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Temperature−Pressure Superposition in SANS χ for an A-*b*-B Diblock Copolymer

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S *Supporting Information*

INTRODUCTION

Block copolymers have drawn tremendous attention since they can self-assemble into nanoscopic arrays of ordered structures such as spheres, cylinders, lamellae, bicontinuous gyroids, and complex networked structures. It is well-known that the phase behavior of a block copolymer is governed by composition ϕ, total number of monomers N, and the Flory−Huggins effective interaction parameter χ_F.[1−6] Typical block copolymers exhibit ordering upon cooling, which is referred to as the order−disorder transition (ODT). Such behaviors of block copolymers have been analyzed in many theoretical approaches based on the assumption of incompressibility.[3,4,7−10] However, there have been numerous recent observations that demonstrate a clear need for compressibility concept to rationalize the response of block copolymers to pressure. In particular, block copolymers exhibiting an ordering transition upon heating, which is referred to as the lower disorder−order transition (LDOT), are in many cases baroplastic, indicating a suppressed ordering by pressure,[11,12] while ODT-type block copolymers are mostly barotropic, indicating an enhanced ordering by pressure.[12,13] Furthermore, the finding of an immiscibility loop in some block copolymers has stimulated the study of pressure effects on phase stability because those materials turned out to be tremendously sensitive to pressure.[14−17]

The LDOT and pressure effects on the ordering transition have been successfully described in recent studies using a random-phase approximation (RPA) approach with finite compressibility developed by one of the authors.[18−23] Compressibility was incorporated into the theory through effective RPA interactions, which is obtained from a molecular equation-of-state (EOS) model by Cho and Sanchez (CS).[18,24] The χ_F was newly interpreted as $\chi_F = \chi_{app} + \chi_{comp}$, where χ_{app} is the conventional exchange energy with proper density dependence and χ_{comp} arises from compressibility difference between constituent blocks. Many block copolymers with unfavorable (positive exchange energy) contributions to χ_{app} would experience typical ODT behavior. However, some block copolymers with directional interactions would develop growing unfavorable contributions to χ_{app} with temperature, due to the entropic penalty of forming such directional pairs. Other block copolymers with large compressibility difference and, thus, large χ_{comp} would gain more entropy due to increase in volume when they phase separate. Such entropic driving forces can be the key factor to induce LDOT-type phase behavior. It was also emphasized that the relative changes of χ_{app} and χ_{comp} upon pressurization determine whether a given system is baroplastic or barotropic.[19,21−23]

There has been found a principle of temperature−pressure (T−P) superposition in static compression behavior of polymeric liquids both semiempirically[25−27] and also theoretically.[18,24] It is stated that compression isotherms (V/V_0) are superposed into a universal function of a dimensionless pressure, $\beta_0(P - P_0)$ or $(P - P_0)/B_0$, where V_0, β_0, and B_0 are volume, isothermal compressibility, and bulk modulus ($B_0 = 1/\beta_0$) at a (low) reference pressure P_0, respectively, which are only a function of temperature. It is the objective of this note to seek for such a T−P superposition in scattering behavior of block copolymers. Because the scattering intensity of microphase segregating block copolymers is influenced by χ_F, and its two components, χ_{app} and χ_{comp}, are dependent on density, it can be intuitively expected that β_0 or B_0 again plays an important role in correlating the scattering intensity profiles upon heating and pressurization. We take deuterated polystyrene-*b*-poly(*n*-propyl methacrylate), which exhibits LDOT and baroplasticity,[12,23] as a model system for our purpose.

