Morphology of Polystyrene-*block*-poly(ethylene-*alt*-propylene) Diblock Copolymers in the Strong-Segregation Limit

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Introduction

Morphological behavior in block copolymers has not yet been thoroughly surveyed, and fascinating experimental observations remain to be discovered. One of them is the thermoreversible morphological transition.[1–4] We have reported thermoreversible sphere–cylinder transitions in polystyrene-*block*-polyisoprene diblock copolymers in bulk[1,2] and in solution.[3] In the course of the study of a morphological transition upon alteration of the primary chemical structures of the segment,[5] we obtained a very curious result on the morphology in the strong-segregation limit (SSL), a cylindrical morphology for polystyrene-*block*-poly(ethylene-*alt*-propylene) (SEP) having the volume fraction of polystyrene (PS), f_{PS}, 0.128. The cylindrical morphology was a very surprising result for such a small volume fraction, because a spherical morphology was expected and actually found for this composition in the case of polystyrene-*block*-polyisoprene diblock copolymers (SI).[6] We discuss the reason from the following two standpoints. The first to be considered is the strong segregation between styrene and ethylene-propylene segments. The results of the SSL theories[7–9] and those of recent theories for all degrees of segregation[10,11] were compared with our experimental results. Except for the result of Semenov,[8] those theoretical results did not agree with our results. The second to be considered is chain asymmetry associated with differences in segment volume and in segment length between styrene and ethylene–propylene segments. It was found that the theoretical result of Vavasour and Whitmore,[12] as obtained by taking into account the effects of chain asymmetry, supported our experimental results.

Experimental Section

The SEP sample coded as SEP-15/74 was used. We first anionically synthesized SI diblock copolymers and then hydrogenated selectively the polyisoprene block chains using Pd/$CaCO_3$ catalyst. The number-average molecular weight, M_n, was determined to be 7.4×10^4 by osmometry and the heterogeneity index, M_w/M_n, was determined to be 1.08 by GPC measurement using columns calibrated for poly(ethylene-*alt*-propylene) alternating copolymers (PEP), where M_w designates the weight-average molecular weight. The weight fraction of PS, w_{PS}, was determined to be 0.153 by ^{1}H-NMR measurement. Then the value of f_{PS} was calculated to be 0.128, using the densities 0.969 g/cm^3 for PS at 413 K ($>T_{g,PS}$; the glass transition temperature of PS domains) and 0.790 g/cm^3 for PEP at 413 K, respectively.[13] The SI diblock copolymer subjected to hydrogenation is coded as SI-16/82, which was used in our previous studies.[1–3] The microstructures in the polyisoprene (PI) blocks before hydrogenation were 93 and 7% for 1,4- and 3,4-linkages, respectively.[2] Therefore, the PEP blocks can be roughly taken to be alternating ethylene–propylene copolymers. For the SI-16/82 sample, $M_n = 8.2 \times 10^4$ and $M_w/M_n = 1.05$. Compared with SI, SEP has a small value of M_n and a large value of M_w/M_n, indicating partial degradation of the sample in the course of hydrogenation. However, it can be considered that the degradation leads to no significant loss of either the styrene or ethylene–propylene segment, because the analyzed value of $w_{PS} = 0.153$ by ^{1}H-NMR measurement for SEP is very close to the calculated value of $w_{PS} = 0.156$ by simply taking into account the increment of segmental weight upon conversion from isoprene to ethylene–propylene segments.

