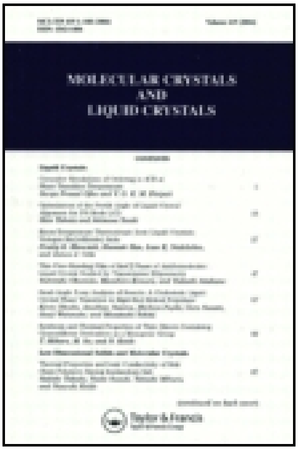

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Self-Assembling Behavior of Amphiphilic Conjugated Block Copolymers Containing an Oligofluorene Rod Segment

Hyun Seok Kim [a], Hyun Jung Kim [a] & Yong Ku Kwon [a]
[a] Department of Polymer Science and Engineering, Inha University, Incheon, Korea

Version of record first published: 12 Mar 2007

To cite this article: Hyun Seok Kim, Hyun Jung Kim & Yong Ku Kwon (2007): Self-Assembling Behavior of Amphiphilic Conjugated Block Copolymers Containing an Oligofluorene Rod Segment, Molecular Crystals and Liquid Crystals, 463:1, 25/[307]-31/[313]

To link to this article: http://dx.doi.org/10.1080/15421400601021463

Mol. Cryst. Liq. Cryst., Vol. 463, pp. 25/[307]–31/[313], 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601021463

Self-Assembling Behavior of Amphiphilic Conjugated Block Copolymers Containing an Oligofluorene Rod Segment

Hyun Seok Kim
Hyun Jung Kim
Yong Ku Kwon
Department of Polymer Science and Engineering, Inha University,
Incheon, Korea

The self-assembling behavior of a conjugated triblock copolymer (PEGMA-b-PF-b-PEGMA) containing an oligofluorene (PF) block and poly[penta(ethylene glycol) methyl ether methacrylate] (PEGMA) blocks was investigated. Due to the amphiphilic nature of PEGMA-b-PF-b-PEGMA, the micellar aggregates of PEGMA-b-PF-b-PEGMA were induced in selective solvents. Photoluminescence spectra of PEGMA-b-PF-b-PEGMA were also measured and compared with the data measured from the SAXS and TEM measurements.

Keywords: amphiphilic triblock copolymer; photoluminescence; self-assembling behavior

INTRODUCTION

Polymer light-emitting diodes (PLED) have been recently developed for commercial applications in the display technology [1–3]. Poly(*p*-phenylene)s (PP), poly(*p*-phenylene vinylene)s (PPV), polyfluorenes (PF) and their derivatives are of special interest because of those excellent electronic and optical properties. Particularly, PF has emerged as an important class of conjugated polymers because of its excellent PL efficiency and thermal stability [1]. However, polymers

Funding for this work was provided by research grant from the Korea Science and Engineering Foundation (KOSEF) through the Optics and Photonics Elite Research Academy (OPERA), an official KOSEF-created engineering research center (ERC) at Inha University, Korea.

Address correspondence to Yong Ku Kwon, Department of Polymer Science and Engineering, Inha University, Incheon 402–751, Korea. E-mail: ykkwon@inha.ac.kr

consisting of phenylene units tend to be aggregated by the π-π interactions, leading to the formation of excimer [4]. To minimize this tendency, several attempts have been made to modify the chemical structures of these aromatic, π-conjugated systems by incorporating various substituents within their main and/or side chains through random, graft and block copolymerization.

Recently, there is growing interest to synthesize block copolymers with conjugated rod segments for photonic and electronic applications. It has been reported that oligothiopene [5], oligo(*p*-phenylene) [6], oligo(phenylene vinylene) [7], three biphenyls connected by vinylene unit [8], oligofluorene [9] are used as a conjugated block and the incorporation of the conjugated rod segment into a heterogeneous polymer chain leads to unique self-assembling structures. It is well known that microphase separation between the blocky segments of coil-coil block copolymers leads to a highly ordered, periodic domain structure of lamellae, columns, and spheres in a nanometer scale [10]. For rod-coil block copolymers, the component block segments are strongly segregated due to the different conformations of rod-like and coil-like molecules [11].

