

Effect of Homopolymer Molecular Weight on Order-Order Transition in Block Copolymer and Homopolymer Blends

Sang-In Lee¹, Wang-Cheol Zin^{1,*}, and Jong-Hyun Ahn^{2,*}

¹Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang, 790-784, Korea

²School of Advanced Materials Science and Engineering, SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon, 440-746, Korea

The order-order transition temperature (T_{OOT}) in blends of poly(styrene-*b*-isoprene-*b*-styrene) (S-I-S) triblock copolymer and polyisoprene (PI) homopolymer was investigated by using synchrotron small-angle X-ray scattering (SAXS). Pure triblock copolymer undergoes an order-order transition (OOT) from hexagonally ordered cylinder (HEX) to body centered cubic (BCC) phases. In order to investigate the effect of the molecular weight of the added homopolymer on T_{OOT} of the triblock copolymer, various low-molecular-weight PI homopolymers were studied. The results revealed that T_{OOT} was affected by the PI molecular weight. T_{OOT} was reduced for blends having low-molecular-weight PI.

Keywords: Block Copolymer, Order-Order Transition, Small-Angle X-ray Scattering.

1. INTRODUCTION

Block copolymers self-assemble into a variety of ordered nanostructures due to unfavorable interaction between the two different blocks.¹⁻² By varying the composition of the block copolymers and the temperature, these nanostructures can be controlled and various order-order transitions (OOT) and order-disorder transitions (ODT) can occur. During the past decade, scattering and rheological methods have been used to investigate OOT between different kinds of microdomain structures of a block copolymer.³⁻¹⁷ Sakamoto et al. and Kim et al. reported OOT from hexagonally ordered cylinders (HEX) to body centered cubic (BCC) phases in poly(styrene-*b*-isoprene-*b*-styrene) (S-I-S) copolymer using small-angle X-ray scattering (SAXS) and rheological measurements.³⁻¹⁰

When a homopolymer is just soluble in selective block component, the nanostructure and OOT of the blends are changed.¹³⁻¹⁵ However, previous investigations have mainly focused on the effect of the volume fraction of the homopolymer on the OOT of blends. Few studies have dealt with the effect of the molecular weight of the added homopolymer on OOT at a fixed composition.²¹ In this study, we examined the effects of homopolymer molecular

weight on OOT in blends of S-I-S triblock copolymer and polyisoprene (PI) homopolymer.

2. EXPERIMENTAL DETAILS

2.1. Materials

The samples were mixtures of S-I-S triblock copolymer (Vector 4111, Dexco Polymers Co. $M_w = 1.4 \times 10^5$ with styrene wt% = 18.3 and styrene vol% = 16.4) and with a small amount of added PI (Polyscience INC). The characteristics of the S-I-S triblock copolymer used are listed in Table I. Blend samples with various Φ_{PS} from 0.158 to 0.164 were prepared by dissolving a predetermined amount of each copolymer in toluene in the presence of an antioxidant (Irganox 1010, Ciba-Geigy Group) and then slowly evaporating the solvent at room temperature. After completely removing the last trace of the solvent, the samples were further annealed at 140 °C for 5 days. Detailed sample information is listed in Table II. The blend samples were designated by a sample label followed by their weight percentages, as in “S-I-S/PIIK (98/2).”

2.2. SAXS Experiment

Synchrotron SAXS measurement was performed at the 4C1 X-ray beam line of the Pohang Accelerator

*Authors to whom correspondence should be addressed.

Table I. Polymer characteristics.

Sample code	M_w	M_w/M_n	Composition (wt%) ^c		
			Styrene	Unsaturation	
				cis 1, 4	trans 1, 4
S-I-S ^a	1.43×10^5	1.11 ^b	18.3		
PI1K	1000	1.2		62.9	30.7
PI30K	30000	1.08		65.3	28.2

^aPoly(styrene-*b*-isoprene-*b*-styrene). ^bBy GPC calibrated with PS standard. ^cBy ¹H-NMR.

Table II. Blend compositions.

Composition (wt)		Predicted composition	
Vector 4111	PI (1 K, 30 K)	PS (total wt. frac.)	PS (total vol. frac.)
0.99	0.01	0.181	0.159
0.98	0.02	0.179	0.158

Laboratory (PAL), Korea (X-ray wavelength was 1.608 Å). A two-dimensional CCD detector (Princeton Applied Research) was located at the distance of 2.1 m from the sample. A beam path was maintained under vacuum to reduce air scattering, and the measured intensity was corrected for background scattering and detector noise. Each sample was heated from room temperature to a temperature far above the OOT temperature (T_{OOT}) at a heating rate of 1 °C/min. During the heating run, each sample was maintained for 20 min at a specific temperature to obtain thermal equilibrium.

