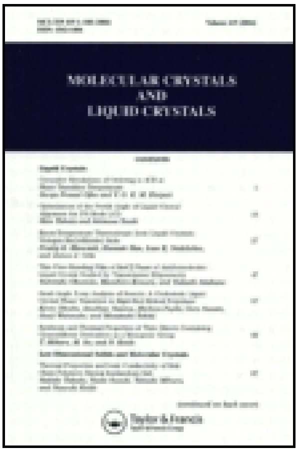


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Selective Dispersion of Porphyrin Metal Complex into Styrene-(Ethylene-co-butylene)-Styrene Triblock Copolymer

Sang-Hee Park [a], Kie-Young Cho [a], Seung Sang Hwang [a] & Kyung-Youl Baek [a]

[a] Center for Materials Architecting, Korea Institute of Science and Technology, Seoul, 136-791, Korea

Version of record first published: 12 Sep 2012.

To cite this article: Sang-Hee Park , Kie-Young Cho , Seung Sang Hwang & Kyung-Youl Baek (2012): Selective Dispersion of Porphyrin Metal Complex into Styrene-(Ethylene-co-butylene)-Styrene Triblock Copolymer, Molecular Crystals and Liquid Crystals, 566:1, 94-99

To link to this article: http://dx.doi.org/10.1080/15421406.2012.701834

Mol. Cryst. Liq. Cryst., Vol. 566: pp. 94–99, 2012
Copyright © Korea Institute of Science and Technology
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.701834

Selective Dispersion of Porphyrin Metal Complex into Styrene-(Ethylene-co-butylene)-Styrene Triblock Copolymer

SANG-HEE PARK, KIE-YOUNG CHO,
SEUNG SANG HWANG, AND KYUNG-YOUL BAEK*

Center for Materials Architecting, Korea Institute of Science and Technology,
Seoul 136-791, Korea

*Porphyrin metal complex covered with polystyrene (PS) arm chains was synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization of styrene from the porphyrin metal (Cu) complex with chain transfer agents (CTA) in the presence of AIBN at 80 °C (PDI < 1.2). Obtained PS covered porphyrin metal complex was then mixed with different molar ratio of styrene-(ethylene-*co*-butylene)-styrene (SEBS) triblock copolymer to give well-defined morphologies such as cylinder and lamella structures, where the porphyrin metal complex was selectively dispersed into the PS domain of the SEBS triblock copolymer. These materials could be expected to show interesting electroactive properties, because of high dielectric constant (k) and elastomeric property from the porphyrin metal complex and the SEBS triblock copolymer elastomer, respectively.*

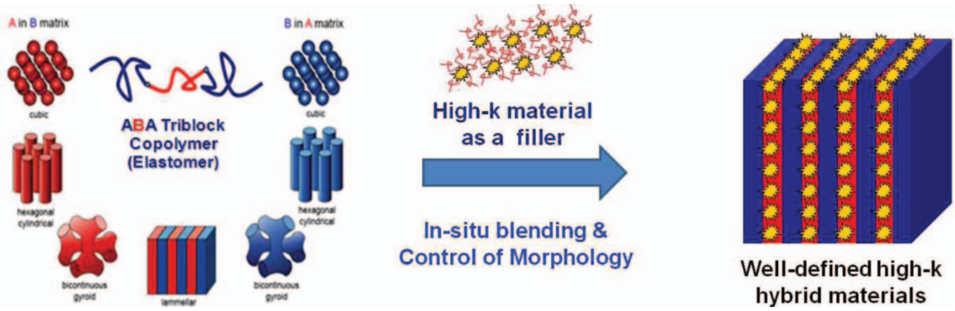
Keywords Porphyrin metal complex; selective dispersion; SEBS; high k