SAXS experiments were conducted according to the method described in detail elsewhere.[2,3,14,15] The measured scattered intensities were corrected for absorption due to the sample, air scattering, thickness of the sample, and thermal diffuse scattering arising from density fluctuations. The SAXS profiles were measured at the edge-view geometry. The cross-section of the incident X-ray beam is rectangular with its long axis set parallel to surfaces of a stack of film samples, the incident beam passes through the stack parallel to their surfaces, and a one-dimensional position-sensitive proportional counter was set parallel to the film normal to detect the scattered X-rays. Because the incident beam has a finite height rather than a point, the measured SAXS profile is smeared. This smearing effect should be corrected for by desmearing the measured SAXS profile. However, it is not possible to desmear the scattered pattern from an oriented system.[16] The purpose of the SAXS measurement is to characterize the morphological features, and therefore the relationship of the peak positions from the lattice scattering is merely needed. Note that the lattice scattering peaks are associated with spatial regularity of the ordered domains. The error due to smearing does not affect the relationship of the lattice peak positions[15] for the collimation optics adopted in this work, so that we can use the measured (smeared) SAXS profiles for the morphological characterization.

Results and Discussion

The SAXS profiles for SEP-15/74 are shown in Figure 1 at several temperatures up to 300 °C. These profiles were measured with raising the temperature of a sample stepwise; i.e., the sample was successively heated to a desired temperature after completing an isothermal SAXS measurement. The profiles are displayed in a semilogarithmic plot of the absolute scattered intensity vs the magnitude of the scattering vector, s, which is given by

$$s = |\mathbf{s}| = (2 \sin \theta)/\lambda \tag{1}$$

with θ and λ being half the scattering angle and the wavelength of X-rays with 0.154 nm, respectively. For all temperatures, the scattering peaks were observed at s values relatively assigned to $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{13}$. These are the lattice scattering peaks of hexagonally-packed cylinders; i.e., the relationship can meet $\sqrt{h^2 + hk + k^2}$ with $h, k = 0, 1, 2, 3, ...$

In order to show that the SAXS results are obtained under the state of thermodynamic equilibrium or quasi-equilibrium, we discuss the temperature dependence of Bragg spacing d which is defined as the inverse of the first-order peak position s^*. The double-logarithmic plot of d vs the absolute temperature, T, is shown in Figure **2**. The result at T = 150 °C seemed to be kinetically constrained[19] by PS domains because the temperature is close to the glass transition temperature of PS ($T_{g,PS}$

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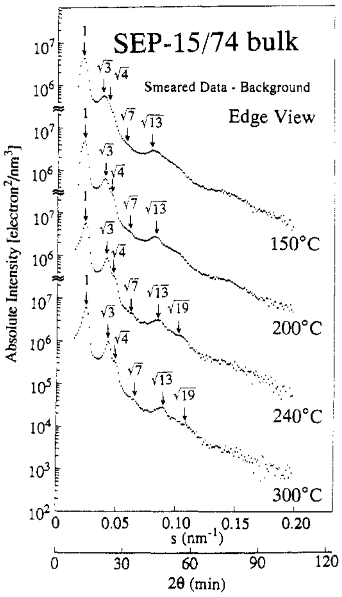

Figure 1. Smeared SAXS profiles (edge view) for SEP-15/74 at several temperatures up to 300 °C.

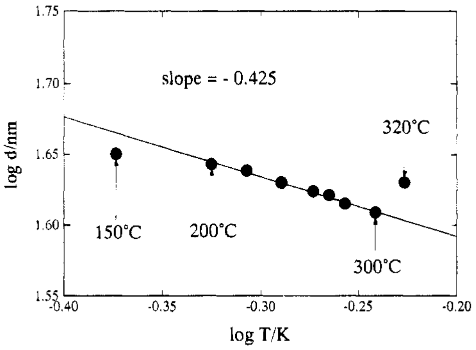

Figure 2. Double-logarithmic plot of Bragg spacing d vs the absolute temperature, T, for SEP-15/74. The Bragg spacing d is defined as the inverse of the first-order peak position s^*. The straight line is the approximation for the data from 200 to 300 °C. The slope of this line is −0.425.

