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Effective Flory interaction parameter and disparity in equation-of-state properties for block copolymers

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Abstract

It has been shown in our recent Landau analyses for a compressible block copolymer that its phase behavior is largely described by an effective Flory interaction parameter, which is subdivided into the density-dependent dimensionless exchange energy and the contribution from the 1,2- and 2,2-elements of the second-order vertex functions. Here, it is further shown that for the symmetric copolymer in the long chain limit those two vertex functions are directly proportional to disparity in equation-of-state properties between blocks and the isothermal bulk modulus, respectively. It is argued that the relative strength of molecular parameters governing each part of the effective Flory parameter determines whether a given copolymer experiences ordering (barotropic) or disordering (baroplastic) upon pressurization. Comparison of theory with experimental results is also mentioned.

Keywords: Effective Flory interaction parameter; Compressible block copolymers; Disparity in equation-of-state properties

1. Introduction

Studies on various behaviors of block copolymers have drawn tremendous interest from the polymer circle, because those materials exhibit self-assembly behavior to form microscopically ordered nanomaterials [1–3]. It is well known from the seminal work by Leibler [4] that the copolymer phase behavior is determined by composition ϕ, Kuhn segmental length N, and Flory's phenomenological interaction parameter χ_F. Typical block copolymers exhibit ordering upon cooling or upper order–disorder transition (UODT). Most of the analyses on block copolymers including Leibler's work are thus based on the common assumption of system incompressibility [3]. However, there have been numerous recent findings that strongly address a clear need for finite compressibility to interpret the compressible nature and the pressure responses of block copolymers. The relevant findings include ordering upon heating or lower disorder–order transition (LDOT) phenomena in styrenic block copolymer melts and films [5,6], loop-forming block copolymers [7,8], and baroplastic copolymers to utilize pressure-induced flow [8–10].

The LDOT and the pressure effects including baroplasticity have been successfully analyzed in a recent series of works by the present author on a compressible random-phase approximation (RPA) theory [11–16]. Finite compressibility was incorporated into the theory through effective RPA interactions, which is obtained from a molecular equation-of-state model by Cho and Sanchez (CS) [11,17]. χ_F was reinterpreted as $\chi_F = \chi_{app} + \chi_{comp}$, where χ_{app} is the density-dependent exchange energy and χ_{comp} represents compressibility difference between constituent blocks. Here in this communication, *it is our objective to express χ_F in more explicit phenomenological terms* in order to broaden our knowledge of pressure effects on block copolymers. We believe that better understanding of copolymer properties will help us to design new nanomaterials from them with aimed purposes such as pressure sensitivity.

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2. Theoretical consideration

Let us consider A–B diblock copolymers with N_i monomers of i-type. Copolymer chains are assumed as perturbed hard sphere chains of uniform size σ in a continuum. The nonbonded perturbed i,j-interactions are characterized by $\bar{\varepsilon}_{ij}$. A hard-core volume fraction of i-monomers on the copolymer chains is defined by $\phi_i \equiv N_i / \sum N_i$. We denote as η_f the fraction of free volume in the system, and as $\eta = 1 - \eta_\mathrm{f}$ the total dimensionless density of all the monomers present. Phase segregation in this system can be probed with the thermally averaged order parameters such as $\psi_i(\vec{r}) \equiv \langle \delta\eta_i(\vec{r}) \rangle = \langle \eta_i(\vec{r}) - \eta_i \rangle$, where $\eta_i = \phi_i \eta$ and $\eta_i(\vec{r})$ are global and local densities of i-block component, respectively. The basic scheme of our compressible RPA theory can be conceptually stated as follows. The Landau free energy F of the system can be obtained from an Edwards Hamiltonian with effective (RPA) interactions W_{ij} as $W_{ij} = \partial^2[a^\mathrm{ni}]/\partial\eta_i\partial\eta_j$, where a^ni is the nonideal (hard chain + nonbonded interaction) part of the Helmholtz free energy density a from the CS model [11–16]. The two contributions to a^ni are given as $\beta a^\mathrm{hc} = 3\eta/2(1-\eta)^2$ for the hard chain part in the long chain limit and $\beta a^\mathrm{nb} = \sum \phi_i \phi_j \beta\,\bar{\varepsilon}_{ij} u(\eta)/2$ for the nonbonded perturbed interaction part, where $u(\eta)$ describes the density dependence of the perturbed interactions as $u(\eta) = 4[(\gamma/C)^4\eta^4 - (\gamma/C)^2\eta^2]$ with $\gamma = 1/\sqrt{2}$, and $C = \pi/6$. The symbol β is $1/kT$ as usual. The proper derivatives of βa^hc and βa^nb, respectively yield $L_{ij}(\eta)$ and $-\beta\varepsilon_{ij}^\mathrm{app}(\eta)$ for βW_{ij} as

