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Effects of Fluctuations and Compressibility on the Phase Behavior of Loop-Forming Diblock Copolymers

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ABSTRACT: The recently developed Hartree analysis for compressible diblock copolymers has been performed to study the thermodynamic origin of an immiscibility loop and its unprecedented pressure dependence observed in a diblock copolymer from polystyrene and poly(*n*-pentyl methacrylate). Certain specific interactions (SI) were incorporated in the theory by adding an entropic component into cross-contact interactions. An effective Flory-type interaction parameter χ_{cRPA}, which carries not only the change in contact interactions but also compressibility difference between blocks, was shown to play a central role here. The χ_{cRPA} plotted against temperature exhibited a loop character with a maximum because of the input SI. The effects of both fluctuations and compressibility difference were found through χ_{cRPA} to yield a loop phase diagram for the copolymer in a feasible temperature range along with the peculiar dependence of the loop on copolymer chain sizes and pressure. The resultant theoretical phase behavior was shown to be harmonious with the experimental observations for the copolymer.

Introduction

Studies on various behaviors of block copolymers, which are obtained from chemically binding different homopolymers, have drawn tremendous interest from the polymer circle. Block copolymers exhibit nanoscale self-assembly behavior to form microscopically ordered structures called microphases. A number of nanoscale ordered structures have been identified up to now. There are classical morphologies such as body-centered-cubic spheres (bcc), hexagonally packed cylinders (hex), and lamellar (lam) structures. Recently found morphologies such as bicontinuous gyroid, hexagonally perforated lamellae, and the latest noncubic triply periodic structures are categorized as complex morphologies. Those materials can be used in a variety of applications such as thermoplastic elastomers, compatibilizers, surface modifiers, and photoresists and also used for potential applications in lithography, patterning, displays, and information storage media. Templates for porous materials such as membranes, catalysts, and drug delivery devices are an emerging class of applications for block copolymers.[1−6]

Block copolymers have been known to exhibit a microphase separation from a disordered state to an ordered state either upon cooling or upon heating, where the former behavior is called the upper order−disorder transition (UODT) and the latter the lower disorder−order transition (LDOT). The UODT behavior is observed in most of block copolymers including typical ones from polystyrene (PS) and polybutadiene (PBD) or from PS and polyisoprene (PI). The unfavorable interactions between dissimilar monomers comprising a given block copolymer are considered to be the cause for such behavior.[5] The LDOT behavior is exhibited by some block copolymers containing PS. It has been recently shown experimentally by Russell and Mayes that the diblock copolymers of PS and several lower *n*-alkyl (ethyl to *n*-butyl) polymethacrylates (PA$_n$MA) reveal LDOT.[7−11] The diblock copolymer of deuterated PS and poly(vinyl methyl ether) (PVME) also revealed a strong evidence of the same behavior.[12] The LDOT behavior, analogous to the lower critical solution temperature (LCST) behavior of the corresponding polymer blends, is of entropic origin and considered to be in twofold ways.[13−16] The difference in volume fluctuations between constituent polymers can drive the observed self-association upon heating. Specific interactions (SI) between dissimilar monomers are another source of the LDOT. Such specific interactions require a particular spatial arrangement of the different monomers to be activated. Without specific interactions, monomer−monomer contacts are treated as nonpolar and cross-contacts as unfavorable. Heating induces more unfavorable contacts as the entropic loss due to the formation of the spatial arrangement of the monomers becomes less acceptable.

There have been in recent decades extensive theoretical developments to analyze the UODT behavior and transitions between equilibrium microstructures for molten block copolymers or systems containing block copolymers in weak to strong segregation regime.[5] Most of the theories developed so far are based on the common assumption of system incompressibility. Among them, Leibler suggested a Landau mean-field analysis based on the random-phase approximation (RPA) for weakly segregating diblock copolymer melts near spinodals.[17,18] It was revealed that asymmetric block copolymers undergo a general sequence of transitions from a disordered state to a metastable bcc, then to a hex, and then finally to a lam morphology upon cooling. A symmetric one was shown to exhibit a continuous transition from the disordered state to the lam morphology. Leibler's mean-field theory was later corrected using a Hartree analysis by Fredrickson and Helfand[19] and then by Mayes and Olvera de la Cruz[20] or by Barrat and Fredrickson[21] in a more general way to include concentration fluctuation effects. It was shown that for a copolymer of finite molecular weight the continuous transition disappears, and the direct transition to hex or lam morphology is possible. It is a central concept in

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all of the works just mentioned that a composite parameter $N\chi$, where N and χ are the copolymer chain size and Flory's interaction parameter, respectively, forms a relevant parameter to describe the phase behavior of block copolymers.

The generalization of Leibler's mean-field Landau analysis and Fredrickson–Helfand's fluctuation theory to compressible block copolymers has recently been made by the present author based on the so-called compressible RPA.[22-29] Finite compressibility was incorporated into the theory through effective RPA interaction fields, which is obtained from an off-lattice equation-of-state (EOS) model by Cho and Sanchez (CS).[22,30] In the earlier part of our work, compressible Landau free energies treating of classical microphase morphologies were formulated to describe the following two cases: first, diblock copolymer melts with favorable cross-contact interactions exhibiting LDOT due to compressibility difference between blocks;[24] second, those exhibiting UODT due to unfavorable energetics.[25,27] The continuous transition was shown to disappear even for a symmetric copolymer in the mean-field situation, and the general sequence of transitions (disorder–bcc–hex–lam) is sustained at all compositions, if there is an appreciable compressibility difference. A fluctuation correction to the latter Landau energy for compressible UODT systems led to the formulation of a Hartree free energy, which is suitable for the analysis of the effects of fluctuations and compressibility on the copolymer phase behavior.[28] The direct transition from the disordered state to hex or to lam morphology with the chain size decrease and the pressure response of the transitions resulted from those two effects. It was shown that a new effective Flory-type interaction parameter χ_{cRPA} together with N now serves a role of the relevant parameter, where χ_{cRPA} carries not only the change in contact interactions but also the compressibility difference between blocks.

