Explanation for the Unusual Phase Behavior of Polystyrene-*b*-poly(*n*-alkyl methacrylate) Diblock Copolymers: Specific Interactions

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ABSTRACT: The observed variation in the nature of the order−disorder transition (lower vs upper temperature phase diagram) with the length of the *n*-alkyl side group in polystyrene-*b*-poly(*n*-alkyl methacrylate) diblock copolymers [PS-*b*-P(*n*AMA)] by Mayes, Russell, and their co-workers (*Macromolecules* **1998**, *31*, 8509) is explained using a simple version of the lattice cluster theory that distinguishes between specific interactions of different united atom groups and that determines the temperature-independent portion of the effective Flory interaction parameter χ solely from the monomer molecular structures without employing adjustable parameters. The presence of this temperature independent part of χ provides the entropic driving force for the lower disorder−order transition in systems with negative enthalpic χ. The only adjustable parameters of the theory are three independent combinations of the specific interaction energies. The theory is developed for arbitrary monomer structures of the two block components (or alternatively for two homopolymer blend species) and is extended to describe A-*b*-C_xD_{1-x} diblock copolymers in which one block is a random copolymer. The calculated disorder−order transition temperatures accord reasonably with experimental data, and the utility of the theory is illustrated further by presenting predictions of how the phase behavior of the PS-*b*-P(*n*AMA$_x$ -*co*-*n*′AMA$_{1-x}$) systems changes with *n* and *n*′ and with the random copolymer composition *x*.

I. Introduction

Despite the commonly assumed equality of the Flory interaction χ parameter between an A-*b*-B diblock copolymer melt and the corresponding binary A/B homopolymer blend and despite the existence of a lower critical solution temperature (LCST) for certain binary blends, there had long been a general perception (supported by numerous experimental examples) that the microphase separation transition in diblock copolymers occurs only upon cooling. Our earlier mean-field lattice cluster theory (LCT) calculations[1] for diblock copolymer melts predicted, on the other hand, that the combined influences of monomer structure, nonrandom mixing effects, and melt compressibility could produce a lower critical disorder−order transition (LDOT) for systems with sufficiently negative exchange energies $\epsilon = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}$ (where $\epsilon_{\alpha\beta}$ denotes the nearest neighbor attractive van der Waals interaction energy between monomers of polymer species α and β). Although the original LCT predictions are not accompanied by an assessment of the generality of the new predicted phenomenon nor by a detailed analysis of the underlying mechanism, the calculations represent the first attempts toward the formulation of a detailed molecular basis for understanding the thermodynamics of diblock copolymers.[1,2]

Further progress has been provided by experiments of Russell and co-workers,[3,4] who verified our prior predictions,[1] finding that diblock copolymers of polystyrene (PS) and poly(*n*-butyl methacrylate) (PBMA) exhibit a microphase separation at both low and high temperatures (with a disordered phase at intermediate temperatures) and by the theoretical analysis of Yeung et al.[5] who combine equation-of-state theory with standard descriptions of the order−disorder transition in diblock copolymer systems and who interpret the observation of Russell et al.[3,4] as a result of finite compressibility effects. The analysis of Noolandi and co-workers[5] therefore builds upon arguments that have been widely used for explaining the appearance of LCST phase diagrams for polymer solutions and homopolymer blends.[6,7]

Our recent applications[8] of the lattice cluster theory (in the high pressure, high molecular weight, fully flexible chain limit) to polyolefin blends suggest, on the other hand, an alternative mechanism for the occurrence of a LCST phase behavior in binary polymer blends and, hence, an alternative mechanism for the LDOT in diblock copolymers. The competition between a positive temperature independent (called “entropic”) contribution χ_s to the effective interaction parameter χ and a negative exchange energy ϵ can also produce a LCST or LDOT in blends or diblock copolymer melts, respectively. In contrast to the previous mechanism based on differing compressibilities of the two components, this simple LCT description even applies within an incompressible model and appears to be appropriate when the two blend or block components retain similar densities as a function of temperature. In addition to the experiments of Russell et al.,[3,4] we also mention recent small-angle neutron scattering studies by Hashimoto and co-workers[9] that support our earlier LCT predictions[1] of a LDOT for poly(styrene)-*b*-poly(vinyl methyl ether) diblock copolymers.[10]