EXPERIMENTAL SECTION

A symmetric dPS-*b*-PPrMA was synthesized by the sequential, anionic polymerization of *d*-styrene and *n*-propyl methacrylate in tetrahydrofuran (THF) at −78 °C in the presence of LiCl under purified argon using *sec*-BuLi as an initiator. LiCl (high purity, Aldrich) was dried overnight at 150 °C under vacuum and then dissolved in dried THF. Refluxed THF from CaH_2 was stirred over fresh sodium benzophenone complex until it showed a deep purple color, indicating an oxygen- and moisture-free solvent. Degassed monomers with CaH_2, *d*-styrene (99.5%, CDN Isotopes), and *n*-propyl methacrylates (Aldrich) were vacuum-distilled over dried dibutylmagnesium and trioctylaluminum, respectively. After sequential adding *d*-styrene and *n*-propyl methacrylates to the reactor, the polymer solution terminated with purified 2-propanol was precipitated in excess methanol/water (90/10 w/w) mixture to remove the impurities including LiCl.

Number-average molecular weights (M_n) and polydispersity (M_w/M_n) of dPS-*b*-PPrMA, characterized by size-exclusion chromatography (SEC) with multiangle laser light scattering (MALLS), were 135 000 g/mol and 1.02, respectively. The volume fraction of one component was

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estimated to be nearly symmetric (0.499), as determined by nuclear magnetic resonance.

SANS experiments were performed at the HANARO (Korea). Scattering intensities were collected on a 2-D area detector for 1 h and then circularly averaged. The sample thickness was set to 1.5 mm (in diameter of 14 mm) by compression molding, followed by thermally annealing it well above T_g (>100 °C) under vacuum for 24 h. A stainless steel (SUS 316) pressure cell devised with sapphire windows was used in hydrostatic pressuring experiments over a range from 1.4 to 82.7 MPa. SANS profiles were obtained at every 10 °C during heating, where the sample was equilibrated for 1 h at each temperature before 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).

SCATTERING PROPERTIES AND χ_F

We focus on a molten A-*b*-B diblock copolymer well above its T_g, but below LDOT, representing a disordered state. The absolute scattering intensity ($I(q)$ in cm^{-1}) is measured as a function of the so-called scattering vector q, which is given by $4\pi/\lambda \sin\theta$ with scattering angle 2θ and wavelength λ. According to Leibler's incompressible RPA analysis,[8] $I(q)$ can be equated to

$$I(q) = v_{\mathrm{ref}}\left(\frac{\bar{b}_1}{v_1} - \frac{\bar{b}_2}{v_2}\right)^2 S(q) \tag{1}$$

where $\bar{b}_i$ is the coherent neutron scattering length and v_i is the monomeric volume for the i-component. The reference volume v_{ref} is defined as $v_{\mathrm{ref}} = (v_1v_2)^{1/2}$. The $S(q)$ is the scattering function of a diblock copolymer melt, which is given by Leibler as follows:[8]

$$S(q)^{-1} = \frac{S_{11}^0 + S_{22}^0 + 2S_{12}^0}{N_e \det[S_{ij}^0]} - 2\chi_F \tag{2}$$

where S_{ij}^0 is the *i,j*-correlation function for incompressible Gaussian A-*b*-B chains. From the experiment, the total number of segments (N_e) is defined as $N_e = (V_{\mathrm{dps}} + V_{\mathrm{PPrMA}})/v_{\mathrm{ref}}$, where V_{dPS} and V_{PPrMA} are respectively the molar volumes of the dPS and PPrMA blocks. The SANS profiles are described by an empirical effective interaction parameter χ_F, which can be obtained by fitting eq 2 to the experimental $S(q)$ data.