The phase behavior of the homologous series of PS-*b*-PA$_n$MA with varying size n of alkyl groups is of our particular interest.[7-11,31-34] According to Russell and Mayes,[7-11] in the case of $n = 1$ or $n \geq 6$, PS-*b*-PA$_n$MA, where the difference in the solubility parameter δ between blocks is appreciable, exhibits common UODT behavior. The pressure dependence of the observed ODT's for UODT-showing PS-*b*-PA$_n$MA is quite diversified. For the copolymers with $n = 1$ (methyl) and $n = 12$ (*n*-lauryl) of typical molecular weights, the pressure coefficients $\Delta T_{\mathrm{UODT}}/\Delta P$ of their UODT's are +23 and +13 K/100 MPa, respectively. In the case of $n = 6$ (*n*-hexyl), PS-*b*-PA$_6$MA shows $\Delta T_{\mathrm{UODT}}/\Delta P$ of −60 K/100 MPa, and the pressure coefficients of the copolymers with $n > 6$ are gradually changed to that of PS-*b*-PA$_{12}$MA. Using our Landau analysis, we have already studied such diversified pressure responses of ODT in UODT-type block copolymers.[26,27] The sign and the absolute value of the pressure coefficients were shown to be the sensitive measure of the difference in compressibility or self-interactions between blocks. The PS-*b*-PA$_1$MA copolymer, like other typical UODT systems such as PS-*b*-PBD[35] and PS-*b*-PI,[36] feels little compressibility difference. The unfavorable energetics in the copolymer are strengthened upon pressurization due to the density increase to yield the positive $\Delta T_{\mathrm{UODT}}/\Delta P$. More compressibility difference is felt by the PS-*b*-PA$_6$MA copolymer than by the PS-*b*-PA$_1$MA. Phase miscibility is always hampered by the compressibility difference, which is suppressed by the applied pressure eventually to yield the negative $\Delta T_{\mathrm{UODT}}/\Delta P$. This so-called anomalous UODT behavior is also observed in poly(ethylene–propylene)-*b*-poly(ethylethylene) copolymers.[37]

In the meantime, PS-*b*-PA$_n$MA with $n = 2-4$ reveals LDOT behavior, where δ's of constituent blocks are quite close.[7-11,38] All of those LDOT copolymers show the enhanced miscibility by the applied pressure. For $n = 2$, 3, and 4, the pressure coefficients $\Delta T_{\mathrm{LDOT}}/\Delta P$ of their LDOT's are respectively 100, 90, and 147 K/100 MPa,[9-11] where the molecular weights of the samples used were varied to have similar ODT's. Meanwhile, Kim and Russell performed very recently small-angle X-ray scattering (SAXS) and neutron scattering (SANS) measurements on PS-*b*-PA$_5$MA with $n = 5$ (*n*-pentyl), which was missing in Russell and Mayes' compendium of LDOT diblock copolymers.[31-34,39] The scattering results demonstrated that PS-*b*-PA$_5$MA revealed an astonishing phase diagram exhibiting an immiscibility loop with both LDOT and UODT. It was further shown that the pressure coefficients of PS-*b*-PA$_5$MA were 725 K/100 MPa and −725 K/100 MPa for LDOT and UODT, respectively.[33] Prior to the experiments on this system, the loop phase behavior at ambient pressure has rarely been reported for either blends or block copolymers of apparently weakly interacting constituents. The measured pressure coefficients are by far larger than any other reported value. It was also found that the loop phase diagram is extremely sensitive to the variation of chain sizes.

In this study, we focus on the investigation of the origin of immiscibility loop phase behavior for PS-*b*-PA$_5$MA with the peculiar pressure coefficients of both ODT's. We intuitively expect that understanding of the phase behavior of PS-*b*-PA$_5$MA is key to the construction of the whole picture of the elusive behavior of these homologous series of LDOT-type PS-*b*-PA$_n$MA copolymers. In searching for a plausible explanation of the observed loop, certain specific (directional) interactions between dissimilar monomers are taken into account.[40] A simple treatment of ten Brinke and Karasz[14] or of Sanchez and Balasz[15] is employed to add an entropic component to cross-contact interactions. To elucidate the observed behavior of PS-*b*-PA$_5$MA, our recent development of the simple Hartree analysis for compressible block copolymers is to be used. It is reemphasized that χ_{cRPA}, which is not a simple exchange energy but a complicated function of various molecular parameters, composition, and even chain sizes, plays a central role here. $N\chi_{\mathrm{cRPA}}$ as the relevant parameter replaces $N\chi$ in Leibler's incompressible theory and the corresponding Hartree theory.

Theory

Let us begin with the system description. The system of interest consists of A–B diblock copolymers with N_{A} monomers of A type and N_{B} monomers of B type to have the overall size N $(= N_{\mathrm{A}} + N_{\mathrm{B}})$. All the monomers in the system are assumed to have the identical diameter σ. The $\phi_{\mathrm{A}} \equiv N_{\mathrm{A}}/N$ defines a volume fraction of A monomers on the copolymer chains. The ϕ_{B} then indicates that of B monomers and thus $\phi_{\mathrm{B}} = 1 - \phi_{\mathrm{A}}$. The system is allowed to be compressible. We denote as η_f the fraction of free volume in the system and as $\eta = 1 - \eta_f$ the total packing density that is the fraction of volume occupied by all the monomers present.

The Landau analysis is a useful tool to probe weakly phase segregating block copolymer systems in the mean-field situation. The difference δF in free energies between ordered and disordered states is expanded as a power series in the order parameter $\bar{\psi}(\vec{r})$ ($\equiv \langle \phi_A(\vec{r}) - \phi_A \rangle/2 - \langle \phi_B(\vec{r}) - \phi_B \rangle/2$), where $\phi_i(\vec{r})$ is the local concentration of i-monomers, and the brackets indicate the thermal average of the difference between the local and the global concentrations.[41] The δF is then rewritten as the power series in the Fourier transformed $\bar{\psi}(\vec{q})$, where the Fourier component $\vec{q}$ implies physically the scattering vector. We define $\bar{\psi}_n/\sqrt{n}$ as the amplitude of the $\bar{\psi}(\vec{q})$ for periodically patterned ordered systems characterized by n reciprocal lattice vectors $\vec{Q}$'s, whose magnitudes are all $|\vec{q}| = q$. The Landau free energy expansion is approximated to the sum only containing the most important contributions from the fastest growing waves with a characteristic wavenumber q^*:[27]

$$N\delta F/\eta kT \approx$$
$$N[2\chi_s - 2\chi_{cRPA}]\bar{\psi}_n^{\,2} - \left[a_n + \frac{N\Delta\bar{\Gamma}_{12}}{\eta\bar{\Gamma}_{22}}\right]\bar{\psi}_n^{\,3} + b_n\bar{\psi}_n^{\,4} \quad (1)$$