$$L_{ij}(\eta) = \frac{3+6\eta}{(1-\eta)^4} \tag{1}$$

in the long chain limit and

$$-\beta\varepsilon_{ij}^\mathrm{app}(\eta) = \beta\,\bar{\varepsilon}_{ij}\frac{u(\eta)}{\eta} + \left(\sum_k \phi_k \beta\{\bar{\varepsilon}_{ik} + \bar{\varepsilon}_{jk}\}\right)\eta\frac{\partial}{\partial\eta}\left(\frac{u(\eta)}{\eta}\right) + \frac{1}{2}\left(\sum_{kl}\phi_k\phi_l\beta\bar{\varepsilon}_{kl}\right)\eta^2\frac{\partial^2}{\partial\eta^2}\left(\frac{u(\eta)}{\eta}\right) \tag{2}$$

The equilibrium bulk density η is determined at a given set of temperature and pressure from the resultant CS equation-of-state as $\beta P v^* = \eta^2(\partial\beta a^\mathrm{ni}/\partial\eta) + \eta/\sum N_i$ [11,17], where v^* $(= \pi\sigma^3/6)$ is the volume of one monomer.

The Landau free energy F for the system can be expanded as a series in the order parameter ψ_i as $\beta F = \sum_{m=2}^{\infty}(1/m!) \int \mathrm{d}\vec{q}_1 \ldots \mathrm{d}\vec{q}_m \Gamma^{(m)}_{i_1\ldots i_m}(\vec{q}_1\ldots\vec{q}_m)\psi_{i_1}(\vec{q}_1)\ldots\psi_{i_m}(\vec{q}_m)$, where $\psi_i(\vec{q})$ is the Fourier transform of $\psi_i(\vec{r})$ with $\vec{q}$ denoting physically the scattering vector. The coefficient $\Gamma^{(m)}_{i_1\ldots i_n}$ is commonly known as the mth-order vertex function. It is well known that $\Gamma^{(2)}_{ij}(\vec{q}_1,\vec{q}_2) = S^{-1}_{ij}(\vec{q}_1,\vec{q}_2)\delta(\vec{q}_1+\vec{q}_2)$, where S_{ij} is the second-order monomer–monomer correlation function and $\delta(\vec{q}_1+\vec{q}_2)$ the Dirac delta function. The compressible RPA treatment yields $S^{-1}_{ij} = S^{0^{-1}}_{ij} + \beta W_{ij}$, where S^0_{ij} is the Gaussian i,j-correlation function for the given copolymers [11–16]. The conventional Gaussian functions for the corresponding incompressible copolymers are equated here to S^0_{ij}/η, where η corrects the diluted contact probabilities by the presence of free volume. While $\Gamma^{(2)}_{ij}$ is strongly dependent on the effective interactions, the higher-order $\Gamma^{(3)}_{ijk}$ and $\Gamma^{(4)}_{ijkl}$ are shown to be purely of entropic origin [12].