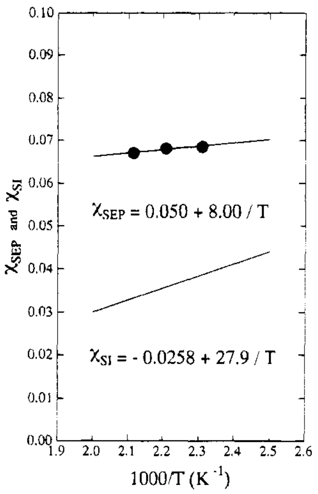

Figure 3. Temperature dependence of χ_{SEP} (=0.050 + 8.00/T) for the SEP-15/74 sample. The temperature dependence of χ_{SI} (=−0.0258 + 27.9/T) for the SI-16/82 sample[2,3] is also shown.

≈ 100 °C). Moreover, the sample turned out to be damaged at T = 320 °C (by GPC measurement). Therefore, we used the results from 200 to 300 °C in order to approximate the temperature dependence of d. Those data can be fitted by a straight line with a slope of −0.425; i.e., the relationship is given by $d \sim T^{-0.425}$. Hashimoto et al.[17] have reported a scaling behavior on the temperature dependence of d for SI diblock copolymers with the exponent of −1/3 ($d \sim T^{-1/3}$). Our results on SEP-15/74 show a stronger temperature dependence. Excepting disagreement of the exponent values, the tendency of d decreasing with an increase of the temperature supports that our SAXS results reflect thermodynamically equilibrium (or quasi-equilibrium) morphological structures.

The SI-16/82 sample, which is a precursory diblock copolymer before hydrogenation, has been found to exhibit a thermoreversible morphological transition between cylinders and spheres.[1,2] The cylindrical and spherical morphologies were formed at temperatures below and above the transition temperature of ca. 175 °C, respectively. The value of f_{PS} is 0.140 for this SI sample. At first glance, it is strange that the SEP sample forms cylindrical structures, because the value of f_{PS} (=0.128) is smaller than that of SI-16/82. We interpret the reason from the following two standpoints. The first to be considered is the strong segregation between the styrene and ethylene−propylene segments. It is reasonable to recognize that the segmental interaction becomes larger upon hydrogenation. As a matter of fact, we obtained a preliminary result on the temperature dependence of the interaction parameter, χ_{SEP}, as

$$\chi_{\mathrm{SEP}} = 0.050 + 8.00/T \qquad (2)$$

which is shown in Figure 3. To obtain (2), the effective χ values (χ_{eff}) were first evaluated for the SEP-15/74 sample in dioctyl phthalate (DOP) solution by analyzing the SAXS profiles from the disordered state on the basis of the random phase approximation.[14] The dilution approximation[18] was used to obtain the relationship between the χ values for the bulk SEP and the effective χ values for the solution, i.e., $\chi_{\mathrm{eff}} = \chi_{\mathrm{SEP}}\phi_{\mathrm{P}}$, where ϕ_{P} denotes the volume fraction of polymer in the solution (ϕ_{P} = 0.43). The result expressed by (2) is considered to be preliminary and approximate, good only for qualitative discussion, because DOP is not a neutral solvent for SEP and the dilution approximation has not been confirmed to be applicable to the SEP/DOP solution with ϕ_{P} = 0.43. Note that the method to evaluate χ_{eff} assumes the neutrality of solvents. Paying attention to this fact, let us make a qualitative comparison of χ_{SEP} with χ_{SI}, which was specifically determined for the SI-16/82 sample. We reported a temperature dependence of $\chi_{\mathrm{SI}} = -0.0258 + 27.9/T$ for the SI-16/82 sample,[2,3] which is also shown in Figure 3. We find that the interaction parameter remarkably increases upon hydrogenation. The SSL theories provide a compositional range for a cylindrical region, such as $0.15 \le f \le 0.33$ by Helfand and Wassermann,[7] $0.12 \le f \le 0.28$ by Semenov,[8] $0.215 \le f \le 0.355$ by Ohta and Kawasaki,[9] $0.15 \le f \le 0.33$ by Vavasour and Whitmore,[10] and $0.195 \le f \le 0.345$ by Lescanec and Muthukumar.[11] Although the theoretical work of Semenov gives a result consistent with our experimental observation of the cylindrical morphology for the SEP sample having f_{PS} = 0.128, the cylindrical morphology is surprising for such a small PS volume fraction.