where k is the Boltzmann constant. We take for convenience that A block is less compressible than B block. The second-order term in eq 1 contains an effective Flory-type interaction parameter, χ_{cRPA}, which is found to be $\chi_{cRPA} \equiv \chi_{app} + \chi_{comp}$.[27,28] The χ_{app} is given by $\chi_{app} \equiv h_z(\Delta\epsilon/kT)(f_p/2)|u(\eta)|$, where $\Delta\epsilon$ is the exchange energy between the characteristic i,j contact interactions ϵ_{ij}'s as $\Delta\epsilon \equiv \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}$. The symbol h_z implies the number of nonbonded nearest neighbors around a given monomer. The $u(\eta)$ in χ_{app}, which is defined as $u(\eta) = (\gamma/C)^4\eta^4 - (\gamma/C)^2\eta^2$ with $\gamma = 1/\sqrt{2}$ and $C = \pi/6$, describes the density dependence of attractive nonbonded interactions in the CS equation-of-state model, and $f_p = 4$ is a numeric prefactor associated with $u(\eta)$. The remaining χ_{comp} is given as $\chi_{comp} = \bar{\Gamma}_{12}^{\,2}/2\eta\bar{\Gamma}_{22}$ evaluated at q^*, where $\bar{\Gamma}_{ij}$ is the proper second-order vertex functions associated with the order parameter $\bar{\psi}(\vec{q})$ for the compressible copolymer system. Those vertex functions are given in the Appendix. It was shown in our previous communications that $\bar{\Gamma}_{12}$ ($\propto$ [$\epsilon_{AA} - \epsilon_{BB}$] at $\phi_A = 0.5$), and thus χ_{comp} represents the compressibility difference between block components in a given system. The $2\chi_s$ is the well-known Gaussian term (eq III-22 in ref 17) in the Landau free energy by Leibler for incompressible UODT diblock copolymer melts. It can also be shown that $\eta[2\chi_s - 2\chi_{app}] = \bar{\Gamma}_{11}$, and thus $\eta[2\chi_s - 2\chi_{cRPA}] = \bar{\Gamma}_{11} - \bar{\Gamma}_{12}^{\,2}/\bar{\Gamma}_{22}$. In eq 1, a_n and b_n are identical with α_n and β_n (eqs V-10, 11, 14, 15, and 26 in ref 17) for a proper microphase morphology, respectively, in Leibler's work. The coefficient Δ can be written as[27]

$$\Delta = \bar{a}_n(\bar{\Gamma}^{(3)}_{112}(1) + \bar{\Gamma}^{(3)}_{121}(1) + \bar{\Gamma}^{(3)}_{211}(1)) \quad (2)$$

where $\bar{\Gamma}^{(3)}_{112}(1)$ and the other two in eq 2 are the coupled third-order vertex functions evaluated in the case that the three wave vectors form an equilateral triangle. Such third-order vertex functions are also summarized in the Appendix. The $\bar{a}_n$ associated with them is given as $\bar{a}_n = (4/3!)(12/(\sqrt{6})^3)$, $(1/3!)(12/(\sqrt{3})^3)$, and 0 for bcc, hex, and lam morphology, respectively. It is shown that $-\Delta\bar{\Gamma}_{12}/\bar{\Gamma}_{22}$ gives a nonvanishing and negative contribution to the free energy for bcc and hex morphologies, if $\bar{\Gamma}_{12}$ is nonzero. This procedure yields the sequence of transition of lam → hex → bcc → disorder upon heating for the entire range of composition again with nonvanishing $\bar{\Gamma}_{12}$. The mean-field continuous transition exists only if the copolymer is symmetric ($a_n \rightarrow 0$ as $\phi_A \rightarrow 0.5$), and there is no compressibility difference ($\bar{\Gamma}_{12} \rightarrow 0$ as $|\epsilon_{AA} - \epsilon_{BB}| \rightarrow 0$).[27]

To include the concentration fluctuation effects, a simplified Hartree analysis adopted by Fredrickson and Helfand for incompressible diblock copolymers[19,42] or by Fredrickson and Leibler for a copolymer in a neutral solvent[43] has been applied to the compressible Landau free energy in eq 1.[28] The Landau energy is taken as a reference and corrected self-consistently. The desired free energy δF_H in the Hartree analysis can be obtained as[28]

$$N\delta F_H/\eta kT =$$
$$\frac{N}{2\Gamma'_4}(S^{-2}(q^*) - {S_D}^{-2}(q^*)) + \frac{3x^*/2\pi}{\sqrt{\tilde{c}}}(\sqrt{S^{-1}(q^*)} -$$
$$\sqrt{{S_D}^{-1}(q^*)}) - [a_n + N\Delta\bar{\Gamma}_{12}/\eta\bar{\Gamma}_{22}]\bar{\psi}_n^{\,3} +$$
$$\left(b_n - \frac{N\Gamma'_4}{2}\right)\bar{\psi}_n^{\,4} \quad (3)$$

where $\eta\Gamma'_4$ is equal to the uncoupled fourth-order vertex function $\bar{\Gamma}^{(4)}_{1111}$ evaluated for four wave vectors of $\pm\vec{Q}$, $\pm\vec{Q}$.[44] Such fourth-order vertex functions are also given in the Appendix. The symbol S^{-1} represents the Hartree correction to the effective second-order vertex term Γ'_2, which is defined as $[2\chi_s - 2\chi_{cRPA}]$. The S^{-1} at q^* satisfies the following self-consistent Hartree equation:

$$S^{-1}(q^*) = \Gamma'_2(q^*) + \Gamma'_4(q^*)\bar{\psi}_n^{\,2} + \frac{\Gamma'_4(q^*)3x^*/2\pi}{N\sqrt{S^{-1}(q^*)\tilde{c}}} \quad (4)$$

The new symbol $\tilde{c}$ is given by $\tilde{c} = Nx^*/3\cdot\partial^2\Gamma'_2/\partial x^2)_{x^*}$, where x implies the squared dimensionless wavenumber as $q^2R_G^{\,2}$ with the gyration radius R_G of chains. The corresponding x^* is then evaluated at q^*. The $S_D^{\,-1}$ represents S^{-1} in the disordered state and can thus be obtained if $\bar{\psi}_n$ in eq 4 is taken to be zero. This Hartree free energy can be shown to converge to the Landau energy in eq 1, as $N \rightarrow \infty$. Transition temperatures and equilibrium microphase morphologies for compressible block copolymers with finite sizes are to be calculated by the minimization of the Hartree free energy in eq 3, along with S^{-1} in eq 4, with respect to $\bar{\psi}_n$. The direct first-order transitions from the disordered state to lam or other morphologies are now allowed, as the chain size N decreases.