In our recent communications, we discussed the physical meaning of χ_F using the compressible RPA theory[18,19,21−23] in connection with C−S EOS model.[18,24] Through the analysis of the second-order vertex functions, χ_F was shown to be subdivided into two terms as $\chi_F = \chi_{\mathrm{app}} + \chi_{\mathrm{comp}}$, where χ_{app} ($\sim \Delta\bar{\varepsilon}/T|u(\eta)|$) is Flory−Huggins-like parameter with density dependence. The symbol $\Delta\bar{\varepsilon}$ ($= \bar{\varepsilon}_{\mathrm{AA}} + \bar{\varepsilon}_{\mathrm{BB}} - 2\bar{\varepsilon}_{\mathrm{AB}}$) implies the exchange energy between characteristic *i,j*-interactions $\bar{\varepsilon}_{ij}$. The $u(\eta)$ describes the dependence of the exchange energy on packing density η, which is defined as the fraction of volume occupied by all the monomers. The functional form for $u(\eta)$ is given by the mean-field description of internal energy. If a simple Bragg−Williams-type (van der Waals) approximation were employed, $u(\eta)$ would become equal to η.[28] In CS EOS model, a more advanced Bethe−Peierls-type approximation is employed for $u(\eta)$.[18,24,28] Therefore, a more complicated functional form is given for $u(\eta)$ as $u(\eta) = (\gamma/C)^4\eta^4 - (\gamma/C)^2\eta^2$ with $\gamma = 1/\sqrt{2}$ and $C = \pi/6$. Nonetheless, $u(\eta)$ is fairly linear in its dependence on η in the useful range. The remaining χ_{comp} ($\sim P_\phi{}^2v^*/T\eta B_T$) represents compressibility difference (disparity in EOS properties) between constituents. Here, P_ϕ denotes the composition derivative of pressure, and v^* is the monomer volume. It can be shown that $P_\phi v^* \sim (\varepsilon_{\mathrm{AA}} - \varepsilon_{\mathrm{BB}})\eta^2\, \mathrm{d}u/\mathrm{d}\eta$ for symmetric copolymers. In general, a block component with larger $\bar{\varepsilon}_{ii}$ has a smaller compressibility (and larger $\eta_{\phi_i\to 1}$) due to the stronger binding energy. Therefore, P_ϕ vanishes if two components have the same compressibility. B_T is the bulk modulus, which is the inverse of isobaric compressibility, to determine the magnitude of χ_{comp}. A more detailed description of CS EOS and the compressible RPA theory is given in the Supporting Information.

A TEMPERATURE−PRESSURE SUPERPOSITION

For a better information of the scattering data, we reproduce the scattering intensity profiles on the absolute scale for dPS-*b*-PPrMA copolymer as a function of scattering vector (q).[21] The scattering intensity profiles at 1.4 MPa, which is taken as our reference pressure P_0, is shown in Figure 1a at various temperatures from 150 to 240 °C during heating process. At lower temperatures (≤180 °C), a weak and broad peak maximum at $q^* = 0.18$ nm^{-1} is seen due to the correlation hole scattering by the compositional fluctuation of block copolymer in disordered (or phase-mixed) state. As temperature increases up to 240 °C, the scattering intensity increases and reaches a sharp maximum, indicating the microphase separation of the block copolymers with the characteristic of an LDOT-type behavior. On the basis of the change in the half-widths of the intensity curves, it can be said that the copolymer experiences LDOT at ∼205 ± 10 °C. Figure 1b also shows a pressure dependence of the scattering intensity profiles at 240 °C, where a sharp primary peak of the scattering intensity at P_0 is observed due to the strong segregation between two components of dPS-*b*-PPrMA copolymer. As pressure increases up to 82.7 MPa, the scattering intensity decreases and the primary peak broadens significantly, leading to a disordered state at higher pressure for baroplastic block copolymers. We analyze those intensities only up to 190 °C to elicit χ_F, while pressure is varied from 1.4 (=P_0) to 82.7 MPa. In this $T-P$ window, the copolymer system stays in the disordered state. The experimental $S(q)$ is fitted to that by Leibler given in eq 2 to determine χ_F, as shown in Figure 1c for an example at 170 °C and at three different pressures, where χ_F is spanning from a positive to a negative value.[29] Necessary numerical values for monomer volume and scattering length to obtain $S(q)$ from eq 1 can be found from the literature as $v_{\mathrm{dPS}} = 97.44$ cm^3/mol, $\bar{b}_{\mathrm{dPS}} = 1.056 \times 10^{-11}$ cm for dPS block and $v_{\mathrm{PPrMA}} = 118.53$ cm^3/mol, $\bar{b}_{\mathrm{PPrMA}} = 1.67 \times 10^{-13}$ cm for PPrMA block.