The observation of a LDOT in the PS-*b*-PBMA diblock copolymers has been followed by interesting experiments by Mayes and Russell and co-workers[11] who investigate the phase behavior for a homologous family

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of diblock copolymers formed from styrene and a series of *n*-alkyl methacrylates. The extremely well studied system of PS-*b*-PMMA [poly(styrene)-*b*-poly(methyl methacrylate)] is known[12] to undergo an upper order−disorder transition (UODT); the short side chain *n*-alkyl methacrylate copolymers (with $n = 2$, 3, and 4) are found to order upon heating (LDOT systems); and diblock copolymers with longer *n*-alkyl groups ($n = 6$, 8, and 12) are observed to order on cooling.[11] Quite remarkably, the block copolymer formed from styrene and a 53−47 wt % random copolymer of methyl ($n = 1$) and lauryl methacrylates ($n = 12$) [PS-*b*-P(MMA$_{0.74}$-LMA$_{0.26}$] orders on *heating*, despite the fact that both PS-*b*-PMMA and PS-*b*-PLMA copolymers individually exhibit the classical upper order−disorder transitions![11] These striking results clearly indicate that the microphase separation in these systems is subtly, but decisively, affected by the molecular monomer structures and interactions.

An explanation for this remarkable variation in the nature of the order−disorder transition with the length of the alkyl side group in the methacrylate (*n*AMA) block component evidently requires a theory that distinguishes not only between the chemical structures of the styrene and *n*-alkyl methacrylate monomers, but also between different *n*-alkyl methacrylate molecules. Flory−Huggins (FH) theory is of no use in these regards since it treats monomers as structureless entities whose only differences are reflected by ascribing varying species dependent monomer−monomer interaction parameters χ_{ij}. The LCT provides[13,14] a more realistic molecular description by specifying united atom type structures for individual monomers, by explicitly computing (with no adjustable parameters) the "entropic" portion of χ from the numbers of tri- and tetrafunctional united atom groups in these monomer structures, and by basing the computation of energetic interactions on the more microscopically faithful interactions between united atom groups. However, to minimize the number of adjustable parameters, prior applications of the LCT employ the simplifying approximation of united atom-united atom interaction energies that are averaged over all (chemically distinct) united atom groups within the monomers of a given species. While the approximation of monomer-averaged interaction energies may suffice as a zeroth-order model for some chemically fairly homogeneous systems such as polyolefins,[8,13,14] the monomer-averaged interaction models are clearly inadequate for explaining the remarkable observed variation in the ordering behavior of styrene-*b*-*n*-alkyl methacrylate diblock copolymers with the length of the alkyl chain.

In the present paper, we develop a simplified version of the LCT in which physically obvious different interaction energies are ascribed to chemically distinct united atom groups, a feature implicitly suggested by mention in the literature of "specific interactions". This new theory represents a generalization of our monomer averaged treatment recently formulated[15] for random copolymer systems and recently applied[16] to binary mixtures of ethylene−norbornene random copolymers. The extension retains united atom models for the individual monomers and is designed to explain the general trends observed by Mayes, Russell, and coworkers,[11] yet it is simple enough to be readily amenable for use by experimentalists. Again, to minimize the number of interaction energies, the chemically distinct united atom groups are taken as aromatic and alkyl CH$_n$ ($n = 0$, ..., 3) units and oxygen atoms. While this may appear to introduce six adjustable interaction energies, detailed analysis for the PS-*b*-P*n*AMA systems indicates the presence of only three independent parameters.

The entropic part χ_s of χ is determined from the monomer structures with no further adjustable parameters. The system is treated as incompressible, so the LDOT emerges solely from a competition between the temperature-independent entropic χ and the attractive enthalpic portion of χ that increases (becoming less attractive) with the elevation of temperature. The main approximation involves the use of Flory−Huggins type counting[17,18] to express the interaction energies in terms of united atom structures. Thus, the enthalpic portion of χ is not corrected for chain connectivities that affect the contact probabilities (often related to "surface fractions") in prior treatments of the LCT with monomer averaged interaction energies.[1,2] The same χ parameter is assumed to apply for binary A/B blends and A-*b*-B blocks despite some differences previously predicted[1] and recently observed[19] as these small differences are unlikely to affect the gross variation of the order−disorder transition type with the length of alkyl chain in poly(*n*-alkyl methacrylates).