It is well documented in our previous publications that $N\chi_{cRPA}(q^*)$ serves a role of relevant parameter in compressible block copolymers.[27,28] On the basis of this understanding, it can be easily seen that the mean-field spinodal condition yields $N\chi_{cRPA}(q^*) = 10.495$ universally for a symmetric copolymer.[27] When the fluctuation effects are considered, our Hartree free energy in eq 3 suggests that $N\chi_{cRPA}(q^*)$ at the disorder-to-lam ODT for a symmetric copolymer is determined solely by the total chain size N as $N\chi_{cRPA}(q^*) = 10.495 + 41.022N^{-1/3}$, regardless of the choice of polymer pairs. The fluctuation effects suppress demixing in the mean-field situation.[28]

In treating a block copolymer system with specific interactions, a simple approach devised by ten Brinke and Karasz or by Sanchez and Balasz is adopted here.[14-16] The central concept is to take A,B cross-

Table 1. Volumetric Data for Homologous PA$_n$MA Series from $n = 2$ to $n = 6$ in the Form of the Isothermal Padé Equation, Which Is Mathematically Stated as $\ln(V/V_0) = \{\omega/(1-\omega)B_1\}[1 - (1 + B_1P/\omega B_0)^{1-w}]$ with $B_1 = 10.2$ and $\omega = 0.9$[a]

n (size of n-alkyl group)	$1/V_0$ (= $c - dT$) (g/cm^3)		B_0 (= $a\mathrm{e}^{-bT}$) (MPa)	
	c	d ($\times10^{-4}$)	ln a	b
2	1.3901	8.2191	9.7384	0.0061
3	1.2848	6.7654	9.1289	0.0049
4	1.2355	6.2635	9.0834	0.0047
5[b]	1.2197	6.4427	9.1548	0.0049
6	1.2212	7.1308	8.9897	0.0049

[a] $1/V_0$ and B_0 are density and bulk modulus at 0.1 MPa, respectively. [b] For $n = 5$ (n-pentyl), the volume data are obtained from the proper interpolation using other four data sets. [c] T and P indicate temperature in K and pressure in MPa, respectively. [d] Data for polymers given above except PA$_5$MA are from Zoller and Walsh's book on the PVT properties of polymers.[46]

contact interaction parameter as a kind of free energy that possesses not only enthalpic but also entropic contributions. Consider that the cross-contact interaction can be nonspecific with a characteristic energy parameter ϵ_{AB} and specific with the energy parameter $\epsilon_{\mathrm{AB}} + \delta\epsilon$. A symbol d denotes the ratio of the statistical degeneracies of nonspecific and specific cross-contact interactions. The fraction θ of the total number of cross-contacts that are specific is given from Boltzmann statistics as

$$\theta = [1 + d\exp(-\delta\epsilon/kT)]^{-1} \tag{5}$$

The free energy $\epsilon^{\mathrm{s}}_{\mathrm{AB}}$ per one cross-contact can be suggested as

$$\epsilon^{\mathrm{s}}_{\mathrm{AB}} = \epsilon_{\mathrm{AB}} + \delta\epsilon - kT\ln[\theta(1 + d)] \tag{6}$$

The previously defined free energy parameter $\epsilon^{\mathrm{s}}_{\mathrm{AB}}$ now replaces the nonspecific ϵ_{AB} in the original formulation.

Calculations of Phase Behavior

To describe the compressibility of PS-*b*-PA$_5$MA, we need the volumetric data of the two constituent homopolymers. Those data for PS can be found elsewhere.[45] However, there have been no reported data for the latter homopolymer. This situation is circumvented by analyzing the volume data of adjacent homologues of PA$_5$MA, which were reported by Zoller and Walsh,[46] to perform proper interpolation for PA$_5$MA. In Table 1, we listed the data for the volume of PA$_2$MA (ethyl) to PA$_6$MA (n-hexyl) in the form of the isothermal Padé equation,[45,47] which represents the published data for the respective polymers in Zoller and Walsh's book. The regression equations for those four homologous polymers are then used to generate the interpolated volume of PA$_5$MA (n-pentyl) at a given set of temperature and pressure. Finally, the whole set of interpolated volume data is used to obtain the desired regression (Padé) equation for PA$_5$MA.

The volume data for PS and PA$_5$MA are now used to fit the requisite molecular parameters for the CS model. Those parameters include the self-interaction parameter $h_z\epsilon_{ii}$, the model monomer diameter σ_i, and the chain size N_i/MW$_i$, where MW$_i$ implies the molecular weight. For PS, all the three homopolymer parameters are adjusted to best fit its volume data to yield $\sigma_{\mathrm{A}} = 4.039$ Å, $h_z\epsilon_{\mathrm{AA}}/k = 4107$ K, and $N_{\mathrm{A}}/\mathrm{MW}_{\mathrm{A}}\cdot\pi\sigma_{\mathrm{A}}{}^3/6 = 0.41857$ cm^3/g. However, the monomer diameter of PA$_5$MA is set to that of PS, and then other two parameters are adjusted to best fit the volume data of PA$_5$MA. For simplicity purposes, the CS model assumes the identical diameter for all the monomers in the system. Those molecular parameters for PA$_5$MA are then as follows: $\sigma_{\mathrm{B}} = 4.039$ Å; $h_z\epsilon_{\mathrm{BB}}/k = 3680.9$ K; $N_{\mathrm{B}}/\mathrm{MW}_{\mathrm{B}}\cdot\pi\sigma_{\mathrm{B}}{}^3/6 = 0.43073$ cm^3/g. It is not necessary to specify h_z at this stage; $h_z\epsilon_{ii}$ together suffices for our need. As all the monomer diameters are identical, the difference in compressibility between constituents is described solely by the difference in self-interaction parameters ϵ_{ii}'s. A constituent with larger ϵ_{ii}, PS in this case, is less compressible.

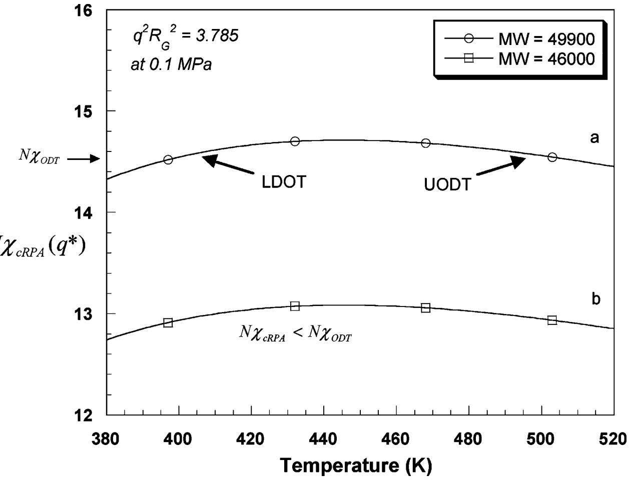

Figure 1. Relevant parameter $N\chi_{\mathrm{cRPA}}(q^*)$ at ambient pressure for the symmetric PS-*b*-PA$_5$MA copolymers of MW = 49 900 (a) and 46 000 (b) plotted as a function of temperature.

