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Anomaly in SANS χ for polydisperse polystyrene-*b*-poly(isooctyl acrylate)

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ABSTRACT

Small-angle neutron scattering (SANS) measurements have been performed on a disordered block copolymer from deuterated polystyrene (dPS) and self-adhesive poly(isooctyl acrylate) (POA) in order to elicit the effective Flory–Huggins χ, which carries the essence of the copolymer phase behavior. The copolymer sample for the measurement was prepared by blending two polydisperse dPS-*b*-POAs of different molecular weights, where the overall average size of the blend was low enough to ensure to be in the mean-field region but high enough to have discernible scattering intensities. The SANS profiles for the copolymer were fitted to Leibler's scattering function for a polydisperse copolymer system described by Schulz-Zimm distribution. The resultant χ as a function of inverse temperature was shown to have a strong entropic contribution and a weak enthalpic contribution. By adopting Sanchez-Balasz or ten Brinke-Karasz-type simple analysis for specific interactions, it was found that the entropically dominated χ for dPS-*b*-POA arises from the steric hindrance of long alkyl side groups of POA.

1. Introduction

Nanoscale materials based on block copolymers have drawn huge attention from polymer society because such a new nanomaterial can lead to a more sophisticated material technology in various applications to microelectronic engineering and bioengineering [1–7]. Block copolymers are obtained from connecting two dissimilar polymers by covalent bonds. These polymers can yield well-defined nanostructured materials through self-assembly behavior. Typical nanostructures consist of classical body centered or face centered cubic, hexagonally packed cylindrical, lamellar structures, and more complex nonclassical structures with cubic or noncubic network structures [8–11]. There have been extensive efforts to understand the self-assembly behavior of block copolymers via experimental investigations [8–11], and also via numerous theoretical approaches in both conventional field [9,12–18] and molecular analyses [19–26].

It has been shown in the previous works that the so-called effective Flory–Huggins interaction parameter χ, which is the dimensionless exchange energy scaled by thermal energy *kT*, is the central concept of nanoscale self-assembly in block copolymers. There is a threshold $N\chi$ value, over which a molten system of block copolymer chains with *N* segments at each composition exhibits ordered nanostructures [9]. A conventional method to determine χ is to fit experimental measurements such as small-angle neutron or X-ray scattering to the scattering function from the phenomenological field theory by Leibler [12] or by Fredrickson and Helfand [14]. The χ of a series of homologous polystyrene-*b*-poly(alkyl methacrylates) (PS-*b*-PAMA) reveal all the aspects ever found in block copolymers [27–38]. PS-*b*-PAMA with methyl group or side groups longer than n-pentyl exhibits the common behavior of order–disorder transition (ODT) upon heating [27,31,36]. On the other hand, PS-*b*-PAMA with side groups between ethyl and n-propyl exhibits the behavior of lower disorder–order transition (LDOT) upon heating [28,29,31,32,36]. PS-*b*-PAMA with n-butyl and n-pentyl side groups showed an immiscibility loop with both LDOT and upper ODT [33–38]. The pressure dependence of the observed transitions for PS-*b*-PAMA falls into two cases. It was observed that the ODT-type PS-*b*-P(methyl MA) reveals ordering upon pressurization (barotropicity) [32,36]. PS-*b*-P(n-hexyl MA), on the other hand, disorders upon pressurization (baroplasticity) [32,36]. All of the LDOT-type homologous copolymers show baroplasticity [30,32,36]. By direct measurement of the transition temperatures at elevated pressures, the pressure coefficients of ODT or LDOT for loop-forming PS-*b*-PAMAs were shown to be unprecedentedly large [34,36,38].