It is often useful to change the order parameters to $\overline{\psi}_1 \equiv (\psi_\mathrm{A} - \psi_\mathrm{B})/2\eta$ and $\overline{\psi}_2 \equiv \psi_\mathrm{A} + \psi_\mathrm{B}$, where the latter is equated to fluctuations in free volume fraction as $\overline{\psi}_2 = -\langle \delta\eta_\mathrm{f}(\vec{r}) \rangle$. The Landau energy F can then be expanded as a series in the Fourier-transformed $\overline{\psi}_i(\vec{q})$ and the mth-order vertex function is accordingly changed to $\overline{\Gamma}^{(m)}_{i_1\ldots i_n}$ as

$$\overline{\Gamma}^{(m)}_{i_1\ldots i_m} = \Gamma^{(m)}_{j_1\ldots j_m} M^{-1}_{j_1 i_1} \ldots M^{-1}_{j_m i_m} \tag{3}$$

where the matrix M_{ij} is defined as

$$[M_{ij}] = \begin{bmatrix} \dfrac{1}{2\eta} & -\dfrac{1}{2\eta} \\ 1 & 1 \end{bmatrix} \tag{4}$$

It can be seen that $\overline{\psi}_i = M_{ij}\psi_j$ [14].

The phase stability condition requires $\overline{\Gamma}_{11} - \overline{\Gamma}^2_{12}/\overline{\Gamma}_{22} > 0$ [11–14,18]. If $\overline{\Gamma}^{(2)}_{ij}$'s are rewritten more explicitly with L_{ij} and $-\varepsilon^\mathrm{app}_{ij}$ after the transformation in Eq. (3), then

$$\overline{\Gamma}^{(2)}_{11} = \eta\left[\eta\left(S^{0^{-1}}_\mathrm{AA} + S^{0^{-1}}_\mathrm{BB} - 2S^{0^{-1}}_\mathrm{AB}\right) - 2\beta\Delta\bar{\varepsilon}/2.|u(\eta)|\right] \tag{5}$$

$$\begin{aligned}\overline{\Gamma}^{(2)}_{12} = {}& \eta/2.\left[\left(S^{0^{-1}}_\mathrm{AA} - S^{0^{-1}}_\mathrm{BB}\right) + (L_\mathrm{AA} - L_\mathrm{BB})\right] \\ & + \beta(\bar{\varepsilon}_\mathrm{AA} - \bar{\varepsilon}_\mathrm{BB})/2.\left[u + \eta^2\frac{\mathrm{d}(u/\eta)}{\mathrm{d}\eta}\right] \\ & - \beta\Delta\bar{\varepsilon}/2.\left(1 - 2\phi_\mathrm{A}\right)\eta^2\frac{\mathrm{d}(u/\eta)}{\mathrm{d}\eta}\end{aligned} \tag{6}$$

$$\overline{\Gamma}^{(2)}_{22} = \left[\sum S^{0^{-1}}_{ij} + \sum L_{ij} + \sum\left(-\beta\varepsilon^\mathrm{app}_{ij}\right)\right]\Big/4 \tag{7}$$

In Eq. (5), $\Delta\bar{\varepsilon}$ is the exchange energy as $\Delta\bar{\varepsilon} = \bar{\varepsilon}_\mathrm{AA} + \bar{\varepsilon}_\mathrm{BB} - 2\bar{\varepsilon}_\mathrm{AB}$. In our previous works [14–16], an effective Flory-type χ_F was given as $\chi_\mathrm{F} = \chi_\mathrm{app} + \chi_\mathrm{comp}$, where χ_app was defined as $\beta\Delta\bar{\varepsilon}/2.|u(\eta)|$, and χ_comp as $\overline{\Gamma}^2_{12}/2\eta\overline{\Gamma}_{22}$. It is seen that $\overline{\Gamma}^{(2)}_{11}/\eta$ is expressed in a conventional form as (Gaussian $- 2\chi_\mathrm{app}$). It is desirable to relate $\overline{\Gamma}^{(2)}_{12}$ and $\overline{\Gamma}^{(2)}_{22}$ of χ_comp to more familiar terms. For simplicity, we consider a symmetric copolymer. The first and the third terms of $\overline{\Gamma}^{(2)}_{12}$ in Eq. (6) then vanish, and as a result the difference in self interactions, $\bar{\varepsilon}_\mathrm{AA} - \bar{\varepsilon}_\mathrm{BB}$, becomes proportional to $\overline{\Gamma}^{(2)}_{12}$. Disparity in equation-of-state properties between constituent blocks can be measured by $P_\phi(\equiv(\partial P/\partial\phi)_{T,v})$, which is obtained from the CS model as

$$P_\phi v^* = 1/2.\{\bar{\varepsilon}_\mathrm{AA} - \bar{\varepsilon}_\mathrm{BB} - \Delta\bar{\varepsilon}(1 - 2\phi_\mathrm{A})\}\eta^2\,\mathrm{d}u/\mathrm{d}\eta \tag{8}$$