We now turn our attention to the cross-interaction parameter $\epsilon^{\mathrm{s}}_{\mathrm{AB}}$ with specific interactions considered. In this case, it is additionally requisite to have explicit h_z and d. In dense polymeric liquids, it is quite natural that nearest neighbors surrounding a monomer consist of h_z nonbonded monomers and two bonded monomers. We then choose $h_z \approx 10$, which is harmonious with the conventional face-centered-cubic lattice. The degeneracy ratio d is simply fixed to 11, implying that the specific interaction pair is formed only in the limited range of spatial arrangements of two dissimilar monomers. The nonspecific part ϵ_{AB} and specific part $\delta\epsilon$ of $\epsilon^{\mathrm{s}}_{\mathrm{AB}}$ are determined from the experimental ODT's (loop) at ambient pressure for the symmetric PS-*b*-PA$_5$MA copolymer of overall MW = 49 900 by Kim and Russell.[31] In this procedure, our Hartree free energy,[28] not the Landau energy, is used to take the fluctuation (finite size) effects into account. The Hartree energy predicts that the copolymer with this size reveals the disorder-to-lamella transition, which is indeed the observed behavior.[31] The nonspecific cross-contact interaction is characterized by $\epsilon_{\mathrm{AB}}/(\epsilon_{\mathrm{AA}}\epsilon_{\mathrm{BB}})^{1/2} = 0.983\,18$, yielding repulsive $h_z\Delta\epsilon/k = 142.5$ K. The specific interaction is adjusted with $\delta\epsilon/\epsilon_{\mathrm{AA}} = 0.18$. The given $\delta\epsilon$ can yield the energy gain per one monomer ($\sigma = 4.039$ Å) as $f_{\mathrm{p}}h_z(\delta\epsilon/2)|u(\eta)|\phi[1 - \phi]\theta$, which only reaches ~0.065 kJ/mol with θ = ~0.1 at ~400 K for a symmetric copolymer. For comparison purposes, the solubility parameter δ of PS or PA$_5$MA, which is usually of ~18 MPa$^{1/2}$, gives the cohesive energy per 1 mol of chemical repeating units of ~32 kJ/mol, as its molar volume is typically ~100 cm^3/mol.

Plot a of Figure 1 shows the $N\chi_{\mathrm{cRPA}}$ for the symmetric PS-*b*-PA$_5$MA of MW = 49 900 ($N = 1019.7$) as a function

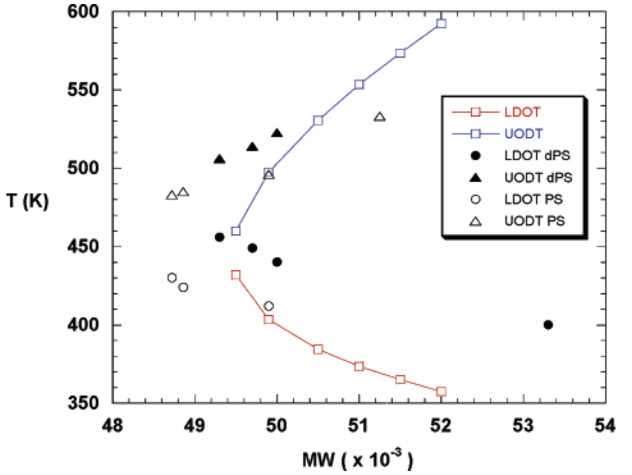

Figure 2. Peculiar chain size dependence of the loop at ambient pressure for the symmetric PS-*b*-PA$_5$MA copolymers. Theoretical ODT's (open squares) are compared with the measured ones for hydrogeneous samples (open circles, triangles) from ref 31 and for deuterated samples (filled circles, triangles) from ref 32.

of temperature. It is seen in this figure that $N\chi_{\mathrm{cRPA}}$ over the temperature range from 380 to 520 K possesses a maximum. The modified exchange energy $\Delta\epsilon$ ($= \epsilon_{\mathrm{AA}} + \epsilon_{\mathrm{BB}} - 2\epsilon^{\mathrm{s}}_{\mathrm{AB}}$) becomes more repulsive with temperature increase, as the entropic penalty of forming specific interaction pairs gets less acceptable. This action makes χ_{app} and thus χ_{cRPA} increase with temperature. Because $\Delta\epsilon$ in χ_{app} is scaled by the thermal energy kT, χ_{app} starts to decrease beyond a certain temperature, around which $N\chi_{\mathrm{cRPA}}$ reveals a maximum. Such a maximum in $N\chi_{\mathrm{cRPA}}$ indicates the loop-type character. It is shown that $N\chi_{\mathrm{cRPA}} > 10.495$, which suggests that the copolymer is fully ordered in the mean-field sense. The concentration fluctuations, however, significantly affect the mean-field picture by the fact that the threshold $N\chi_{\mathrm{cRPA}}$ at ODT ($= 10.495 + 41.022\,N^{-1/3}$) is equal to 14.57 according to our Hartree analysis.[28] This condition then suggests that the copolymer is ordered only between 404 and 497 K, i.e., the loop with LDOT and UODT together. The Hartree free energy yields that the ordered pattern of the copolymer in between these two ODT's is lamellar. We applied the same argument to the symmetric PS-*b*-PA$_5$MA of MW = 46 000 ($N = 940.0$) shown in plot b of Figure 1. The mean-field condition yields this copolymer also in the ordered state over the same temperature range. The reduction in chain size, however, renders the copolymer fully disordered, as the threshold $N\chi_{\mathrm{cRPA}}$ at ODT is rather increased to 14.68 due to the fluctuation effects.

In Figure 2, the chain size dependence of the ODT at 0.1 MPa is depicted, where not only calculated values but also the measured ones for hydrogeneous PS-*b*-PA$_5$MA (open symbols)[31] and for deuterated PS-*b*-PA$_5$MA (filled symbols)[32] are drawn together. It should be mentioned that the calculated ODT for the hydrogeneous copolymer of MW = 49 900 are very close to those measured because the adjustment of the molecular parameters, ϵ_{AB} and $\delta\epsilon$, is performed for this particular sample. The extraordinary chain size dependence of the ODT is clearly demonstrated in this figure, even though the theoretical prediction is somewhat stronger than the experimental results. Such behavior is caused by the fluctuation effects. The reduction in N lowers $N\chi_{\mathrm{cRPA}}$, but the threshold $N\chi_{\mathrm{cRPA}}$ value at ODT is conversely increased due to the fluctuations.

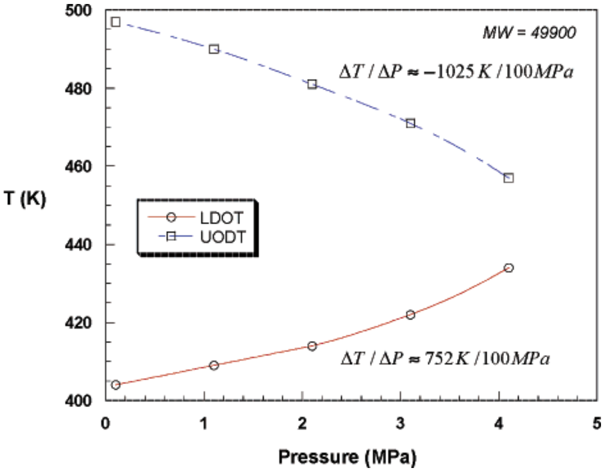

Figure 3. Theoretically calculated LDOT and UODT comprising the loop as a function of pressure for the hydrogeneous PS-*b*-PA$_5$MA of MW = 49 900 ($N = 1019.7$) at $\phi = 0.5$. It needs to be mentioned that the loop completely disappears at 4.37 MPa.