In this study, the self-assembling behavior of an amphiphilic conjugated symmetric triblock copolymer of poly[penta(ethylene glycol) methyl ether methacrylate]-*block*-poly(9,9-didodecylfluorene-2,7-diyl)-*block*-poly[penta(ethylene glycol) methyl ether methacrylate] (denoted PEGMA-*b*-PF-*b*-PEGMA) was investigated. Recently we synthesized a series of conjugated block copolymers of polyfluorene by atom transfer radical polymerization (ATRP). PEGMA was chosen as a hydrophilic end block, due to its excellent solubility in both hydrophobic and hydrophilic media. Due to the dissimilarities in the molecular structure and polarity between the PEGMA and PF blocks, both block segments are expected to be segregated. We also investigated the PL properties and self-assembling behavior of PEGMA-*b*-PF-*b*-PEGMA in selective solvents.

EXPERIMENTAL

PEGMA-*b*-PF-*b*-PEGMA synthesized by atom transfer radical polymerization was used in this study. The detailed synthetic procedure was reported in our publication. The thermogravimetric analysis (TGA) was carried out with a Thermal Analysis Q50, under nitrogen over a temperature range from 25°C to 700°C at a scan rate of 20 °C/min. The PL emission spectra were obtained with a RF-5301PC spectrofluorophotometer (Shimadzu, Japan). Transmission electron microscopy (TEM, Philips CM-200) was used to measure the self-assembled micellar structure of PEGMA-*b*-PF-*b*-PEGMA.

The XRD measurements were conducted on Beamline 4C2 at the Pohang Accelerator laboratory, Pohang, Korea. The X-ray beam was generated from synchrotron radiation using Co Kα radiation ($\lambda = 1.608$ Å) and the storage ring was operated at energy level of 2 GeV. The XRD apparatus employs a point focusing optics with a *Si* double crystal monochromator followed by *Au* coated flat mirror. The sample-to-detector distance was 2000 mm and the data were collected in a range in momentum transfer of $0.003 \leq Q(\text{nm}^{-1}) \leq 1.421$, $Q = (4\pi/\lambda)\sin\theta$. The intensity of the beam was monitored by ionization chamber for the minor decrease of primary beam intensity during measurement. The scattering data profiles were corrected for background and detector efficiency.

RESULTS AND DISCUSSION

Figures 1(a) and (b), show the TGA data of the polyfluorene macroinitiator and PEGMA-*b*-PF-*b*-PEGMA, respectively, measured during heating from room temperature to 700°C at a heating rate of 10°C/min. The polyfluorene macroinitiator was thermally decomposed in the

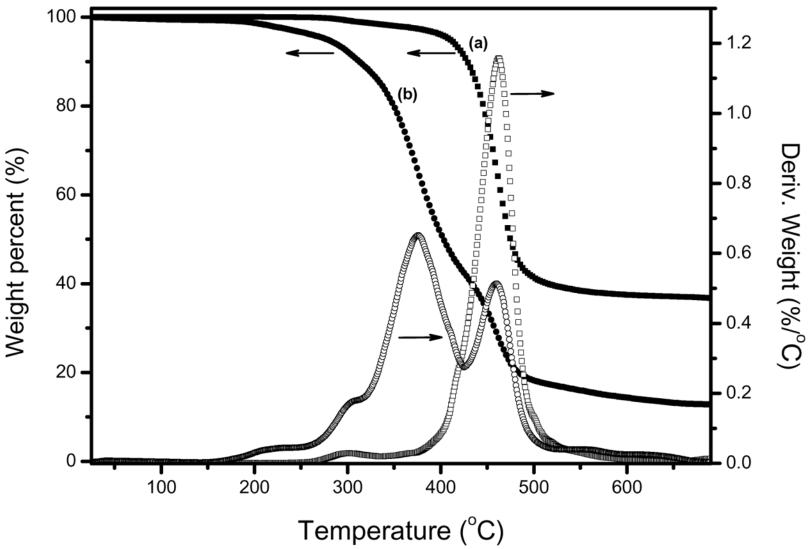

FIGURE 1 TGA data of (a) the polyfluorene macroinitiator and (b) PEGMA-*b*-PF-*b*-PEGMA.