The manipulation of $u(\eta)$ gives $[u + \eta^2\,\mathrm{d}/\mathrm{d}\eta(u/\eta)] = \eta\,\mathrm{d}u/\mathrm{d}\eta$. Therefore, it is seen at $\phi_\mathrm{A} = 1/2$ that

$$\eta\overline{\Gamma}^{(2)}_{12} = \beta P_\phi v^* \tag{9}$$

The remaining $\overline{\Gamma}^{(2)}_{22}$ is mostly determined by the given sum of L_{ij}'s and $\varepsilon^\mathrm{app}_{ij}$'s in the long chain limit, as $S^{0^{-1}}_{ij} \sim \mathrm{O}(1/N)$.

It can be further shown that $\sum L_{ij}/4 = 3(1+2\eta)/(1-\eta)^4$, and $\sum[-\beta\varepsilon_{ij}^{\mathrm{app}}]/4 = \sum \beta\,\bar{\varepsilon}_{ij}/4 \times 2[20(\gamma/C)^4\eta^3 - 6(\gamma/C)^2\eta]$. The isothermal bulk modulus B_T ($\equiv \eta\,\partial P/\partial\eta$) can be given again from the CS equation-of-state as $B_T = B_T^{\mathrm{hc}} + B_T^{\mathrm{nb}}$, where $\beta B_T^{\mathrm{hc}} v^* = 3\eta^2(1+2\eta)/(1-\eta)^4$ from the a^{hc} part in the long chain limit and $\beta B_T^{\mathrm{nb}} v^* = \sum \phi_i\phi_j\beta\,\bar{\varepsilon}_{ij}.2[20(\gamma/C)^4\eta^5 - 6(\gamma/C)^2\eta^3]$ from the a^{nb} part. It is then clear that

$$\eta^2\overline{T}_{22}^{(2)} \approx \beta B_T v^* \tag{10}$$

Therefore, it is concluded from Eqs. (9) and (10) that

$$2\chi_{\mathrm{comp}} = \overline{T}_{12}^2/\eta\overline{T}_{22} \approx \beta v^* P_\phi^2/\eta B_T \tag{11}$$

As $B_T > 0$, $\chi_{\mathrm{comp}} \geq 0$ and always hampers miscibility [19].

3. Discussion

The dependence of $|u(\eta)|$ on η in its useful range is fairly linear. It is typical that polymer density or volume changes by ~8% with $\Delta P = 100$ MPa. The increase of η then yields a similar increase of $|u(\eta)|$ and thus χ_{app} if $\Delta\bar{\varepsilon} > 0$. Meanwhile, P_ϕ changes by less than 8%. However, B_T, which is more dependent on B_T^{hc} than on B_T^{nb}, increases by ~80% along with $\Delta P = 100$ MPa. As a result, χ_{comp} decreases strongly upon pressurization. Therefore, the magnitudes of $\Delta\bar{\varepsilon}$ and $\bar{\varepsilon}_{\mathrm{AA}} - \bar{\varepsilon}_{\mathrm{BB}}$ determine the relative strength of χ_{app} and χ_{comp}, which in turn decides whether a given copolymer exhibits ordering (barotropic) or disordering (baroplastic) upon pressurization. We will give some illustrations in the following paragraph.