Introduction

Among presently available elctroactive materials, electroactive polymer (EAP) is most promising material for compact actuators, sensors, artificial muscles and micro robotics applications because of its light-weight, inexpensive, mechanical resilience, and good processability, which was not achieved by conventional ceramic electroactive materials[1]. Dielectric elastomer (DE) is one the class of EAPs, which are especially adjustable for artificial muscle because of large deformation and fast response with relatively low electric field. Spontak et al. recently reported an interesting DE material, organogels, derived from SEBS triblock copolymer with mineral oil, which showed unexpected high electroactuation strains (∼300%) at relatively low electric field (<20 kV/mm)[2]. However, the SEBS triblock copolymer consisted of non-polar carbon based polymers, thus more polar and higher dielectric components in the block copolymers were more preferable to maximize the electroactuation property. For this, we synthesized novel polystyrene (PS) covered porphyrin-metal complex as high-k filler by reversible addition-fragmentation chain transfer (RAFT) polymerization of styrene from a porphyrin metal (Cu) complex with chain transfer agents (CTA) and blended with the SEBS triblock copolymer to increase dielectric

---

*Address Correspondence to Kyung-Youl Baek, 39-1 Hawalgok-dong, Seougbuk-gu, Seoul 136-791, Korea. Phone: +82-2-958-5313; Fax: +82-2-958-5309. E-mail: baek@kist.re.kr constant, where the PS covered porphyrin metal complex was selectively dispersed into a micro-phase separated polystyrene domain of the SEBS triblock copolymers (Scheme 1). We also examined the morphologies with different weight fraction ratio of PS covered porphyrin and the SEBS triblock copolymer and their electrical properties such as dielectric constant.



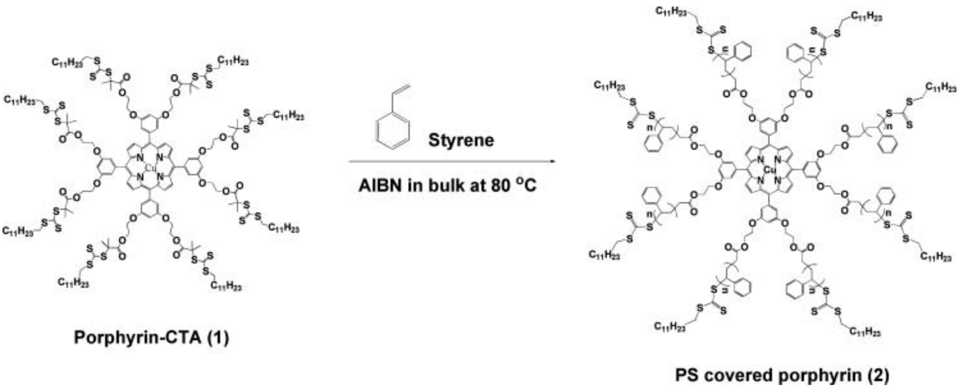
Scheme 1. Selective dispersion of polystyrene covered porphyrin high-k filler into self-assembled polystyrene domain of the SEBS triblock copolymer.

Experimental

Materials

Copper dichloride ($CuCl_2$, Sigma-Aldrich) was used without further purification. S-1-dodecyl-S′-(a,a′-dimethyl-a″-acetic acid)trithiocarbonate as chain transfer agent (CTA) was prepared according to the literature[3]. Styrene (PS, Sigma-Aldrich) was distilled from calcium hydride before use. Azobisisobutyronitrile (AIBN) as initiator was purified by recrystallization from methanol. Dimethylformamide (DMF, Sigma-Aldrich) were distilled from calcium hydride before use. Poly[styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene] (Kraton G1650; $M_w = 110{,}000$; 30 wt.% of polystyrene) was used without further purification.

Synthetic procedure for polystyrene covered porphyrin metal (Cu) complex (2) Scheme 2. Porphyrin metal (Cu) complex with chain transfer agents (Porphyrin-CTA) (**1**) was



Scheme 2. Synthesis of polystyrene covered porphyrin (**2**) by RAFT polymerization of styrene from porphyrin-CTA (**1**) in the presence of AIBN at 80 °C.

Table 1. SEBS composite films with different molar ratio of PS covered porphyrin metal (Cu) complexes.