temperature range between 375°C and 500°C, while thermal decomposition of PEGMA-*b*-PF-*b*-PEGMA triblock copolymer was occurred in two steps: the degradation of the end blocks of poly[(ethylene glycol) methyl ether methacrylate] in the temperature range between 200°C and 375°C, followed by the decomposition of the thermally stable aromatic polyfluorene moieties in the temperature range between 375°C and 500°C. It was proposed that the weight loss at ~225°C in the early stage was probably due to the thermal decomposition of 9,9-didodecyl units, attached to the C9 positions of 9,9-didodecylfluorene-2,7-diyl moieties. The relative weight loss during the degradation of the end blocks of PEGMA was approximately 60%, which was almost the same as one measured from GPC.

Figures 2(a) and (b) show the photoluminescence (PL) spectra of PF macroinitiator and PEGMA-*b*-PF-*b*-PEGMA triblock copolymer in THF. In Fig 2(a), we found a PL maximum at $\lambda = 422\,\text{nm}$ and two vibronic bands at $\lambda = 442\,\text{nm}$ and 475 nm. For PEGMA-*b*-PF-*b*-PEGMA, these peaks were slightly shifted to the shorter wavelength and the peak intensities corresponding to vibronic bands were also reduced. The reduction of the intensity was attributed to the suppression of the 0–1 and 0–2 radiation transition by the presence of the PEGMA blocks.

Figure 2(c) through (f) showed the PL spectra of PEGMA-*b*-PF-*b*-PEGMA in a mixed solvent of THF and methanol with a THF: methanol volume ratio of (c) 10:0; (d) 8:2; (e) 6:4 and (f) 5:5. The PL intensities of the peaks at $\lambda = 440\,\text{nm}$ and 475 nm (vibronic band) were slightly increased due to the aggregation of PEGMA-*b*-PF-*b*-PEGMA which enhanced the 0–1 and 0–2 radiation transition by π-π interactions between the neighboring aromatic moieties.

The self-assembling micellar behavior of amphiphilic PEGMA-*b*-PF-*b*-PEGMA was investigated in THF and THF/methanol mixed solvent and confirmed by TEM measurements. The PEGMA block segments are easily dissolved in both THF and THF/methanol mixed solvent and may be located in the corona of PEGMA-*b*-PF-*b*-PEGMA. On the contrary, the PF blocks, composed of aromatic moieties may be associated to form a core in a micelle. Figure 3 shows the TEM images of the micellar aggregates of PEGMA-*b*-PF-*b*-PEGMA prepared in (a) THF and (b) a mixed solvent of THF and methanol. In these images, the diameter of micellar aggregates induced in THF was smaller than one measured from a mixed solvent of THF and methanol. The result indicates that the increased number of PEGMA-*b*-PF-*b*-PEGMA is aggregated in a THF/methanol mixed solvent because of methanol which reduced the solubility of PEGMA-*b*-PF-*b*-PEGMA in the solution. This aggregation behavior also confirmed the increased PL intensities of the peaks at $\lambda = 440\,\text{nm}$ and 475 nm (vibronic band)