χ_F's obtained in such a way are plotted against a dimensionless pressure $\Delta P/B_0$ ($= [P - P_0]/B_0$) at indicated temperatures in Figure 2a, where $\tilde{\chi}_F \equiv [\chi_F - \chi_F(P_0)]/\chi_F(P_0)$ is displayed instead of χ_F itself. The bulk modulus B_0 for the symmetric copolymer at P_0 is estimated as the average of those for dPS and PPrMA given in the literature.[30] The copolymer exhibits a baroplastic behavior, which yields diminishing $\tilde{\chi}_F$ with increase in pressure. This action is, however, shown to be more pronounced with decreasing temperature. Intriguingly, it is seen in this plot that the isotherms of $\tilde{\chi}_F$ may be superposed into a single characteristic curve by a

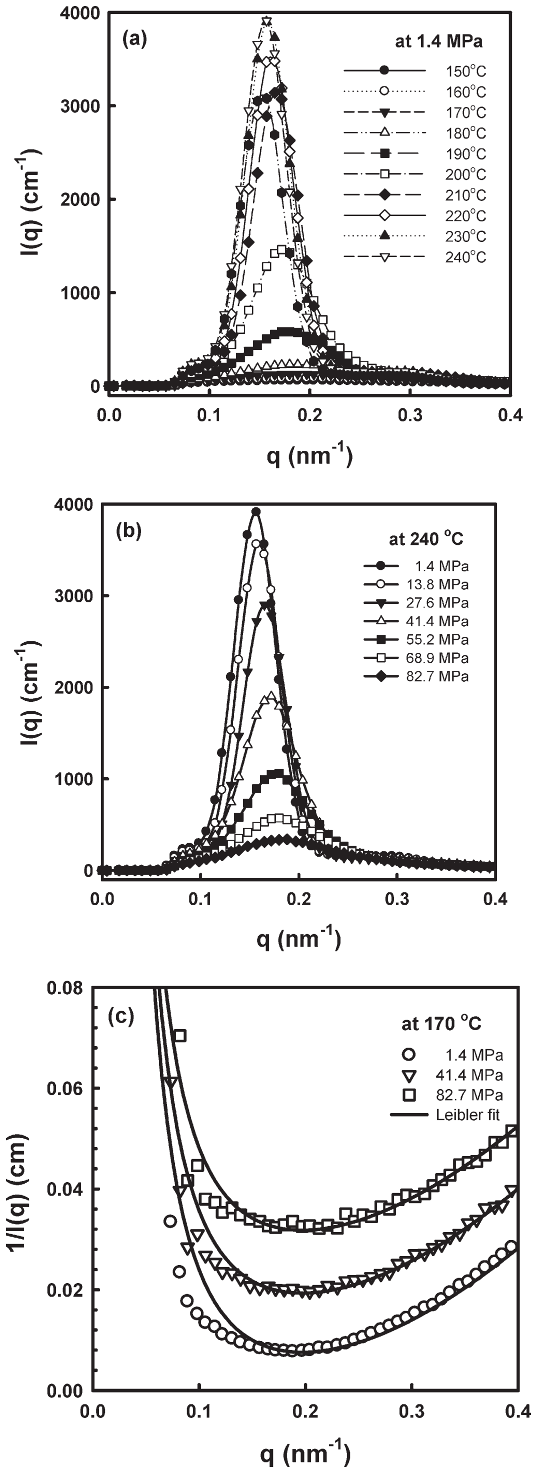

Figure 1. (a) SANS intensity profiles on absolute scale for dPS-*b*-PPrMA copolymer (M_n = 135 000 g/mol; N_e = 1125) at P_0 = 1.4 MPa as a function of scattering vector q at indicated temperatures. (b) Those intensity profiles at 240 °C as a function of q with the indicated changes in pressure. (c) Fitting the experimental $1/I(q)$ data to that by Leibler (eq 2) for the copolymer at 170 °C and at 1.4, 41.4, and 82.7 MPa, which yields χ_F = 0.006 46, 0.002 02, and −0.002 71, respectively.