An incompressible model is used here solely to develop the simplest description and to minimize the number of adjustable parameters. Indeed, the LDOT systems (and the corresponding LCST binary blends) exhibit a significant pressure sensitivity in accord with our LCT predictions[1,2,20] and subsequent experimental observations.[21−23] Hence, a full theory for the pressure variation of the LDOT and UODT transitions in PS-*b*-P*n*AMA systems obviously must include equation of state effects. In addition, reliable tests of this theory would require the availability of more detailed data. We, therefore, focus attention on understanding the nontrivial variation in the nature of the ODT with the alkyl chain length, a restricted goal for which a simplifying incompressible model suffices.

The next section outlines the derivation of the simple expressions for χ pararmeter of A-*b*-B (and A-*b*-C$_x$-*co*-D$_{1-x}$) diblock copolymers which are modeled by structured monomer chains with specific interactions for individual chemically distinct united atom groups. Section III compares the theory with the experiments of Russell, Mayes, and co-workers.[11] After explaining the variation in transition type with alkyl chain length, a secondary goal lies in roughly reproducing transition temperatures which are only approximately determined for several of the systems. We also provide predictions of the transition types for random PS-*b*-P(*n*AMA$_x$-*co*-*n*′AMA$_{1-x}$) diblocks as a function of the copolymer composition x and the alkyl chain lengths n and n'. In addition, we assess the ranges of molecular weights for which the calculated transition temperature is less sensitive to χ_s than is found for a few of the experimental samples.

II. Theory

The classic FH theory for A-*b*-B and A-*b*-C$_x$-*co*-D$_{1-x}$ diblock copolymers is extended here by introducing two significant improvements. The first improvement consists of including explicit formulas for computing the temperature independent contribution χ_s to the Flory interaction parameter χ, while the second one involves describing the enthalpic portion of χ in terms of more realistic interactions between united atom groups that are allowed to have specific interactions. The presence of the "entropic" portion of χ does not lead to the appearance of extra adjustable parameters because χ_s is completely determined[13,14] from the lattice cluster theory (see below), but the departure from the our prior assumption of monomer averaged interactions inevitably leads to an increased number of nearest neighbor van der Waals interaction energies, i.e., of adjustable parameters.

The high pressure, high molecular weight, fully flexible chain limit of the LCT yields the temperature independent component χ_s of the interaction parameter χ for a binary A/B homopolymer blend (or an A-*b*-B diblock copolymer) in the compact form[8]

$$\chi_s = \sqrt{s_\alpha s_\beta}\,(1/z^2)(r_\alpha - r_\beta)^2 \tag{1}$$

where the subscript α refers to monomers of species A and the subscript β designates monomers of species B, s_γ ($\gamma \equiv$ A, B) denotes the number of united atom groups in a single monomer of species γ (equal to the number of lattice sites occupied by this monomer), and the partial entropic structure parameters r_γ ($\gamma \equiv$ A, B) are defined in terms of the numbers $s_\gamma^{(\mathrm{tri})}$ and $s_\gamma^{(\mathrm{tetr})}$ of tri- and tetrafunctional united atom groups, respectively, in a single monomer of species γ

$$r_\gamma = \frac{s_\gamma + s_i^{(\mathrm{tri})} + 3s_\gamma^{(\mathrm{tetr})}}{s_\gamma}, \quad \gamma \equiv \mathrm{A, B} \tag{2}$$

As described in our previous papers,[15,16] chain semiflexibility affects the partial entropic structural parameters r_γ. For example, the presence of $n_{2,\mathrm{stiff}}^{(\gamma)}$ stiff pairs of bonds in a monomers of species γ leads to the following modification of eq 2:

$$r_\gamma = \frac{s_\gamma + s_i^{(\mathrm{tri})} + 3s_\gamma^{(\mathrm{tetr})} - n_{2,\mathrm{stiff}}^{(\gamma)}}{s_\gamma}, \gamma \equiv \mathrm{A, B} \tag{3}$$

The factor $\sqrt{s_\alpha s_\beta}$ in eq 1 converts the LCT χ_s, which is computed per united atom group, to an interaction parameter per monomer.