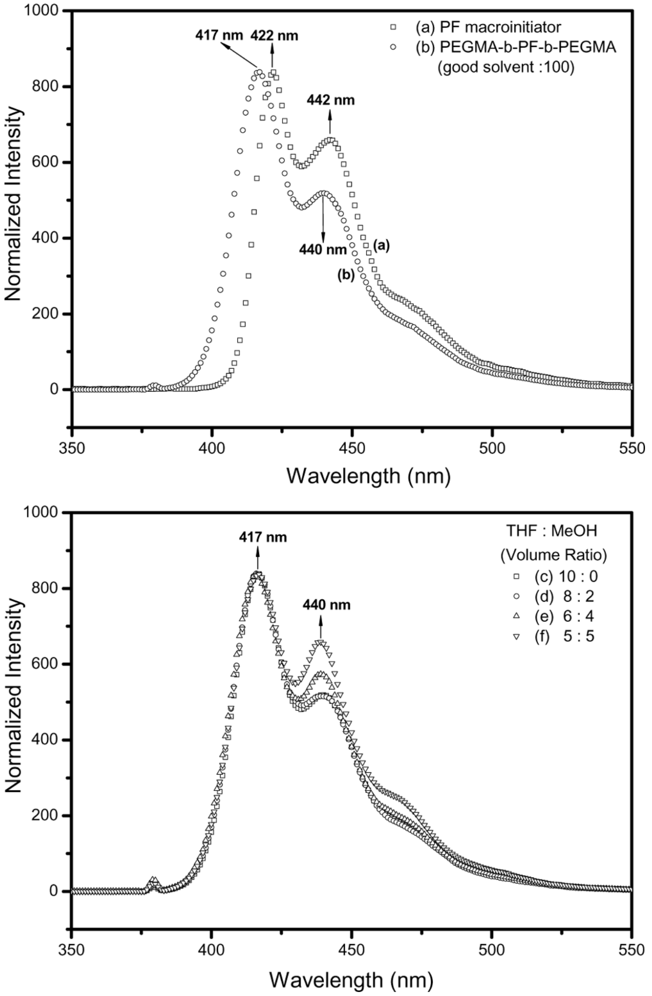

FIGURE 2 PL data of (a) the polyfluorene macroinitiator and (b) PEGMA-*b*-PF-*b*-PEGMA in THF and PL data of PEGMA-*b*-PF-*b*-PEGMA in a mixed solvent of THF and methanol with a THF:methanol volume ratio of (c) 10:0; (d) 8:2; (e) 6:4 and (f) 5:5.

shown in Figure 2, measured during the gradual addition of methanol in PEGMA-*b*-PF-*b*-PEGMA/THF solution.

Figure 4 shows a typical example of SAXS scan data, measured from the as-prepared powder of PEGMA-*b*-PF-*b*-PEGMA at room temperature. In this scan, the broad peak was found at $Q \approx 0.35\,\mathrm{nm}^{-1}$,

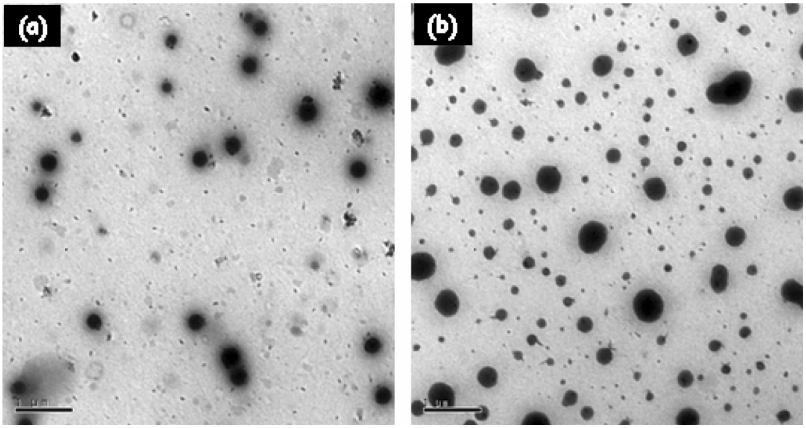

FIGURE 3 TEM micrographs of PEGMA-*b*-PF-*b*-PEGMA in (a) THF and (b) the mixed solvent of THF and methanol with a volume ratio of 5:5 for THF : methanol.

which corresponded to a *d*-spacing of ~18 nm. The broadness of the peak, along with the absence of higher order peaks appeared to be due to the disordered morphology of phase-separated domain structure. The absence of the long-range nanoscopic order of the domain

