the absorption and the fluorescence spectra of compound 3, dissolved in (a) THF as a good solvent for both blocks; (b) a mixed solvent of THF:methanol=1:9(v/v). Methanol was used as a poor solvent for the PF blocks of 3. In THF, we found an absorption maximum at 386 nm and a fluorescence maximum at 422 nm (blue), which appeared to be due to the photoemission of the 9,9-didodecylfluorene-2,7-diyl blocks. In a mixed solvent of THF and methanol, both absorption and the fluorescence maxima were shifted to 401 and 435 nm. The red-shift of both maxima in THF/methanol was due to the increase of the effective length of the conjugated PF blocks, which resulted from the molecular association of PHEMA-*b*-PF-*b*-PHEMA. The addition of the PHEMA end blocks and the resulting microphase separation between both PF and PHEMA blocks increases the effective molecular length of the molecular association of the conjugated PF moieties. The following equation indicates that the emission of conjugated polymers is inversely proportional to the effective molecular length of conjugated chains:  $\alpha(\lambda) = \alpha(\lambda)/N$  where  $\alpha(\lambda)$  is molecular absorption cross-section;  $\alpha(\lambda)$  is absorption coefficient and  $N$  is the number molecular entities contained in a unit volume of the absorbing medium along the light path.<sup>16</sup>

Figure 3 shows the surface topology of the dip-coated PHEMA-*b*-PF-*b*-PHEMA onto an ITO glass, obtained by AFM. The thin films were cast from 0.05 mg/mL solutions of (a) THF and (b) THF:methanol=1:9(v/v). They were kept at room temperature for 1 day prior to the measurement.<sup>17</sup> Applied in a THF solution, the hydrophilic PHEMA blocks are strongly adsorbed and form a wetting layer on



**Figure 2.** UV/Vis(top) and PL(bottom) spectra of PHEMA-*b*-PF-*b*-PHEMA (3) in (a) THF and (b) mixed solvent of THF/MeOH (1/9, v/v).

the ITO surface. Due to the unfavorable interaction with ITO surface, the PF blocks are likely to dewet to yield isolated nanoclusters onto the PHEMA blocks. Unlike thick block copolymer films, both blocks form part of surface, thus resulting in a chemically heterogeneous surface structure of less polar PF domains surrounded by the highly polar PHEMA adsorbate layer. In Figure 3(a), the protruding PF clusters are displayed as brighter areas. In this Figure, the height of the clusters, their lateral diameter and the average spacing were measured. In the image represented here, the average height of the cluster varies from 0.8 to 1 nm, the cluster diameter from 96 to 98 nm. In Figure 3(b) measured from the sample, dip-coated from THF:methanol=1:9 (v/v), we observed a string-like morphology on the ITO glass. Since methanol was a poor solvent for the PF blocks of 3, an increased number of PF blocks were associated to form into the string-like morphology, preferentially oriented on the ITO glass. This AFM image indicates that the  $\pi$ -conju-



**Figure 3.** AFM image of the dip-coated **3**, cast from. (a) THF and (b) mixed solvent of THF/MeOH (1/9, v/v).

gated PF chains of **3**, dissolved in the mixed solvent of THF and methanol, form one-dimensional  $\pi$ -stacks, aligned parallel to each other by supramolecular  $\pi$ - $\pi$  interactions between neighboring PF chains.

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## References

- (1) E. Mena-Osteritz, A. Meyer, B. M. W. Langeveld-Voss, R. A. J. Janssen, E. W. Meijer, and P. Bäuerle, *Angew. Chem., Int. Ed.*, **39**, 2679 (2000).
- (2) (a) A. D. Child and J. R. Reynolds, *Macromolecules*, **27**, 1975 (1994). (b) P. B. Balanda, M. B. Ramey, and J. R. Reynolds, *Macromolecules*, **32**, 3970 (1999). (c) G. Widawski, M. Rawiso, and B. François, *Nature*, **369**, 387 (1994). (d) B. François, O. Pitois, and J. François, *Adv. Mater.*, **7**, 1041 (1995).
- (3) A. J. Heeger, *Angew. Chem. Int. Ed.*, **40**, 2591 (2001).
- (4) P. K. Tzolakis and J. K. Kallitsis, *Chem. Eur.*, **9**, 936 (2003).
- (5) G. Klärner, J. -I. Lee, V. Y. Lee, E. Chan, J. -P. Chen, A. Nelson, D. Markiewicz, R. Siemens, J. C. Scott, and R. D. Miller, *Chem. Mater.*, **11**, 1800 (1999).
- (6) J. Liu, E. Sheina, T. Kowalewski, and R. D. McCullough, *Angew. Chem. Int. Ed.*, **41**, 329 (2002).
- (7) L. Yu, H. Wang, H. H. Wang, V. S. Urban, K. C. Littrell, P. Thiyagarajan, and L. J. Yu, *J. Am. Chem. Soc.*, **122**, 6855 (2000).
- (8) L. Yu, W. Li, H. Wang, T. L. Morkved, and H. M. Jaeger, *Macromolecules*, **32**, 3034 (1999).
- (9) J. Jo, C. Chi, S. Höger, G. Wegner, and D. Y. Yoon, *Chem. Eur.*, **10**, 2681 (2004).
- (10) P. Leclère, A. Calderone, D. Marsitzky, V. Francke, Y. Geerts, K. Müllen, J. L. Brédas, and R. Lazzaroni, *Adv. Mater.*, **12**, 1042 (2000).
- (11) C. L. Chochos, P. K. Tzolakis, V. G. Gregoriou, and J. K. Kallitsis, *Macromolecules*, **37**, 2502 (2004).
- (12) (a) M. Surin, D. Marsitzky, A. C. Grimsdale, K. Müllen, R. Lazzaroni, and P. Leclère, *Adv. Funct. Mater.*, **14**, 708 (2004). (b) B. Liu and G. C. Bazan, *J. Am. Chem. Soc.*, **126**, 1942 (2004).
- (13) M. Fukuda, K. Sawada, and K. Yoshino, *J. Polym. Sci., Polym. Chem.*, **31**, 2465 (1993).
- (14) S. Lu, L. Fan, and S. J. Chua, *Macromolecules*, **36**, 304 (2003).
- (15) X. Gong, D. Moses, A. J. Heeger, and S. Xiao, *Synthetic Metals*, **141**, 17 (2004).
- (16) B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH Verlag GmbH, Paris, 2002, Chap.2, p.24.
- (17) J. Gunther and S. I. Stupp, *Langmuir*, **17**, 6530 (2001).