One of the merits of the present analysis with finite compressibility is the ability to predict the effects of hydrostatic pressure on the phase behavior of the copolymer. Figure 3 shows the calculated pressure dependence of ODT for the copolymer of MW = 49 900. There is nonlinearity in the ODT change upon pressurization. However, we can provide rough values for the pressure coefficient by estimating the temperature change ΔT_{ODT} over the range of pressure shown in the figure. It is obtained that $\Delta T_{\mathrm{ODT}}/\Delta P$ is 752 K/100 MPa and −1025 K/100 MPa for the LDOT and UODT of the loop, respectively. Those values are indeed comparable to the measured ones of ±725 K/100 MPa for the deuterated copolymer with MW = 50 000, which are by far larger than any other reported ones for polymeric systems.[33] It can be understood that this unprecedented pressure coefficient is the outcome of compressibility difference between PS and PA$_5$MA ($|\epsilon_{\mathrm{AA}} - \epsilon_{\mathrm{BB}}|/\epsilon_{\mathrm{AA}} = 0.104$) along with the effect of concentration fluctuations on the phase behavior of the loop-forming PS-*b*-PA$_5$MA system. It was discussed in our previous publications that the response of χ_{app} and χ_{comp} to pressure contribute to phase miscibility differently.[26-28] The χ_{app}, if $\Delta\epsilon > 0$, increases upon pressurization to hamper miscibility. On the contrary, the applied pressure reduces χ_{comp} to enhance miscibility because of the suppressed compressibility difference. Figure 4 depicts $N\chi_{\mathrm{app}}$ and $N\chi_{\mathrm{comp}}$ at 450 K as a function of pressure for the same copolymer used in Figure 3. The overall behavior of $N\chi_{\mathrm{app}}$ and $N\chi_{\mathrm{comp}}$ reduces $N\chi_{\mathrm{cRPA}}$ upon pressurization because $N\chi_{\mathrm{comp}}$ changes more rapidly than $N\chi_{\mathrm{app}}$. The loop is existent only when $N\chi_{\mathrm{cRPA}}$ is greater than the threshold value at ODT. The application of pressure up to 4.34 MPa is enough to diminish $N\chi_{\mathrm{cRPA}}$ below the threshold value.

It has been shown that there is a need for a certain specific interaction to understand the loop character of the phase behavior of PS-*b*-PA$_5$MA. We believe that similar arguments can be made on the energetics of other LDOT-showing PS-*b*-PA$_n$MA series, which is indeed the topic of our future work. The specific interactions do not have to be strong in an absolute sense to induce microphase separation. Even a weak directional

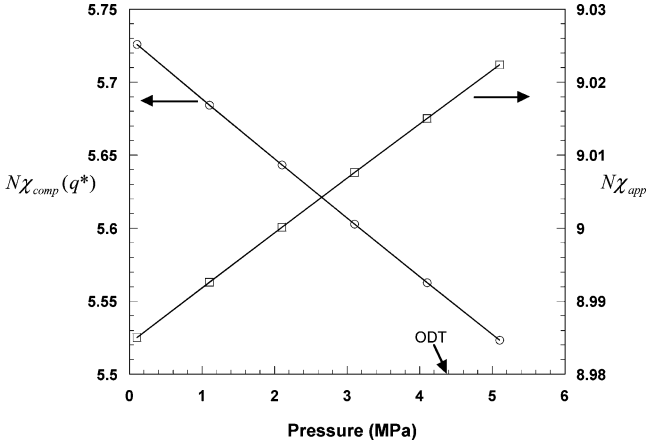

Figure 4. $N\chi_{\rm app}$ and $N\chi_{\rm comp}(q^*)$ at 450 K plotted against pressure for the same copolymer used in Figure 3. It is seen that $N\chi_{\rm cRPA}(q^*)$ $(= N\chi_{\rm app} + N\chi_{\rm comp})$ is a decreasing function of pressure. The copolymer system at 450 K is ordered ($N\chi_{\rm cRPA}(q^*) > N\chi_{\rm ODT}$) at 0.1 MPa, but becomes disordered ($N\chi_{\rm cRPA}(q^*) < N\chi_{\rm ODT}$) at $P > 4.34$ MPa.

interaction put into the system was shown to still cause self-assembly because the combinatorial entropy scales as $1/N$.[16,48] It is difficult in the present approach to reveal the precise description of specific interactions involved. However, one might conjecture from Ziaee and Paul's work[49–51] on the blends containing PS that the electron density distribution of styrene around the phenyl ring and the polar ester group of PA$_5$MA are possible contributors to such specific interactions. To verify this speculation, some spectroscopic methods such as Raman or IR spectroscopy are required to scrutinize the behavior of suspicious groups.

In closing, we should recognize certain limitations of the present work. The off-lattice CS model does not take chain flexibility issue into account. The difference in glass transition temperature T_g between PS and PA$_5$MA is large. Such disparity in chain flexibility between the two polymers in connection with concentration fluctuations could then affect the formation of specific interaction pairs near or below T_g of less flexible constituent, i.e., PS in this case. Therefore, the present theory is considered to better work at $T > T_g$ of PS. In the small-angle neutron scattering experiments by Kim and Russell, the deuterated PS-*b*-PA$_5$MA of MW = 46 000 in the fully disordered state exhibits the increase in the scattering intensity as temperature is lowered from T_g of PS.[32] This part is thus left out of our consideration here.

Concluding Remarks

To study the thermodynamic origin of an immiscibility loop and its unprecedented pressure dependence observed in the PS-*b*-PA$_5$MA diblock copolymer, we have performed the recently developed Hartree (fluctuation correction) analysis for compressible diblock copolymers based on the CS equation-of-state model. Aiming at the loop, certain specific interactions (SI) were incorporated in the theory by adding an entropic component into cross-contact interactions. The requisite molecular parameters (ϵ_{ii}, σ_i, N_i/MW_i) of the CS model to describe the two homopolymers, PS and PA$_5$MA, were first obtained from fitting the equation of state to their respective volume data. The nonspecific $\epsilon_{\rm AB}$ and specific $\delta\epsilon$ comprising the cross-contact interaction parameter $\epsilon^{\rm s}_{\rm AB}$ were determined from the experimental ODT data for the symmetric PS-*b*-PA$_5$MA copolymer using the Hartree free energy.