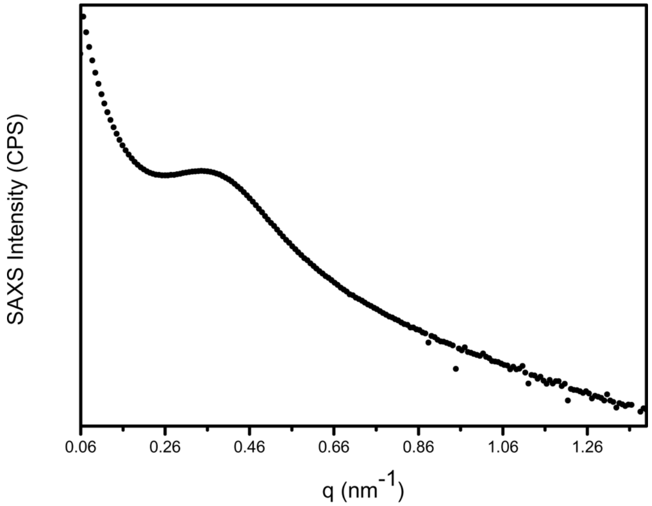

FIGURE 4 SAXS data of the as-received specimen of PEGMA-*b*-PF-*b*-PEGMA at room temperature.

structure was caused by the weak segregation between PEGMA and alkyl-substituted PF blocks in its bulk state.

CONCLUSIONS

The self-assembling micellar structures of amphiphilic, rod-coil triblock copolymer of PEGMA-*b*-PF-*b*-PEGMA has been successfully demonstrated in a good and poor solvent. It formed a highly-associated micellar structure in THF/methanol mixed solvent, whereas a smaller number of PEGMA-*b*-PF-*b*-PEGMA was loosely-associated in THF. The chemical structure of PEGMA-*b*-PF-*b*-PEGMA was confirmed by TGA. We observed that the position of the fluorescence maximum from PEGMA-*b*-PF-*b*-PEGMA was slightly shifted to a shorter wavelength and the intensities of its vibronic bands were slightly reduced, as compared with those measured from the PF macroinitiator. Also, the intensities of these vibronic bands increased with the addition of methanol. The PL intensities of the peaks at $\lambda = 440\,\text{nm}$ and 475 nm (vibronic band) were slightly increased due to the aggregation of PEGMA-*b*-PF-*b*-PEGMA in a THF/methanol mixed solvent which enhanced the 0–1 and 0–2 radiation transition by π-π interactions between the neighboring aromatic moieties.

REFERENCES

[1] Bernius, M. T., Inbasekaran, M., O'Brien, J., & Wu, W. (2000). *Adv. Mater.*, *12*, 1737.
[2] Jenekhe, S. A., Zhang, X., Chen, X. L., Choong , V.-E., Gao, Y., & Hsieh, B. R. (1997). *Chem. Mater.*, *9*, 409.
[3] Scherf, U. & List, E. J. W. (2002). *Adv. Mater.*, *14*, 477.
[4] Klaerner, G., Lee, J.-I., Lee, V. Y., Chan, E., Chen, J.-P., Nelson, A., Markiewicz, D., Siemens, R., Scott, J. C., & Miller, R. D. (1999). *Chem. Mater.*, *11*, 1800.
[5] Henze, O., Fransen, M., Jonkheijm, P., Meijer, E. W., Feast, W. J., & Schenning, A. P. H. J. (2003). *J. Polym. Sci., Polym. Chem.*, *41*, 1737.
[6] Nueesch, F., Si-Ahmed, L., Francois, B., & Zuppiroli, L. (1997). *Adv. Mater.*, *9*, 222.
[7] Urban, V., Wang, H. H., Thiyagarajan, P., Littrell, K. C., Wang, H. B., & Yu, L. (2000). *J. Appl. Crystallogr.*, *33*, 645.
[8] Lee, M., Kim, J.-W., Hwang, I.-W., Kim, Y.-R., Oh, N.-K., & Zin, W.-C. (2001). *Adv. Mater.*, *13*, 1363.
[9] Tsolakis, P. K. & Kallitsis, J. K. (2003). *Chem. Eur. J.*, *9*, 936.
[10] Antonietti, M., Heinz, S., Schmidt, M., & Rosenauer, C. (1994). *Macromolecules*, *27*, 3276.
[11] Radzilowski, L. H. & Stupp, S. I. (1994). *Macromolecules*, *27*, 7747.