An Observation on the Microphase Separation of Poly(methyl methacrylate)-block-Polystyrene Copolymer

Jie DENG, Xin Song LI*, Zheng Mei WANG, Gang SHAO, Ju Zheng LIU

Department of Chemical Engineering, Southeast University, Nanjing 210096

Abstract: The phase behavior of a well-defined poly(methyl methacrylate)-b-polystyrene block copolymer was studied by transmission electron microscope. The results show that a microphase transition may have occurred in the copolymer film. A kind of lamellae and an ordered bicontinuous double-diamond morphology are observed clearly. The lamellar morphology reveals a larger period of about 400 nm.

Keywords: Block copolymer, phase separation, atom transfer radical polymerization, TEM.

The well-ordered structures of block copolymer formed by self-assemble have attracted much attention as potentially interesting optical materials, especially as photonic crystals[1,2]. In order to achieve desirable photonic crystal properties, the morphologies of block copolymers should be controlled, including obtaining the correct size of domains for the optical frequencies of interest and attainment of long-range domain order and appropriate orientation. We know that the morphology of one block copolymer is controlled not only by its components but also by its synthesis and processing history[3]. Anionic copolymerization is often used to prepare block copolymer. The copolymer usually shows the regular morphology with the period of about 10 nm[4]. Recently, Thomas *et al* studied the regular morphology of block copolymer-homopolymer blends with the period of about 160 nm[2]. The pioneering work shows the potential use of the blends as photonic crystals. In order to obtain the proper size of domains for the optical frequencies of interest and attainment of long-range domain order, it is very important to study new polymerization method and control the morphology of block copolymers.

Atom transfer radical polymerization (ATRP), discovered in 1995 by Wang[5] and Sawamoto[6] independently, is based on a redox reaction between transition metals (*eg* Cu^+/Cu^{2+}), providing living radical polymerization of styrene, (meth)acrylates, and other radically polymerizable monomers. The end-up group is C-X (X represents halogen)[7], and adding new monomers block copolymers can be achieved in the presence of catalysts. Much progress in the research of ATRP have been achieved in the past several years. But, the morphology of block copolymer synthesized by ATRP has not attracted attention.

In this study, we describe the synthesis of poly(methyl methacrylate)-block-polystyrene copolymer (PMMA-b-PSt) by ATRP. Especially, we report the special morphology of PMMA-b-PSt block copolymer observed by transmission electron microscope.

Experimental

Poly(methyl methacrylate) (PMMA) was synthesized by ATRP. CuBr/2,2'-bipyridine (bpy) was used as catalyst, ethyl 2-bromoacetate (EBA) used as initiator. The mol ratio of CuBr : EBA : bpy is 1:1:3. The polymerization was carried out at 100°C. PMMA was obtained by precipitation in methanol and purified by dissolution and precipitation three times. Then it was dried under vacuum overnight. PMMA was used as macroinitiator in the preparation of PMMA-b-PSt. The molecular weight distribution was analyzed using a Waters 244 SEC. The number average molecular weight (M_n) of PMMA is 4.42×10^4, and the polydispersity index (PDI) is 1.40.

PMMA-b-PSt was prepared by ATRP according to the procedure for synthesizing PMMA except that equal mol of the macroinitiator (PMMA) was used in place of EBA and styrene was used as monomer instead of MMA. The ratio of CuBr:PMMA:Bpy is 1:1:3. The polymerization was conducted at 130°C. PMMA-b-PSt was obtained by similar treatments. The GPC curve of PMMA-b-PSt is a single peak, which shows the M_n of 4.76×10^4 and the PDI of 1.49. The IR spectrum of PMMA-b-PSt collected with Nicolet 5DX shows C-H out-of-plane bending vibrations of aromatic ring at 700 cm^{-1} and 760 cm^{-1}, together with stretching vibrations of aromatic ring backbone at 1460 cm^{-1}, 1500 cm^{-1} and 1600 cm^{-1}. The weight fraction of the PMMA block is 28%, which is calculated by ^{1}H-NMR collected with a Bruker AM 500.