Sample No.	SEBS (g)	porphyrin metal (Cu) complex (g)	polystyrene (wt.%)
SEBS-neat	0.050	0	30
SEBS_PCu-10	0.045	0.005	35.3
SEBS_PCu-20	0.040	0.010	40.5
SEBS_PCu-30	0.035	0.015	45.8

first prepared by a little modification of the original literature [4]. The porphyrin-CTA (**1**) (0.045 mmol, 174 mg), AIBN (0.0045 mmol, 0.73 mg), degassed styrene (71.4 mmol, 8.18 mL) were added sequentially to a 50-mL flame-dried round-bottom flask equipped with a three-way stopcock under an argon atmosphere. The solution was stirred for 10 minutes at 25°C and was then placed in an oil bath at 80°C. The polymerization was terminated by cooling to –78°C after 150 minutes. The reaction mixture was diluted with THF and then poured into cold methanol. Precipitated purple powder was then filtered and dried overnight under vacuum at room temperature. The number averaged molecular weight (M_n) by size exclusion chromatography (SEC) was 19,600 and polydispersity was 1.08. ^{1}H-NMR ($CDCl_3$), δ: 6.4–7.5 ($-C_6H_5$ of benzene ring), 1.2–2.5 ($-CH-$ and $-CH_2-$ of the styrene backbone).

Preparing SEBS composite films with porphyrin metal (Cu) complex. The composite samples were prepared with different molar ratio of SEBS triblock copolymer and PS covered porphyrin metal (Cu) complex as shown in Table 1. Bulk samples were casted on the petri-dish after dissolving in toluene and then pressed at 105°C for 10 minutes to give 2 × 2 cm with 200 um of thickness. Thin film was casted on the silicon wafer treated with piranha solution by drop casting method after dissolving in toluene. Both samples were additionally annealed at 170°C for 40 h for small angle X-ray scattering (SAXS) and atomic force microscopy (AFM) analyses.

Measurements

The electron absorbance properties of porphyrin-OH and porphyrin metal (Cu) complex were measured by UV/Vis spectrophotometer (UV/Vis, Hewlett Packard, 8453). The number average molecular weight (M_n) and molecular weight distributions (M_w/M_n) of the PS covered porphyrin metal (Cu) complex were measured by gel permission chromatograph (GPC, Jasco) equipped with a Ri-2031 plus refractive index detector and UV-2075 plus ultraviolet detector of 254 nm wavelength using THF as the mobile phase and a flow rate of 1 mL/min. ^{1}H-NMR spectrum was recorded in $CDCl_3$ at 25°C on a varian 300 (^{1}H : 300 MHz) spectrometer. The structure properties of bulk composite films were characterized by small angle X-ray scattering (SAXS) analysis in 4C1 beam-line at Pohang Accelerator Laboratory. The surface morphologies of thin composite films were characterized by an atomic force microscopy (AFM, Veeco, di-NanoScope 5. The dielectric constant (k) of the bulk composite films was measured by HP1492A Impedance analyzer with Agilent dielectric test fixture 16451B at 1 kHz at room temperature.

Result And Discussion

Series of the blending composites with PS covered porphyrin metal complexes and SEBS triblock copolymers were then characterized their morphologies both in bulk and in thin film states by SAXS and AFM analyses, respectively. All samples were annealed at 170°C for 40 h to generate well-defined phase separation by self-assembly of the block copolymers. Figure 1 shows SAXS profiles of the SEBS triblock copolymer and the blending composites with different molar ratios of the PS covered porphyrin metal complexes. Long ranged scattering patterns of the SEBS triblock copolymers (q*, 2q*, 3q*, and 4q*) indicated that well-defined lamella structures were formed in bulk states with 32 nm of the domain size ($d = 2\pi/q^*$)[5]. This domain size was gradually increased as the amount of the PS covered porphyrin increased in the blending composites with the SEBS triblock copolymer (Fig. 1B), because the PS of the porphyrin was selectively mixed into the PS domain of the block copolymer, which indicated that porphyrin, high-k filler, was selectively dispersed into the well-defined lamella structured the PS domain. However, this lamella structure was changed to more complicated morphology, perhaps gyroid structure, when the weight fraction of the PS covered porphyrin metal complex was over 20%. AFM images of the thin films with above samples showed only the SEBS triblock copolymers and the blending composites with 10 wt.% of the PS covered porphyrin metal complex induced micro-phase separations but no specific images were not achieved from the other composites (Fig. 2). UV-vis spectroscopy of the SEBS blending composites showed the absorption peaks derived from the porphyrin metal complex at 300 nm, 410 nm, 530 nm, 610 nm, and 645 nm, which was not detected in the SEBS triblock copolymer. Figure 3 shows dielectric constant (k) of the SEBS triblock copolymer and the blending composites with different molar ratios of the PS covered porphyrin metal complexes. As the amount of the PS covered porphyrin metal complex increased, the dielectric constant linearly increased. In comparison to neat SEBS triblock copolymer (k = 2.38), the dielectric constant of the blending sample with 30 wt.% of the PS covered porphyrin metal complex was 3.09.