3. RESULTS AND DISCUSSION

Figure 1 shows the SAXS profiles of a representative blend, S-I-S/PI1K (98/2) (with a total volume fraction of styrene in the blends, Φ_{PS} , of 0.158) at different temperatures during the heating process. The profiles were plotted in semi logarithmic scale against the magnitude of the scattering vector, q , defined by $q = 4\pi\lambda^{-1} \sin(\theta/2)$, where λ and θ are the wavelength of the incident X-ray and the scattering angle, respectively. At room temperature, the blend had an HEX structure with a peak position ratio of $1:\sqrt{3}:\sqrt{4}$ against the first-order scattering peak. At 170 °C, the scattering profile showed a new peak at the peak position ratio of $\sqrt{2}$, indicated by the arrow, which suggested the initial transformation from HEX to BCC phase. After subsequent heating to 176 °C the SAXS pattern clearly exhibited three peaks at the $1:\sqrt{2}:\sqrt{3}$ position, indicating the complete transformation from HEX to BCC phases.

When a small amount of PI is added to the S-I-S triblock copolymer, it is difficult to define the exact position of T_{OOT} using the SAXS profile. To increase the sensitivity of the SAXS data near T_{OOT} , a plot of the reciprocal first-order scattering maximum ($1/I_m$) as a function of the reciprocal absolute temperature ($1/T$) is useful.²² Figure 2

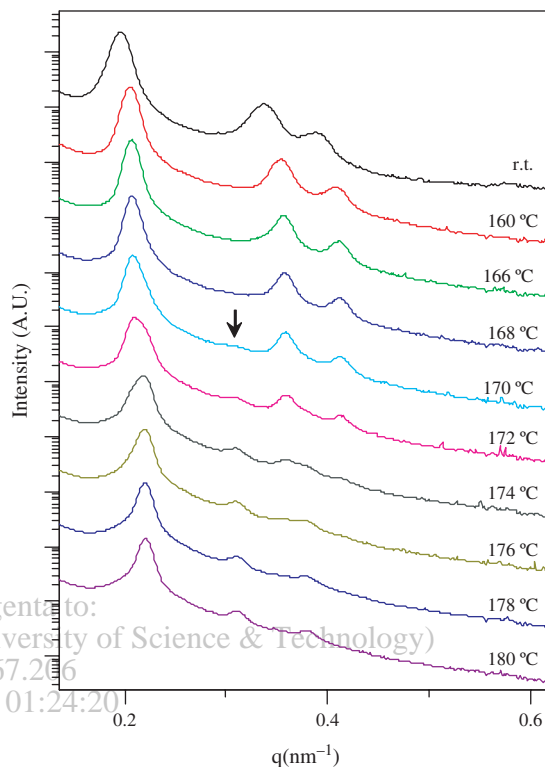


Fig. 1. Temperature dependence of SAXS profiles for S-I-S/PI1K (98/2) blends at various temperatures during heating.

presents the plots of $1/I_m$ versus $1/T$ for the blends and the pure S-I-S triblock copolymer. In this figure, the value of T_{OOT} can be defined by the maximum position of the quadratic curve in the $1/I_m$ versus $1/T$ plots. T_{OOT} of S-I-S/PI1K (99/1) was 177.4 °C, which was 4.6 °C lower than that of the pure S-I-S triblock copolymer. T_{OOT} of S-I-S/PI1K (98/2) was 174.5 °C which was 2.9 °C lower than those of the blend containing with 1 wt% PI. These values were in good agreement with those determined from the SAXS profile. On the other hand, T_{OOT} values of S-I-S/PI30K (99/1) and S-I-S/PI30K (99/2) were 180 °C and 177 °C, respectively, and were higher than those of the blends containing with PI1K.

Figure 3 shows the interdomain distances, $D (= 2\pi/q^*)$, against the reciprocal absolute temperature ($1/T$) for mixtures of S-I-S/PI between 150 °C and 220 °C. D exhibited a discontinuous change at the OOT region as the temperature increases, which is consistent with T_{OOT} determined from the change of $1/I_m$ as a function of $1/T$, as shown in Figure 2.²³

The change of T_{OOT} was related to the molecular weight of the added PI. The D values of S-I-S/PI blends were slightly shifted to lower values compared with those of pure S-I-S triblock copolymer. Winey et al. reported a decrease in the microdomain spacing of block copolymers with homopolymer addition.²⁴ In the blend system of poly(styrene-*b*-isoprene) (S-I)/PS, they found that low-molecular-weight PS (about 2 K) decreased D of the