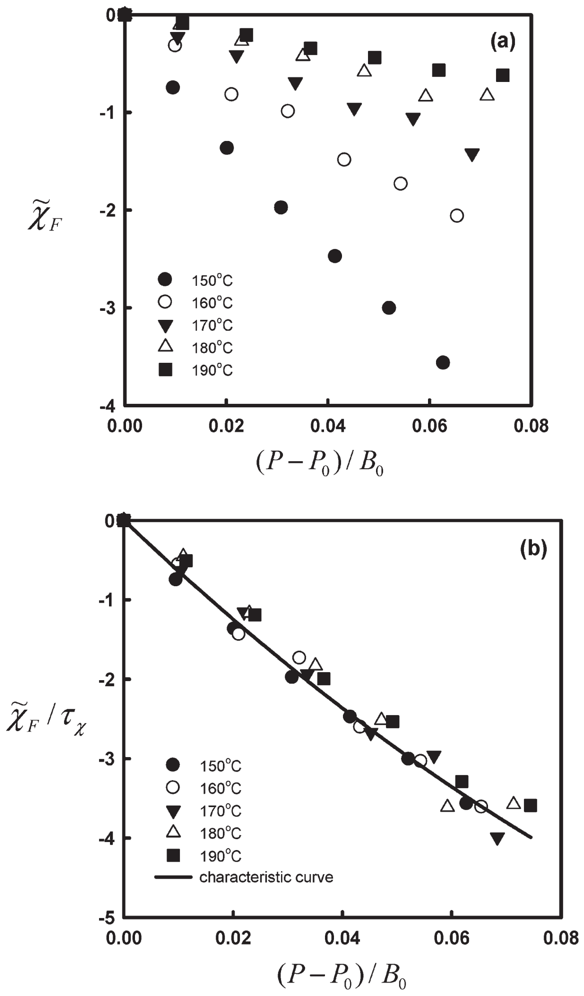

Figure 2. (a) Plot of $\tilde{\chi}_F$ for the copolymer at the indicated temperatures as a function of dimensionless pressure variable $\Delta P/B_0$, where $\Delta P \equiv P - P_0$ is the pressure increment. (b) Plot of $\tilde{\chi}_F/\tau_\chi$ against $\Delta P/B_0$, where a temperature−pressure superposition in $\tilde{\chi}_F$ is revealed: $\tilde{\chi}_F$ data are superposed into a characteristic curve that is regressed as $\tilde{\chi}_F/\tau_\chi = a(\Delta P/B_0) + b(\Delta P/B_0)^2$ with $a = -61.380$ and $b = 114.138$ by $\tau_\chi(T)$.

scale factor $\tau_\chi(T)$, into which all the temperature dependence is absorbed. Figure 2b vividly depicts that $\tilde{\chi}_F/\tau_\chi$ becomes a sole function of $\Delta P/B_0$ with $\tau_\chi(T)$ given in Figure 3. The scale factor τ_χ turns out to be deeply correlated to a bulk property B_0. The $\tau_\chi(T)$ values nicely fit to $\tau_\chi(T) = ae^{b/(T-c)}$ with $a = 0.0017$, $b = 660.9175$ K, and $c = 319.4994$ K. As B_0 decays exponentially ($B_0 = \alpha e^{-\lambda T}$ with $\alpha = 7870.035$ MPa, $\lambda = 0.0043$ K^{-1} for the copolymer), a near linear relationship between ln τ_χ and ln B_0 can be constructed. These results in Figures 2 and 3 give a profound interpretation. In measuring the scattering intensities and eliciting SANS χ_F from them, changes in thermodynamic variables (T and P) are not independent. The effects of temperature and pressure on χ_F are interconvertible. The SANS χ_F can be predicted at any point in a given temperature−pressure window only with the minimal number of measurements by using the characteristic curve in Figure 2b. All that is required is a bulk property B_0. This phenomenon can be considered as a variation of $T-P$ superposition in χ_F for block copolymers.[31]