The next to be considered is chain asymmetry associated with differences in segment volume and in segment length between the styrene and ethylene−propylene segments. Vavasour and Whitmore[12] have constructed the phase diagram by taking into account the effects of chain asymmetry. They have introduced an index ϵ characterizing the degree of chain asymmetry, which is given by

$$\epsilon = \frac{f_A/f_B}{{R_{gA}}^2/{R_{gB}}^2} = \frac{\rho_B {b_B}^2}{\rho_A {b_A}^2} \tag{3}$$

where f_K, R_{g_K}, ρ_K, and b_K denote respectively the volume fraction, radius of gyration, number density, and statistical segment length for the K component (K = A or B). Here the number density ρ_K is mass density divided by the molecular weight of the *K* segment ($M_{u,K}$). The phase boundaries between the disordered state and spherical region, between the spherical and cylindrical regions, and between the cylindrical and lamellar regions were found to shift toward $f_A = 0$ with an increase of the ϵ value, where PS was taken as the A component. If the value of ϵ increases upon hydrogenation, then the cylindrical region shifts toward $f_{PS} = 0$. Actually, the calculated ϵ value increases upon hydrogenation; i.e., the ϵ value is 1.24 for SI-16/82 and 1.56 for SEP-15/74. In these calculations, the literature values 0.969, 0.830, and 0.790 g/cm^3 for the densities of PS, PI, and PEP, respectively, and $b_{PS} = 0.67$ nm, $b_{PI} = 0.65$ nm, and $b_{PEP} = 0.76$ nm at 413 K were used,[13] and $M_{u,PS} = 104$, $M_{u,PI} = 68$ and $M_{u,PEP} = 70$ were also used. Thus the effects of chain asymmetry can account for our experimental observation of cylindrical morphology at $f_{PS} = 0.128$ for SEP. According to the phase diagram constructed by Vavasour and Whitmore[12] for $\epsilon = 1.67$, we found the sperical region of $34.8 \le \chi r_C < 55.5$ and the cylindrical region of $\chi r_C \ge 55.5$ at $f_{PS} = 0.128$, where χr_C is a product of the interaction parameter (χ) and the reduced degree of polymerization (r_C) defined as

$$r_C = (v_A N_A + v_B N_B)/v_0 \tag{4}$$

where v_A and v_B denote molar volumes of segment A and B, respectively, and v_0 designates a molar volume of reference cell. v_K is given by $1/\rho_K$, and $v_0 = (v_A v_B)^{1/2}$ is assumed. Using the density values listed above, we evaluated $r_C = 1009$ for SEP-15/74. In order to check that our experimental result is in accord with their phase diagram, we make a comparison using the preliminary result given by (2) and shown in Figure 3. Combining (2) with $r_C = 1009$, the condition of $\chi r_C \ge 55.5$ for the cylindrical region turns to $T \le 1325$ °C. This indicates that we can only access the cylindrical region in the ordinary experimental temperature range, and it is consistent with our experimental observation of the cylindrical morphology for the SEP-15/74 sample.

In conclusion, the SEP-15/74 sample shows the cylindrical morphology at all temperatures covered in this study despite the small value of $f_{PS} = 0.128$, for which the precursory SI-16/82 before hydrogenation shows a spherical morophlogy at high temperatures. Since the segmental interaction between styrene and ethylene–propylene is very large, the observed cylinder is considered to be the morphology appropriate in the strong-segregation limit. However, the ordinary SSL theories do not account for our experimental observation of the cylindrical morphology at $f_{PS} = 0.128$. It was concluded that the effects of chain asymmetry associated with differences in segment volume and in segment length for the styrene and ethylene–propylene segments play important roles. The theoretical result of Vavasour and Whitmore[12] which takes into account the effects of chain asymmetry supported our experimental observation of cylindrical morphology at $f_{PS} = 0.128$.

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