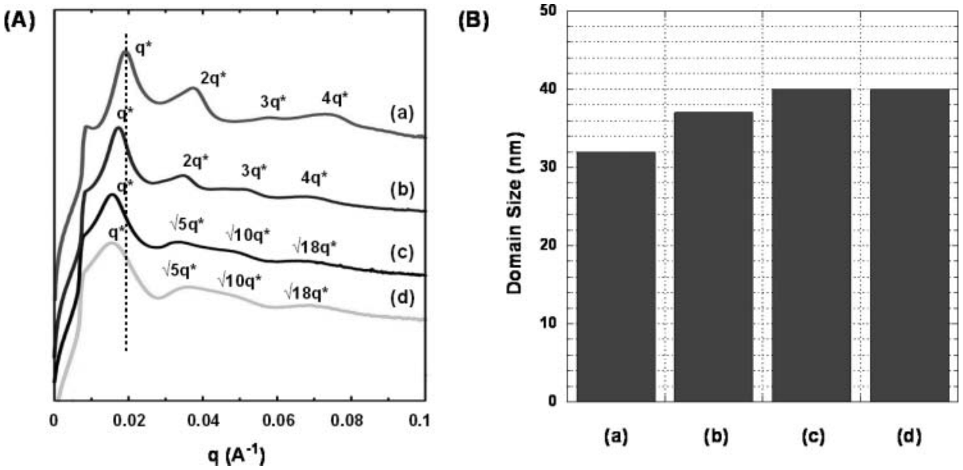


Figure 1. SAXS profile (A) and domain size (B) of the SEBS triblock copolymer (a) and the blending composites with the PS covered porphyrin metal complex: (b) 10%; (c) 20%; (c) 30%.

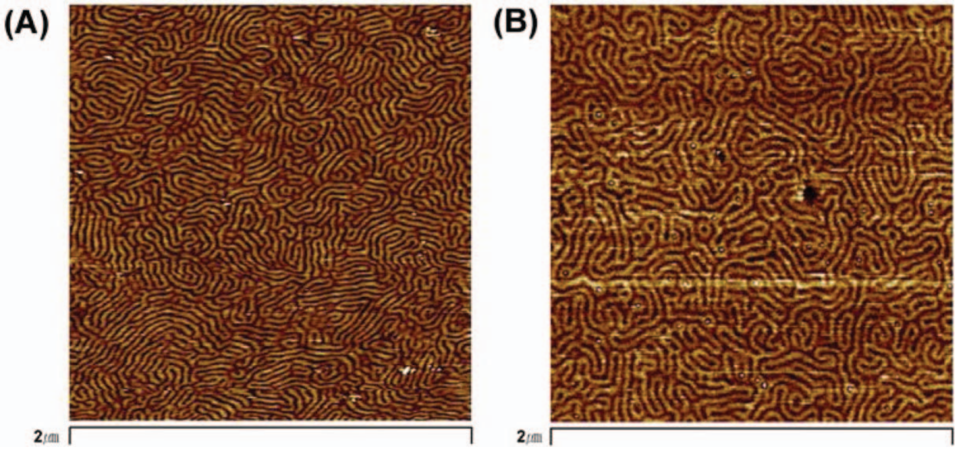


Figure 2. AFM images of the SEBS triblock copolymer (A) and the blending composites with 10 wt.% of the PS covered porphyrin metal complex.