Meanwhile, polyacrylates (PA) with a long alky side groups form a class of materials called pressure sensitive adhesives, which are

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widely used for packaging, taping, semiconductor fabrication processes, and also drug delivery because of their self-adhesiveness to almost any surface upon a light pressurization [39–42]. By introducing a block copolymer of the self-adhesive PA and polymers incompatible with it, one can prepare nanostructured adhesive materials for desired applications. In this study, we report χ of the block copolymer from deuterated dPS and poly(isooctyl acrylate) (POA) at ambient pressure as our first step towards developing useful materials based on POA. Our tool to probe dPS-*b*-POA is small-angle neutron scattering (SANS). The SANS intensity profiles for a fully disordered dPS-*b*-POA copolymer, which is made by mixing the copolymers of two different molecular weights, are used to obtain the empirical Flory–Huggins χ as a function of inverse temperature. Leibler's scattering function with polydispersity included in the mean-field picture is used to elicit χ in the present study. It is found that χ has a relatively weak enthalpic contribution, but a strong entropic contribution, which is caused by the steric hindrance of long alkyl side groups of POA block.

2. Experimental

The two dPS-*b*-POA copolymers with different molecular weights, denoted as dPS$_1$-*b*-POA$_1$ and dPS$_2$-*b*-POA$_2$, used in this study were purchased from Polymer Source Inc. The copolymers were synthesized by the transesterification of the deuterated polystyrene-*b*-poly(tert-butyl acrylate) diblock copolymer in the presence of isooctanol. The molecular weights M_j, the polydispersity indices (PDI), the degree of polymerization N_j, and the fraction f_j of block components are given in Table 1.

To prepare a target molecular weight of 17,400 for dPS-*b*-POA at the similarly symmetric composition, the binary mixtures of the copolymers with φ_1 (volume fraction of dPS$_1$-*b*-POA$_1$) = 0.440 were prepared by the freeze-drying method from their solution [43]. For instance, a predetermined amount of mixture was dissolved in benzene (~10 wt% in solute) and the quenched solution was evaporated under vacuum for 24 h, followed by sequential annealing at $T = 110$–120 °C for 24 h to thermally equilibrate the sample and to remove the solvent completely.

SANS experiments were performed at the HANARO 40 m SANS of Korea Atomic Energy Research Institute (KAERI) in Korea with a $\lambda = 0.60$ nm and $\Delta\lambda/\lambda = 0.12$ with a sample-to-detector distance of 5.75 m. Scattering intensities were collected on a 2-D area detector for 10 min and then circularly averaged. The sample thickness was set to 1 mm (in diameter of 9 mm) by compression molding, followed by thermally annealing it well above T_g of dPS block. SANS profiles were obtained at every 10 °C from 120 to 240 °C during heating, where the sample was equilibrated for 1 h at each temperature before the measurement. The absolute intensity was calibrated by a porous silica material as a standard with the Guinier radius of 31 Å, which was provided by NCNR (NIST Center for Neutron Research, US).

3. Scattering functions and Flory–Huggins χ

The essence of block copolymer phase behavior is concentrated on the phenomenological Flory–Huggins interaction parameter χ. If we denote as ε_{ij} the characteristic *ij*-pair interaction parameter for the copolymer, where *i* and *j* indicate the corresponding block components, then χ is defined as an exchange energy scaled by thermal energy as $\chi \equiv \Delta\varepsilon/kT = (\varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB})/kT$. The empirical effective $\chi(T)$ is elicited by fitting the scattering intensity $I(q)$ to the theoretical one derived from Leibler's incompressible scattering function $S(q)$ [12,44]. Here, $q\ (\equiv (4\pi/\lambda)\sin\theta)$ implies the scattering vector with 2θ and λ being the scattering angle and wavelength, respectively. The $I(q)$ is given by

$$I(q) = k_n \cdot S(q) = \frac{k_n}{\sum S^0_{ij}(q)/\det\left[S^0_{ij}(q)\right] - 2N\chi} \tag{1}$$

where the contrast factor k_n comes from the difference between neutron scattering lengths (b_j) of phase segregating components as $k_n = (b_A/v_A - b_B/v_B)^2 \cdot (v_A v_B)^{1/2}$ along with *j*-monomer volume v_j. The S^0_{ij} is the *i,j*-correlation functions of Gaussian chains. The S^0_{AA} or S^0_{BB} is determined by the Debye function $g_j\,(= 2\cdot(f_j x + e^{-f_j x} - 1)/x^2)$ as $S^0_{jj} = N \cdot g_j$, where x implies the squared dimensionless wave number as $x = q^2 \cdot Nb^2/6$ with b being a monomer diameter. The cross correlation, S^0_{AB}, is given by the multiple of the connecting functions, $g_{cj}\,(= (1 - e^{-f_j x})/x)$, as $S^0_{AB} = N \cdot g_{cA} \cdot g_{cB}$. Now, we need to modify the scattering functions to accommodate in general blending two polydisperse samples. All that is required is to change accordinglyS^0_{ij}.