An example of barotropic systems is polystyrene-*b*-polyisoprene [20]. It was shown that $\Delta\bar{\varepsilon}/\bar{\varepsilon}_{\mathrm{AA}} = 0.0093$ and $(\bar{\varepsilon}_{\mathrm{AA}} - \bar{\varepsilon}_{\mathrm{BB}})/\bar{\varepsilon}_{\mathrm{AA}} = 0.012$ well explain the experimental phase behavior [13]. This system reveals dominant χ_{app} and vanishingly small χ_{comp}, so that it becomes barotropic with $(\partial T_{\mathrm{UODT}}/\partial P)_\phi = 20$–$30$ K/100 MPa. The theory gives the positive volume of disordering of $\Delta V_{\mathrm{mix}}/V = 3.8 \times 10^{-4}$, which is consistent with the observed value of $\Delta V_{\mathrm{mix}}/V = 4.5 \times 10^{-4}$ by Hadjuk et al. [20]. Polystyrene-*b*-poly(*n*-pentyl methacrylate) of $M_{\mathrm{w}} = 50\,000$, which exhibits an immiscibility loop between 443 and 528 K, is a marvelous example of baroplastic materials [7,8]. In this case $(\bar{\varepsilon}_{\mathrm{AA}} - \bar{\varepsilon}_{\mathrm{BB}})/\bar{\varepsilon}_{\mathrm{AA}} = 0.104$. The cross interaction parameter $\bar{\varepsilon}_{\mathrm{AB}}$ requires a free-energy-like character to describe weak directional interactions in the system. At 473 K, $\bar{\varepsilon}_{\mathrm{AB}}/\bar{\varepsilon}_{\mathrm{AA}} = 0.947$ or $\Delta\bar{\varepsilon}/\bar{\varepsilon}_{\mathrm{AA}} = 0.0024$. The ratio $\chi_{\mathrm{comp}}/\chi_{\mathrm{app}}$ reaches ~0.6, which results in the largest ever baroplastic response for this loop-forming copolymer with $(\partial T_{\mathrm{LODT}}/\partial P)_\phi > 700$ K/100 MPa [15]. The theory predicts the negative volume of disordering of $\Delta V_{\mathrm{mix}}/V = -6.5 \times 10^{-4}$ at 473 K, while it was measured that $\Delta V_{\mathrm{mix}}/V = -1.5$ to -1.9×10^{-3} over the loop [8].

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References

[1] Goodman I, editor. Developments in block copolymers - I. New York: Applied Science Publishers; 1982.
[2] Holden G, Legge NR, Quirk RP, Schroeder HE, editors. Thermoplastic elastomers. New York: Hanser; 1996.
[3] Hamley IW. The physics of block copolymers. New York: Oxford University Press, Inc.; 1998.
[4] Leibler L. Macromolecules 1980;13:1602.
[5] Russell TP, Karis TE, Gallot Y, Mayes AM. Nature 1994;386:729.
[6] Mansky P, Tsui OKC, Russell TP, Gallot Y. Macromolecules 1999;32:4832.
[7] Ryu DY, Jeong U, Kim JK, Russell TP. Nat Mater 2002;1:114.
[8] Ryu DY, Lee DH, Kim JK, Lavery KA, Russell TP, Han YS, et al. Phys Rev Lett 2003;90:235501.
[9] Gonzalez-Leon JA, Acar MH, Ryu SW, Ruzette A-V, Mayes AM. Nature 2003;426:424.
[10] Ruzette A-V, Mayes AM, Pollard M, Russell TP, Hammouda B. Macromolecules 2003;36:3351.
[11] Cho J. Macromolecules 2000;33:2228.
[12] Cho J. Macromolecules 2001;34:1001.
[13] Cho J. Macromolecules 2002;35:5697.
[14] Cho J. J Chem Phys 2003;119:5711.
[15] Cho J. Macromolecules 2004;37:10101.
[16] Cho J. Macromolecules 2006;39:4576.
[17] Cho J, Sanchez IC. Macromolecules 1998;31:6650.
[18] Yeung C, Desai RC, Shi AC, Noolandi J. Phys Rev Lett 1994;72:1834.
[19] The bulk thermodynamic arguments on this contribution to the stability for polymer blends were first made by Sanchez. See: Sanchez IC, Panayiotou CG. In: Sandler SI, editor. Models for thermodynamics and phase equilibria calculation. New York: Marcel Dekker Inc.; 1994.
[20] Hajduk DA, Gruner SM, Erramilli S, Register RA, Fetters LJ. Macromolecules 1996;29:1473.