It was shown that an effective Flory-type interaction, $\chi_{\rm cRPA} \equiv \chi_{\rm app} + \chi_{\rm comp}$, where $\chi_{\rm app}$ indicates the exchange energy density and $\chi_{\rm comp}$ characterizes the compressibility difference between the constituent blocks, plays a key role in understanding of the phase behavior and the pressure responses of various thermodynamic transitions for the copolymers. The finite but small SI put into the system was shown to yield the relevant parameter $N\chi_{\rm cRPA}(q^*)$ possessing a loop character with a maximum when plotted against temperature. The copolymer of MW = 49 900 was shown to exhibit a loop with both LDOT and UODT in a feasible temperature range after the application of the threshold $N\chi_{\rm cRPA}(q^*)$ at ODT $(= 10.495 + 41.022N^{-1/3})$ due to fluctuations. The fluctuation effects yielded a strong chain size dependence of the loop. The reduction in the chain size by less than 10% was enough to completely remove the loop. It was revealed that the combination of fluctuations and compressibility difference between blocks caused the unprecedentedly large pressure coefficients of both ODT's of the loop. The resultant theoretical phase behavior was found to be harmonious with the experimental observations for the copolymer.

Finally, it needs to be noted that the validity of the Hartree theory, when applied to copolymers with experimentally available sizes, is in principle restricted to a region in the vicinity of the mean-field continuous transition point. We believe that the present work on the symmetric PS-*b*-PA$_5$MA yields the valuable interpretation of the astonishing phase behavior of the copolymer, as $|\epsilon_{\rm AA} - \epsilon_{\rm BB}|$, the measure of the compressibility difference in this system, merely amounts to ~10% of $\epsilon_{\rm AA}$. Predictions on the variety of phase behavior in other LDOT-showing homologous copolymers are thus being undertaken using the present methodology.

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Appendix. A Compressible RPA and Vertex Functions

A RPA is an approximation method to calculate the second-order monomer−monomer correlation function $G^{(2)}_{ij}$, or equivalently S_{ij}, and higher-order correlation functions $G^{(n)}$'s for the analysis of phase segregation in polymer blends and block copolymers.[17,18] Recently, the present author successfully combined the RPA with the CS equation-of-state model to analyze compressibility effects.[22−28]

We consider a system of A-*b*-B diblock copolymers with a volume fraction ϕ_i for i-monomers. Phase segregation in the system is characterized by proper order parameters. A natural choice of order parameters can be given as ψ_i $(\equiv \eta\langle\phi_i(\vec{r}) - \phi_i\rangle)$. The Landau expansion of the free energy is expressed as a series in the order parameter ψ_i, where the coefficients in the Landau expansion are called the vertex functions $\Gamma^{(n)}$. The ψ_i can also be expanded as a series in U_i, which is conjugate to the order parameter ψ_i. The coefficients appearing in the series for ψ_i are the correlation functions $G^{(n)}$'s. In estimating ψ_i, the correlation functions $G^{(n)}$ are supposed to be equal to those of noninteracting Gaussian copolymer chains, which are denoted as $G^{(n)0}$. The external potential U_i is then substituted with U_i^{eff}, which is corrected as $U_i^{\text{eff}} = U_i + W_{ij}\psi_j$ to properly take the interaction effects into account by an interaction field W_{ij}. The W_{ij} is formulated from the CS model to include the desired compressibility effects and thus includes attractive i, j interactions and excluded-volume interactions. The resultant self-consistent-field equation is solved by an iterative technique to obtain correlation functions. The correlation functions then yield the vertex functions. The second-order vertex function is related to energetic terms as

$$\Gamma_{ij}^{(2)} = S_{ij}^{\ -1} = S_{ij}^{0\ -1} + W_{ij}/kT \tag{A1}$$

where S_{ij}^0 is the second-order correlation function for the Gaussian chains. The third- or higher-order vertex functions are purely entropic and not involved in energetics.

The interaction field W_{ij} for a given block copolymer system is obtained from the nonideal part of the free energy of the CS model.[22-28] The W_{ij} consists of the two terms L_{ij} and $\epsilon_{ij}^{\text{app}}$ as

$$W_{ij}/kT = L_{ij}(\eta) - \epsilon_{ij}^{\text{app}}(\eta)/kT \tag{A2}$$

where L_{ij} and $\epsilon_{ij}^{\text{app}}$ are given as

$$\begin{aligned} L_{ij}(\eta) = \frac{3}{2}\Bigg[&\frac{4}{(1-\eta)^3} + \frac{6\eta}{(1-\eta)^4} - \\ &\left(2 - \frac{1}{N_i} - \frac{1}{N_j}\right)\frac{1}{(1-\eta)^2} - \left(\eta - \frac{\eta}{\bar{N}}\right)\frac{2}{(1-\eta)^3}\Bigg] + \\ &\left(\frac{1}{N_i} + \frac{1}{N_j}\right)\frac{1}{1-\eta} + \frac{\eta}{\bar{N}}\frac{1}{(1-\eta)^2} \end{aligned} \tag{A3}$$

and

$$\begin{aligned} -\epsilon_{ij}^{\text{app}}(\eta) = \\ h_z\epsilon_{ij}f_{\text{p}}\frac{u(\eta)}{\eta} + \Big(\sum_k \phi_k h_z\{\epsilon_{ik} + \epsilon_{jk}\}\Big)f_{\text{p}}\eta\frac{\partial}{\partial\eta}\left(\frac{u(\eta)}{\eta}\right) + \\ \frac{1}{2}\Big(\sum_{kl}\phi_k\phi_l h_z\epsilon_{kl}\Big)f_{\text{p}}\eta^2\frac{\partial^2}{\partial\eta^2}\left(\frac{u(\eta)}{\eta}\right) \end{aligned} \tag{A4}$$

In eq A3, N_{A} and N_{B} are the chain sizes of A and B blocks, respectively, and $\bar{N}$ is their average defined as $\bar{N} = [\sum\phi_i/N_i]^{-1}$.

For the analysis of compressible UODT diblock copolymer systems, it is more convenient to use the order parameters $\bar{\psi}$ and $\bar{\psi}_2$ in the main text instead of the original ψ_i.[25,27,28] The vertex function $\Gamma^{(n)}$ in the Landau expansion of the free energy in ψ_i is then replaced with the proper vertex function $\bar{\Gamma}^{(n)}$. It should be noted that the subscripts in $\bar{\Gamma}^{(n)}$ take 1 and 2, which respectively indicate $\bar{\psi}$ and $\bar{\psi}_2$, not the block components. The first three vertex functions $\bar{\Gamma}^{(n)}$'s are only written here as

$$[\bar{\Gamma}_{ij}^{(2)}] = \begin{bmatrix} \eta^2(\Gamma_{11}^{(2)} - 2\Gamma_{12}^{(2)} + \Gamma_{22}^{(2)}) & (\eta/2)(\Gamma_{11}^{(2)} - \Gamma_{22}^{(2)}) \\ (\eta/2)(\Gamma_{11}^{(2)} - \Gamma_{22}^{(2)}) & \Gamma_{11}^{(2)}/4 + \Gamma_{12}^{(2)}/2 + \Gamma_{22}^{(2)}/4 \end{bmatrix} \tag{A5}$$