It can be further shown that such a $T-P$ superposition is revealed in the scattering intensity maximum for block copolymers under pressure. In Figure 4a, we plot the scaled intensity maximum, $\tilde{I}_{max}$ ($\equiv [I_{max} - I_{max}(P_0)]/I_{max}(P_0)$), against $\Delta P/B_0$ at indicated temperatures. It was again possible to superpose

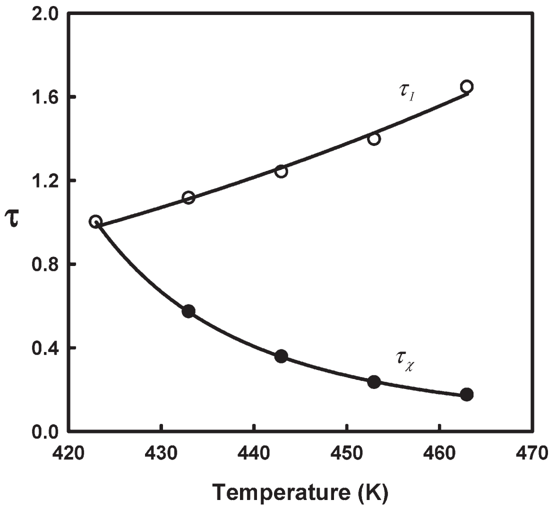

Figure 3. Plots of τ_χ and τ_I as a function of temperature. Data are well fitted to $\tau_\chi = 0.0017\mathrm{e}^{660.92/(T-319.45)}$ and $\tau_\mathrm{I} = -0.1701 + 0.011\mathrm{e}^{0.011(T/\mathrm{K})}$.

them into a single characteristic curve by a scale factor $\tau_\mathrm{I}(T)$, into which all the temperature dependence is absorbed. The plot of $\tilde{I}_\mathrm{max}/\tau_\mathrm{I}$ as a function of $\Delta P/B_0$ is depicted in Figure 4b. It is shown in Figure 3 that $\tau_\mathrm{I}(T)$ is correlated to B_0 in the same way as $\tau_\chi(T)$. The plot for $\tau_\mathrm{I}(T)$ is regressed to $\tau_\mathrm{I} = a + b\mathrm{e}^{b(T/\mathrm{K})}$ with $a = -0.1701$ and $b = 0.0110$. This equation can be used to construct a mathematical equation to relate τ_I to B_0.

Let us discuss what causes the observed $T-P$ superposition. It was found by one of the authors that volumetric properties of polymeric liquids including mixtures satisfy a principle of $T-P$ superposition, which states that the effects of temperature and pressure on compression strain ($\ln(V/V_0)$) are solely described by a unified variable $\Delta P/B_0$.[25−27] It can be easily shown that the bulk modulus at any arbitrary pressure also follows $T-P$ superposition as $B/B_0 = f(\Delta P/B_0)$, because $B^{-1} = \beta = -\partial \ln(V/V_0)/\partial\Delta P$. It is recalled that $\chi_\mathrm{app} \sim u(\eta)$ and $\chi_\mathrm{comp} \sim P_\phi{}^2/\eta B_T$. As V ($\sim\eta^{-1}$) is an apparent function of $\Delta P/B_0$ and so is B, both $\chi_\mathrm{app}/\chi_\mathrm{app}(P_0)$ and $\chi_\mathrm{comp}/\chi_\mathrm{comp}(P_0)$ are $T-P$ superposable. Such a procedure is helped by the notion that $u(\eta)$ reveals a fairly linear dependence on η in its proper range. As χ_F is the sum of χ_app and χ_comp, the scaled $\tilde{\chi}_\mathrm{F}$ is not expected to be in a $T-P$ superposable form. There is $\mu \equiv [\chi_\mathrm{comp}/\chi_\mathrm{comp}]_{P\to P_0}$ that gives an additional temperature-dependent contribution to $\tilde{\chi}_\mathrm{F}$ other than being a sole function of $\Delta P/B_0$. The scale factor τ_χ resolves this problem to merge the isotherms into the given characteristic curve. The ingredients of the ratio μ are η_0 and B_0. These two properties are not independent of each other. A dense system with higher η_0 should resist compression more strongly, which implies higher B_0. It is then clear that the ratio μ is deeply related to B_0, and so is τ_χ. Meanwhile, the scattering intensity, $I(q)$, at q^* for the symmetric diblock copolymers yields its maximum that is inversely proportional to quench depth as $I_\mathrm{max} \propto (10.495 - N\chi_\mathrm{F})^{-1}$. Therefore, the scaled intensity maximum, $\tilde{I}_\mathrm{max}$, is mainly dependent on the behavior of $\chi_\mathrm{F}(P)$. This in turn implies that $\tilde{I}_\mathrm{max}$ can be $T-P$ superposable with the scale factor $\tau_I(T)$. It is conjectured that other block copolymers with barotropicity (enhanced demixing upon pressurization) reveal the same phenomena because the physical cause underneath is $T-P$ superposition in bulk density (volume) and modulus.[32] In the Supporting Information, we provide the scaled analysis of our CS EOS and the corresponding compressible RPA theory to support the observation presented here.