The total chain size N of dPS$_1$-*b*-POA$_1$ is given by its block sizes as $N = N_{A,1} + N_{B,1}$. For dPS$_2$-*b*-POA$_2$, its block size $N_{j,2}$ is determined by $y_j \equiv N_{j,2}/N$, so that its total chain size becomes $(y_A + y_B)\cdot N$. To simplify the calculations, we assume that the individual polydispersity of each block is described by the conventional Schulz-Zimm distributions, of which the probability of the given block having the chain size in between N_j and N_j+dN_j is obtained as $n(N_j)\mathrm{d}N_j = kN_j^{\nu} e^{-aN}\mathrm{d}N_j$, where a, ν, and k are obtained by a shifted polydispersity index $u_j\ (\equiv \langle N_j \rangle_w / \langle N_j \rangle_n - 1)$ as

$$a = 1/\left(\langle N_j \rangle_n u_j\right); \quad \nu = 1/u_j - 1; \quad k = a^{\nu+1}/\Gamma(\nu + 1) \tag{2}$$

In the above expressions, the subscripts *w* and *n* imply the weight and the number average of a given quantity, respectively. As a Gaussian chain only correlates with itself, S^0_{ij} for the polydisperse dPS$_j$-*b*-POA$_j$ copolymer becomes the weight average of those for the corresponding monodisperse copolymer. The averaging procedure yields $\langle S^0_{jj} \rangle_w = \langle N \rangle_n \cdot 2 \cdot (\bar{f}_j \bar{x} + \langle e^{-f_j x} \rangle_n - 1)/\bar{x}^2$ and $\langle S^0_{AB} \rangle_w = \langle N \rangle_n \cdot \prod (1 - \langle e^{-f_j x} \rangle_n)/\bar{x}^2$. The average of $e^{-f_j x}$ is obtained as $\langle e^{-f_j x} \rangle_n = (1 + \bar{f}_j u_j \bar{x})^{-1/u_j}$. Here, $\bar{f}_j = \langle N_j \rangle_n / \sum \langle N_j \rangle_n$ and $\bar{x} = q^2 \cdot \langle N \rangle_n b^2/6$. Finally, the individually weight averaged $\langle S^0_{ij} \rangle_w$'s are linearly added as $S^0_{ij} = \varphi_1 \langle S^0_{ij} \rangle^1_w + \varphi_2 \langle S^0_{ij} \rangle^2_w$ for the blend of dPS$_1$-*b*-POA$_1$ and dPS$_2$-*b*-POA$_2$ copolymers.

4. Results and discussion

SANS intensity profiles for the blend of dPS$_1$-*b*-POA$_1$ and dPS$_2$-*b*-POA$_2$, measured at various temperatures during heating from 120 to 240 °C, are shown in Fig. 1(a) as a function of the scattering vector q. There can be seen a broad and diffuse maximum of the intensity profile over the entire temperature range, which is the

Table 1
Molecular characteristics of two dPS-*b*-POA diblock copolymers and the blend.

Sample code	M_n	M_w/M_n	Φ_{PS}	N_e	Remark (wt. ratio)
dPS$_1$-*b*-POA$_1$	5500-*b*-5700	1.09	0.4502	33.3-*b*-40.6	Pristine, 11.2k overall
dPS$_2$-*b*-POA$_2$	10500-*b*-11500	1.06	0.4366	63.0-*b*-81.2	Pristine, 22k overall
Blend[a]	8377-*b*-9038	–	0.4403	–	11.2k/22k (0.273/0.727)

[a] The binary mixtures of dPS-*b*-POAs were prepared by the freeze-drying method from the polymer solution in benzene.