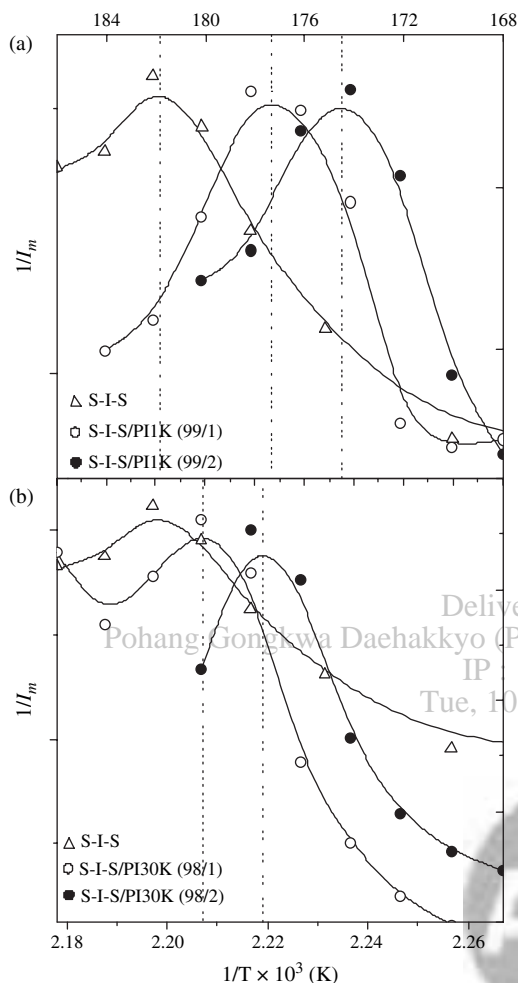


Fig. 2. Plots of the reciprocal of the first-order peak intensity ($1/I_m$) versus the reciprocal of the absolute temperature ($1/T$) for both S-I-S/PI30K and S-I-S/PI1K, which were prepared from SAXS experiments conducted during heating.

microdomain structure of S-I, which was attributed to the uniform localization of the low-molecular-weight PS homopolymer between the junction points at the PS-PI interfaces. Thus, the addition of low-molecular-weight PI homopolymer induces a slight lateral contraction of the PI domain of the S-I-S triblock copolymer.

Figure 4 shows a phase diagram of the S-I-S/PI blends with different molecular weight of PI. The PI weight fraction of the blend was converted to the overall isoprene volume fraction Φ_{PI} . When the molecular weight of PI is sufficiently low compared with that of S-I-S, it tends to dissolve completely into the PI microdomain of S-I-S. In the phase diagram, T_{OOT} of the block copolymer decreased with increasing PI volume fraction and decreasing molecular weight. The addition of PI to S-I-S induced a more asymmetric composition in the block copolymer, thereby decreasing OOT. The addition of high-molecular-weight homopolymer increased the T_{OOT} of the blends, which was attributed to the variation of

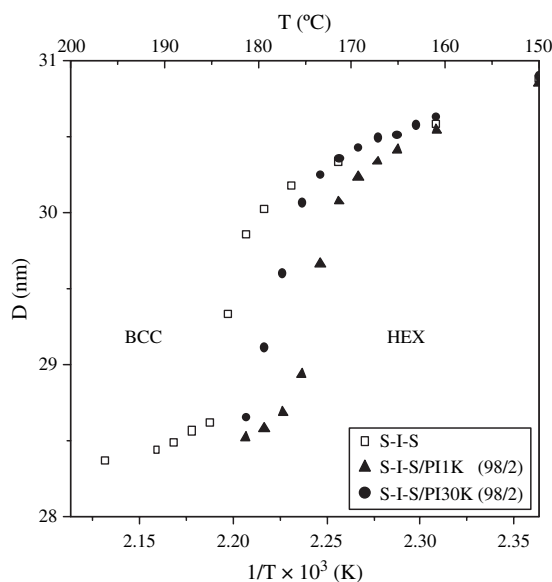


Fig. 3. Temperature dependence of the interdomain distance (D) for S-I-S/PI blends at temperatures ranging from 150 to 220 °C. D was determined from the scattering vector q^* at the first-order scattering maximum.

product χN , the quantity that controls the degree of segregation between two blocks in the S-I-S/PI blend. The high-molecular-weight homopolymer tends to form a well-defined microstructure by localization at the center of the corresponding domain.²⁵ Thus, the addition of high-molecular-weight PI increased the degree of segregation, whereas the addition of low-molecular-weight PI to the block copolymer tended to disorder the nanostructure due to the tendency of small PI to distribute uniformly throughout the block copolymer melt. This was confirmed by the different tendency of D depending on the molecular weight of the added PI, as shown in Figure 3. Moreover, the addition of low-molecular-weight PI may have exerted a reduction effect on the mean molecular weight of the block

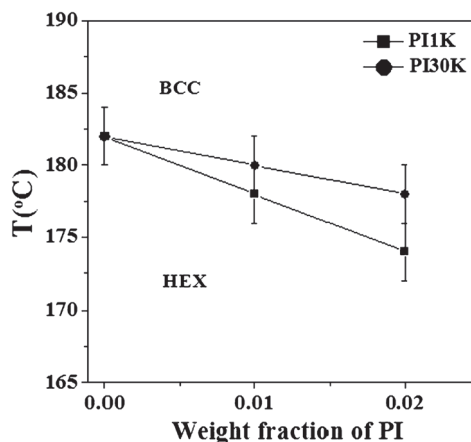


Fig. 4. Phase diagrams of S-I-S/PI blends with different PI molecular weights.

copolymer. Thus, the addition of low-molecular-weight PI decreased the segregation temperature and, therefore, T_{OOT} .