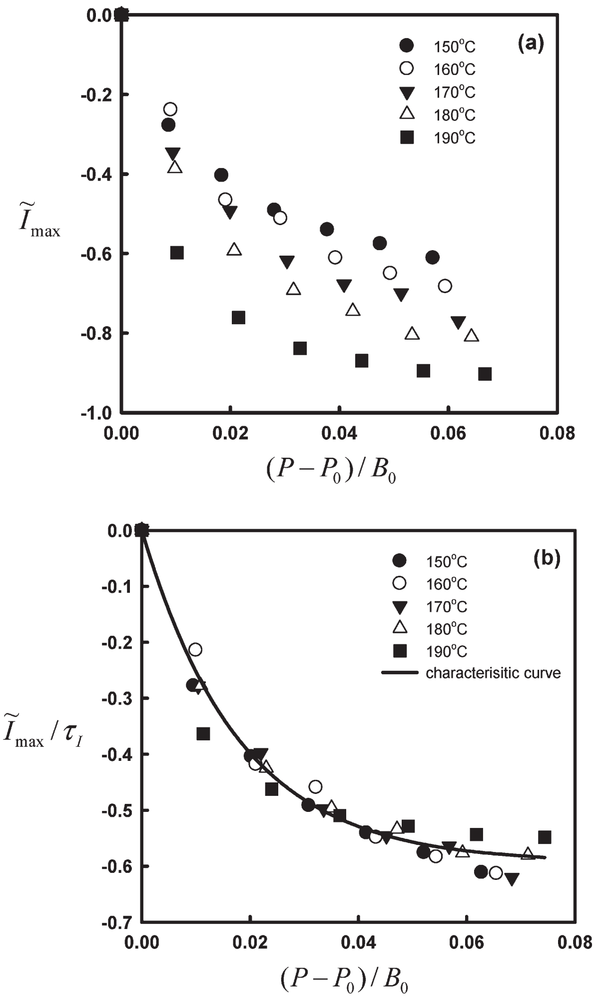

Figure 4. (a) Plot of $\tilde{I}_\mathrm{max}$ for the copolymer at the indicated temperatures as a function of dimensionless pressure variable $\Delta P/B_0$. (b) Plot of $\tilde{I}_\mathrm{max}/\tau_\mathrm{I}$ against $\Delta P/B_0$ where a temperature−pressure superposition in $\tilde{I}_\mathrm{max}$ is revealed: $\tilde{I}_\mathrm{max}$ data are superposed into a characteristic curve that is regressed as $\tilde{I}_\mathrm{max}/\tau_\mathrm{I} = a[1 - \mathrm{e}^{-b(\Delta P/B_0)}]$ with $a = -0.5906$ and $b = 57.87$ by $\tau_I(T)$.