These result indicated that the PS covered porphyrin metal complex was worked as high-k filler. These obtained high-k SEBS blending composites with well-defined morphologies are expected to show better actuation performance in comparison to conventional neat SEBS triblock copolymers because deformation (strain) is strongly depended on dielectric constant (k) [$S_z = k\varepsilon_0(V/Z)2/Y$, where k is dielectric constant, ε_0 is permittivity at free space, V is voltage, Z is thickness, and Y is modulus].

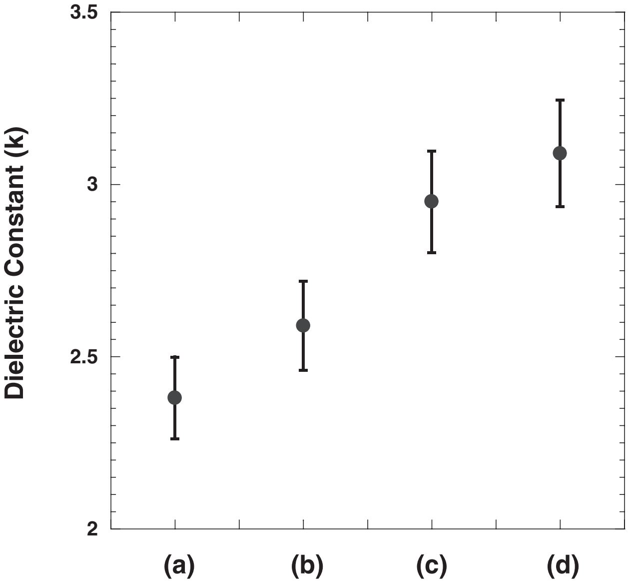


Figure 3. Dielectric constant (k) of the SEBS triblock copolymer (a) and the blending composites with the PS covered porphyrin metal complex: (b) 10%; (c) 20%; (d) 30%.

Conclusions

Polystyrene covered porphyrin metal (Cu) complex was selectively introduced into well-defined polystyrene domain of the SEBS triblock copolymers both in bulk and in thin film states. These SEBS blending composites possessed relatively high dielectric constant (k) in comparison to neat SEBS triblock copolymer, which will give better electroactive performance.

Acknowledgements

This work was financially supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea and partially by a grant from Nanohybrids Research Center of Korea Institute of Science and Technology (KIST).

References

[1] (a) Zhang, Q. M., Bharti V., & Zhao, X. (1998). *Science, 280*, 2101. (b) Zhang, Q. M., Li, H., Poh, M., Xia, F., Cheng, Z., Xu, H., & Huang, C. (2002). *Nature, 419*, 284. (c) Michael, W., & Edoardo, M. (2005). *Sens. Actuators A, 120*, 184. (d) Brochu, P., & Pei, Q. (2010). *Macromol. Rapid Commun.*, **31**, 10.

[2] (a) Shankar, R., Ghosh, T. K., & Spontak, R. J. (2007). *Adv. Mater. 19*, 2218. (b) Shankar, R., Krishnan, A. K., Ghosh, T. K., & Spontak, R. J. (2008). *Macromolecules*, *41*, 6100.

[3] Wakamatsu, J., Nishimura T., & Hattori A. (2004). *Meat Science 67*, 95.

[4] (a) Dichtel, W. R., Baek, K.-Y., Frechet, J. M. J., Rietveld, I. B., & Vinogradov, S. A. (2006). *J. Polym. Sci. Part A: Polym. Chem.*, *44*, 4939. (b) Baek, K.-Y., Lee, S. H., & Hwang, S. S. (2011). *Macromolecular Research 19*, 461.

[5] Bates, F. S., & Fredrickson, G. H. (1990). *Ann. Rev. Phy. Chem.*, *41*, 525.