4. CONCLUSIONS

The order-order phase transition induced by homopolymers was investigated in the S-I-S/PI blends. For the binary mixtures with low molecular weight of PI (≤ 2 wt%), the morphological transitions of a block copolymer depended on the molecular weight of the added homopolymer. The low-molecular-weight PI tended to decrease T_{OOT} of the block copolymer. This effect of homopolymer addition on T_{OOT} was explained by the variation of product χN , which is the quantity that controls the degree of segregation between the two blocks of the S-I-S/PI blends.

Acknowledgments: This paper was supported by Samsung Research Fund from Sungkyunkwan University, 2008 and the Korea Research Foundation Grant (KRF-2008-314-000128). The assistance of the Pohang Accelerator Laboratory in performing in SAXS measurements is gratefully acknowledged.

References and Notes

1. L. Leibler, *Macromolecules* 13, 1602 (1980).
2. L. Song and Y. M. Lam, *J. Nanosci. Nanotechnol.* 6, 3904 (2006).
3. N. Sakamoto, T. Hashimoto, C. D. Han, D. Kim, and N. Y. Vaidya, *Macromolecules* 30, 1621 (1997).
4. N. Sakamoto and T. Hashimoto, *Macromolecules* 31, 8493 (1998).
5. J. K. Kim, H. H. Lee, M. Ree, K. B. Lee, and Y. Park, *Macromol. Chem. Phys.* 199, 641 (1998).
6. M. D. Whitmore and J. Noolandi, *Macromolecules* 18, 2486 (1985).
7. T. Hashimoto, H. Tanaka, and H. Hasegawa, *Macromolecules* 23, 4378 (1990).
8. H. Tanaka, H. Hasegawa, and T. Hashimoto, *Macromolecules* 24, 240 (1991).
9. H. Tanaka and T. Hashimoto, *Macromolecules* 24, 5713 (1991).
10. E. Kim, H. Ahn, D. Y. Ryu, W. Joo, J. K. Kim, J. Jung, and T. Chang, *Macromolecules* 41, 9875 (2008).
11. H. H. Lee, W. Y. Jeong, J. K. Kim, K. Y. Ihn, J. A. Kornfield, Z. G. Wang, and S. Qi, *Macromolecules* 35, 785 (2002).
12. K. Kimishima, T. Koga, and T. Hashimoto, *Macromolecules* 33, 968 (2000).
13. M. W. Matsen and F. S. Bates, *Macromolecules* 29, 7641 (1996).
14. S. H. Lee and K. Char, *Macromolecules* 33, 7072 (2000).
15. N. Y. Vaidya, C. D. Han, D. Kim, N. Sakamoto, and T. Hashimoto, *Macromolecules* 34, 222 (2001).
16. W. K. Lee, H. Lim, and E. Y. Kim, *J. Nanosci. Nanotechnol.* 8, 4771 (2008).
17. K. I. Winey, E. L. Thomas, and L. J. Fetters, *Macromolecules* 25, 2045 (1992).
18. J. Bodycomb, D. Yamaguchi, and T. Hashimoto, *Macromolecules* 33, 5187 (2000).
19. L. Yang, S. P. Gido, J. W. Mays, S. Pispas, and N. Hadjichristidis, *Macromolecules* 34, 4235 (2001).
20. U. Jeong, D. Y. Ryu, D. H. Kho, D. H. Lee, J. K. Kim, and T. P. Russell, *Macromolecules* 36, 3626 (2003).
21. J. H. Ahn and W. C. Zin, *Macromolecules* 27, 10238 (2002).
22. J. Bodycomb, D. Yamaguchi, and T. Hashimoto, *Polym. J.* 28, 821 (1996).
23. M. W. Matsen and F. S. Bates, *J. Polym. Sci., Part B: Polym. Phys. Ed.* 35, 945 (1997).
24. K. I. Winey, E. L. Thomas, and L. J. Fetters, *Macromolecules* 24, 6182 (1991).
25. M. W. Matsen and F. S. Bates, *Macromolecules* 29, 1091 (1996).

Received: 10 October 2008. Accepted: 16 March 2009.

AMERICAN
SCIENTIFIC
PUBLISHERS