■ CONCLUSIONS

For a baroplastic dPS-*b*-PPrMA copolymer in the disordered state, it has been shown that effective interaction parameter χ_F from small-angle neutron scattering measurements over a temperature−pressure ($T-P$) window forms a characteristic curve that is a function of dimensionless pressure variable $\Delta P/B_0$. Each isotherm of χ_F is superposed into the curve by a scale factor $\tau_\chi(T)$, which is completely determined by the bulk modulus B_0 at a reference pressure P_0. It has been further shown that the scattering intensity maxima I_max also reveal the same kind of superposition with a scale factor $\tau_I(T)$. Using the obtained characteristic curve, the effects of temperature and pressure on χ_F or on I_max become interconvertible. A plausible cause for the observation of such a $T-P$ superposition concept was given here. χ_F is subdivided into two components, χ_app and χ_comp. Each component is described by compression strain and bulk modulus, which eventually conserve the $T-P$ superposition as being solely described by $\Delta P/B_0$. Therefore, their linear sum, χ_F, becomes similarly $T-P$ superposable when it is divided by a scale factor $\tau_\chi(T)$, which resolves an additional temperature dependence arising from $[\chi_{\mathrm{comp}}/\chi_{\mathrm{app}}]_{P\rightarrow P_0}$. The same argument is given to $I_{\max}$ along with τ_I due to its relation to χ_F.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Detailed description of the compressible RPA theory in connection with CS EOS model and a fully theoretical view of $T-P$ superposition in χ_F. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) It should be pointed out that the dPS-*b*-PPrMA copolymer reveals chain stretching, signified by a shift in q^*, upon the growth of unfavorable energetics and concentration fluctuation effects. Meanwhile, the region of $\chi_F < 0$ suggests the presence of directional interactions, weak though, between dPS and PPrMA.[21,23]

(30) Volumetric data for PS and PPrMA in the selected temperature range can be given in the form of the isothermal Padé equation, which is mathematically stated as $\ln(V/V_a) = \{\omega/(1-\omega)B_1\}[1-(1+B_1P/\omega B_a]^{1-\omega}$ with $B_1 = 10.2$ and $\omega = 0.9$, where V_a and B_a are volume and bulk modulus at ambient pressure.[26,27] Those are $1/V_a = 1.2247 - 5.3781 \times 10^{-4}T$, $\ln B_a = 8.8737 - 0.0038T$ for PS, and $1/V_a = 1.2848 - 6.7654 \times 10^{-4}T$, and $\ln B_a = 9.1289 - 0.0049T$ for PPrMA. See ref 21 and references therein. We take the regressed volumetric data for PS as those for dPS in estimating the bulk modulus. Now, the Padé equations yield the modulus values at any point in the temperature−pressure window for the two constituent blocks. As a result, the bulk modulus B_0 at P_0 for the symmetric copolymer is estimated as the average of those of the two blocks as $\ln B_0 = 8.9708 - 0.0043T$.

(31) The scattering function based on Hartree one-loop correction can be used to yield a different χ for the copolymer, where a slightly flawed free energy functional by Fredrickson and Helfand[9,20−23] at fixed $(q^*R_g)^2$ or a better one by Olvera de la Cruz[10] with chain stretching allowed can be employed. It is considered that χ from the Hartree scattering function, when scaled by $\chi(P_0)$, is still dependent on density and bulk modulus, which is then to reveal temperature−pressure superposition.

(32) It is worth mentioning a previous work by Rabeony et al. to correlate interaction strength in some polyolefin blends as a sole function of density. Their approach worked well for the UCST blends but did not for the LCST blends. See: Rabeony, M.; Lohse, D. J.; Garner, R. T.; Han, S. J.; Graessley, W. W.; Migler, K. B. *Macromolecules* **1998**, *32*, 6511.