$$\begin{aligned} \bar{\Gamma}_{ijk}^{(3)}(\vec{q}_1,\vec{q}_2,\vec{q}_3) = \\ -V_{mi}(\vec{q}_1)\, G_{mno}^{(3)\ 0}(\vec{q}_1,\vec{q}_2\vec{q}_3)\, V_{nj}(\vec{q}_2)\, V_{ok}(\vec{q}_3) \end{aligned} \tag{A6}$$

$$\begin{aligned} \bar{\Gamma}_{abcd}^{(4)}(\vec{q}_1,\vec{q}_2,\vec{q}_3,\vec{q}_4) = \\ [\textstyle\int d\vec{q}\ S_{ko}^{0\ -1}(\vec{q})\{G_{ijk}^{(3)0}(\vec{q}_1,\vec{q}_2,\vec{q})\, G_{opr}^{(3)0}(-\vec{q},\vec{q}_3,\vec{q}_4) + \\ G_{ipk}^{(3)\ 0}(\vec{q}_1,\vec{q}_3,\vec{q})\, G_{ojr}^{(3)0}(-\vec{q},\vec{q}_2,\vec{q}_4) + \\ G_{irk}^{(3)0}(\vec{q}_1,\vec{q}_4,\vec{q})\, G_{ojp}^{(3)\ 0}(-\vec{q},\vec{q}_2,\vec{q}_3)\} - \\ G_{ijpr}^{(4)\ 0}(\vec{q}_1,\vec{q}_2,\vec{q}_3,\vec{q}_4)]V_{ia}(\vec{q}_1)\, V_{jb}(\vec{q}_2)\, V_{pc}(\vec{q}_3)\, V_{rd}(\vec{q}_4) \end{aligned} \tag{A7}$$

where $G^{(n)^0}$ implies again the nth-order correlation function for the Gaussian chains. A new tensor V_{ij} in eqs A6 and A7 is given as

$$[V_{ij}] \equiv \begin{bmatrix} \eta(S_{\text{AA}}^{0\ -1} - S_{\text{AB}}^{0\ -1}) & \phi_{\text{A}}S_{\text{AA}}^{0\ -1} + (1-\phi_{\text{A}})S_{\text{AB}}^{0\ -1} \\ \eta(S_{\text{BA}}^{0\ -1} - S_{\text{BB}}^{0\ -1}) & \phi_{\text{A}}S_{\text{BA}}^{0\ -1} + (1-\phi_{\text{A}})S_{\text{BB}}^{0\ -1} \end{bmatrix} \tag{A8}$$

It should be noted that V_{i1} in eq A8 is independent of η because S_{ij}^{0-1} is proportional to $1/\eta$. The V_{i1} is indeed frequently employed to obtain higher-order vertex functions Γ_3 and Γ_4 in the incompressible RPA by Leibler.[17]

Using those expressions for L_{ij} and $\epsilon_{ij}^{\text{app}}$, $\bar{\Gamma}_{ij}^{(2)}$ can be rewritten explicitly as

$$\bar{\Gamma}_{11}^{(2)} = \eta^2(S_{\text{AA}}^{0\ -1} + S_{\text{BB}}^{0\ -1} - 2S_{\text{AB}}^{0\ -1}) - h_z(\Delta\epsilon/kT)f_{\text{p}}|u(\eta)|\eta \tag{A9}$$

$$\begin{aligned} \bar{\Gamma}_{12}^{(2)} = \frac{\eta}{2}[(S_{\text{AA}}^{0\ -1} - S_{\text{BB}}^{0\ -1}) + (L_{\text{AA}} - L_{\text{BB}})] + \\ \frac{h_z(\epsilon_{\text{AA}} - \epsilon_{\text{BB}})}{2kT}f_{\text{p}}\left[u(\eta) + \eta^2\frac{d}{d\eta}\left(\frac{u(\eta)}{\eta}\right)\right] + \\ \frac{\eta^2 h_z}{kT}\left[\left(\phi_{\text{A}} - \frac{1}{2}\right)(\epsilon_{\text{AA}} - \epsilon_{\text{AB}}) + \right. \\ \left.\left(\phi_{\text{B}} - \frac{1}{2}\right)(\epsilon_{\text{AB}} - \epsilon_{\text{BB}})\right]f_{\text{p}}\frac{d}{d\eta}\left(\frac{u(\eta)}{\eta}\right) \end{aligned} \tag{A10}$$

$$\begin{aligned} \bar{\Gamma}_{22}^{(2)} = \frac{1}{4}\Bigg[(S_{\text{AA}}^{0\ -1} + S_{\text{BB}}^{0\ -1} + 2S_{\text{AB}}^{0\ -1}) + \\ (L_{\text{AA}} + L_{\text{BB}} + 2L_{\text{AB}}) - \frac{\epsilon_{\text{AA}}^{\text{app}} + \epsilon_{\text{BB}}^{\text{app}} + 2\epsilon_{\text{AB}}^{\text{app}}}{kT}\Bigg] \end{aligned} \tag{A11}$$

It can be seen that $\bar{\Gamma}_{12}^{(2)} \propto (\epsilon_{\text{AA}} - \epsilon_{\text{BB}})$ for a symmetric diblock copolymer with $\phi_{\text{A}} = 1/2$ because the first and the third terms in eq A10 vanish in that case. Even for asymmetric copolymers, $\bar{\Gamma}_{12}^{(2)}$ is dominated by the second term with $(\epsilon_{\text{AA}} - \epsilon_{\text{BB}})$, as $S_{ij}^{0-1} \sim O(1/N)$ and $L_{\text{AA}} \approx L_{\text{BB}}$ for high polymers. As is mentioned in the main text, $\bar{\Gamma}_{11}^{(2)}$ becomes identical to $\eta[2\chi_{\text{s}} - 2\chi_{\text{app}}]$. The remaining $\bar{\Gamma}_{22}^{(2)}$ is shown to be mostly determined by the given sum of L_{ij}'s and $\epsilon_{ij}^{\text{app}}$'s.

Meanwhile, the equilibrium bulk density η is determined at a given set of temperature and pressure from the following CS equation of state:[22]

$$\begin{aligned} \beta P = \frac{1}{v^*}\left[\frac{3}{2}\frac{(\eta^2 + \eta^3)}{(1-\eta)^3} + \frac{\eta}{\bar{N}}\frac{(1+\eta/2)}{(1-\eta)^2}\right] + \\ \frac{f_{\text{p}}}{2}\frac{\beta\bar{\epsilon}}{v^*}[4(\gamma/C)^4\eta^5 - 2(\gamma/C)^2\eta^3] \end{aligned} \tag{A12}$$

where $\bar{\epsilon}$ (= $\sum\phi_i\phi_j\bar{\epsilon}_{ij}$) implies the average interaction parameter for the given copolymer system. All the monomers in the system are assumed for simplification to have the identical diameter σ so that v^* (= $\pi\sigma^3/6$) implies the monomer volume.

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