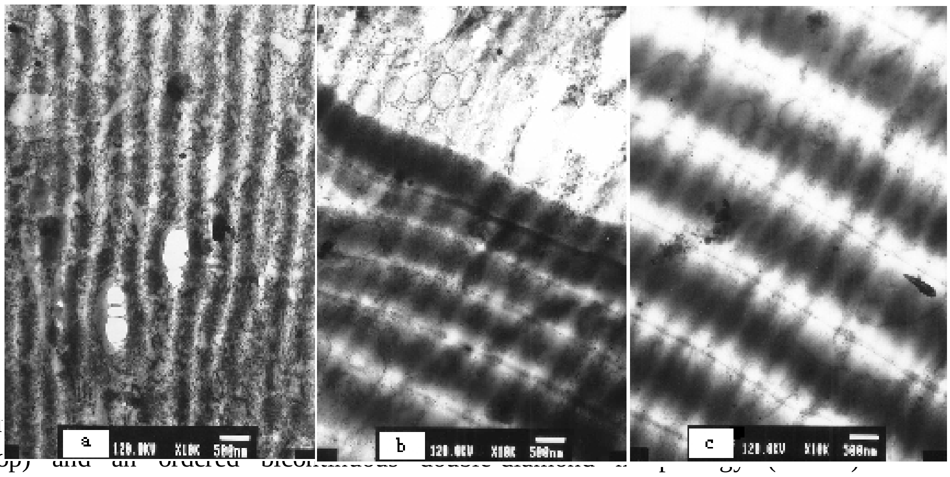
Transmission electron microscope (TEM) measurement was carried out by a Hitachi H-500. For the observation of the morphology of the block copolymer, an ultrathin section of the copolymer film was prepared as follows. The film was dipped in a 1wt % aqueous solution of ruthenium tetraoxide (RuO_4) as the fixing and staining reagent for 20 min. After being dried, the film was embedded in an epoxy resin and cut into ultrathin sections (700-1000 Å thick) by an ultramicrotome with a diamond knife.

Results and Discussion

The well-defined PMMA-b-PSt diblock copolymer with the M_n of 4.76×10^4 and the PDI of 1.49 has been synthesized by atom transfer radical polymerization (ATRP). The weight fraction of the PMMA block in the PMMA-b-PSt copolymer is 28%. In order to have an insight into the phase behavior of the block copolymer synthesized by ATRP, we observed the morphology of the copolymer carefully with TEM.

Figure 1 shows the transmission electron micrographs of an ultrathin section of a PMMA-b-PSt film cast from THF solution. Distinct microphase separation can be observed in the micrographs because the two components of the block copolymer are not compatable[8]. In **Figure 1a**, a kind of lamellar morphology is observed. The lamellae is reasonably well ordered and has a dominant in-plane orientation due to the influence of the substrate and air interfaces on the lamellar organization during evaporation.

Figure 1 TEM of an ultrathin section of poly(methyl methacrylate)-block-polystyrene copolymer film observed at different positions (a, b and c), the scale bar is 500 nm



ru

(top) and an ordered bicontinuous double-diamond morphology ( ) microphase transition may have occurred in the PMMA-b-PSt film. In **Figure 1c**, the ordered bicontinuous double-diamond morphology is shown clearly.

The TEM data presented here indicate a regular symmetric lamellar morphology with a period of about 400 nm. This value is much larger than that of the block copolymer synthesized by anionic copolymerization observed by other groups[4]. And It is also larger than that of the lamellar morphology from self-assembled block copolymer-homopolymer blend[2]. The existence of the larger layer spacing of the block copolymer may be attributed to the somewhat larger polydispersity (PDI = 1.49). The molecules with lower molecular weights might thus swell the microdomains. We are astonished to find the ordered bicontinuous double-diamond morphology (OBDD) with one period of about 1000 nm and the other period of about 400 nm in **Figure 1c**. It is very interesting that the OBDD shows one period of 400 nm which equals to that of the lamellar morphology in **Figure 1a**. Another period of the OBDD morphology is about 1000 nm. We noted that the larger period of OBDD morphology decreases as the lamellar region is approached. But the period of the lamellar morphology remains to be 400 nm. Therefore, the morphology of block copolymer prepared by ATRP may be controlled, including obtaining the correct size of domains and attainment of long-range domain order and appropriate orientation.

Conclusions

Atom transfer radical polymerization has produced well structured PMMA-b-PSt diblock copolymer. The block copolymer with a weight fraction of the PMMA block of 28% shows an ordered lamellar morphology with a constant period of about 400 nm, which is of the order of UV-Vis wavelength. This special morphology may have application in the optical field such as photonic crystals.

Acknowledgments

Thanks are due to Dr Chun Xiang XU for helpful discussions (Department of Electronic Engineering, Southeast University). This work has been supported by the Talent Foundation of Southeast University.

References

1. S. A. Jenekhe, X. L. Chen, *Science,* **1999**, *283*, 373.
2. A. Urabs, Y. Fink, E. L. Thomas, *Macromolecules,* **1999**, *32*, 4748.
3. Z. R. Chen, J. A. Kornfield, S. D. Smith, J. T. Grothaus, M. M. Satkowski, *Science,* **1997**, *277*, 1248.
4. F. S. Bates, G. H. Fredrickson, *Annu. Rev. Phys. Chem.,* **1990**, *41*, 525.
5. J. S. Wang, K. Matyjaszewski, *J. Am.. Chem. Soc.,* **1995**, *117*, 5614.
6. M. Kato, M. Kamigatio, M. Sawamoto, T. Higashimura, *Macromolecules,* **1995**, *28*, 1721.
7. J. S. Wang, K. Matyjaszewksi, *Macromolecules,* **1995**, *28*, 7901.
8. A. E. Woodward, *Atlas of Polymer Morphology*, Hanser Publishers, Munich, **1988**, 189.
9. R. Xie, B. X. Yang, B. Z. Jiang, *Macromolecules,* **1993**, *26*, 7097.

Received 27 October, 2000