Let a monomer of polymer species A have s_{A_1}, s_{A_2}, ..., s_{A_k} united atom groups of type A_1, A_2,..., A_k, respectively, (where $s_{\mathrm{A}_1} + s_{\mathrm{A}_2} + ... + s_{\mathrm{A}_k} = s_\mathrm{A}$) and a monomer of polymer species B have s_{B_1}, s_{B_2}, ..., s_{B_l} united atom groups of type B_1, B_2, ..., B_l, respectively, (with $s_{\mathrm{B}_1} + s_{\mathrm{B}_2} + ... + s_{\mathrm{B}_l} = s_\mathrm{B}$), so the interactions between united atom groups involve the specific interactions $\epsilon_{\gamma_i\mu_j}$ where $\gamma, \mu = \{\mathrm{A, B}\}$. The enthalpic portion χ_h of the interaction parameter χ can be expressed as

$$\chi_h = \sqrt{s_\alpha s_\beta}\,\frac{(z-2)}{2kT}[\epsilon_{\alpha\alpha} + \epsilon_{\beta\beta} - 2\epsilon_{\alpha\beta}] \tag{4}$$

where the individual polymer−polymer effective attractive van der Waals energies $\epsilon_{\alpha\alpha}$, $\epsilon_{\beta\beta}$, and $\epsilon_{\alpha\beta}$ are explicit functions of the specific group site occupancy indices s_{α_i} and s_{β_i} and the specific interaction energies $\epsilon_{\alpha_i\beta_j}$

$$\epsilon_{\alpha\alpha} = \sum_{i=1}^{k} \epsilon_{\mathrm{A}_i\mathrm{A}_i}\left(\frac{s_{\mathrm{A}_i}}{s_\mathrm{A}}\right)^2 + 2\sum_{i=1}^{k}\sum_{j>i}^{k} \epsilon_{\mathrm{A}_i\mathrm{A}_j}\frac{s_{\mathrm{A}_i}s_{\mathrm{A}_j}}{s^2_{\ \mathrm{A}}} \tag{5}$$

$$\epsilon_{\beta\beta} = \sum_{i=1}^{l} \epsilon_{\mathrm{B}_i\mathrm{B}_i}\left(\frac{s_{\mathrm{B}_i}}{s_\mathrm{B}}\right)^2 + 2\sum_{i=1}^{l}\sum_{j>i}^{l} \epsilon_{\mathrm{B}_i\mathrm{B}_j}\frac{s_{\mathrm{B}_i}s_{\mathrm{B}_j}}{s^2_{\ \mathrm{B}}} \tag{6}$$

and

$$\epsilon_{\alpha\beta} = \sum_{i=1}^{k}\sum_{j=1}^{k} \epsilon_{\mathrm{A}_i\mathrm{B}_j}\frac{s_{\mathrm{A}_i}s_{\mathrm{B}_j}}{s_\mathrm{A}s_\mathrm{B}} \tag{7}$$

The specific interaction energies $\{\epsilon_{\alpha_i\beta_j}\}$ are the adjustable parameters of the theory, but as shown below for the PS-*b*-P*n*AMA systems, not all are independent. The factor $\sqrt{s_\alpha s_\beta}$ again converts χ_h from united atom-united atom interaction parameter to the more traditional monomer−monomer interaction parameter χ_h, and the standard Flory scaling factor $z/2$ between χ_h and the exchange energy $\epsilon = \epsilon_{\alpha\alpha} + \epsilon_{\beta\beta} - 2\epsilon_{\alpha\beta}$ is replaced by $(z-2)/2$ to be consistent with the simple incompressible limit of LCT for high molecular weight binary homopolymer blends[8] and with the arguments of Guggenheim[24] that each interior unit in a linear chain is linked by chemical bonds to two nearest neighbors and therefore has two fewer neighboring sites available for possible interactions. The total effective interaction parameter χ is a sum of the entropic and enthalpic contributions of eqs 1 and 4

$$\chi = \chi_s + \chi_h = \chi_s + \frac{\chi'_h}{T} \tag{8}$$

The interaction energies in eqs 5−7 are linear combinations of specific group interactions, which makes these equations similar in spirit to those derived from group additivity models. However, more extensive LCT theory indicates that all such group additivity treatments represent leading approximations, and important correction terms, describing the influence of the connectivities between the various groups, are required in a more detailed analysis.[25]

When one of the blocks is a random copolymer (e.g., $\beta \equiv \mathrm{C}_x\mathrm{D}_{1-x}$), eqs 1−3 maintain their validity by setting $s_\beta = s_\mathrm{C}x + s_\mathrm{D}(1-x)$, but the entropic partial structure parameter r_β and the interaction energies $\epsilon_{\beta\beta}$ and $\epsilon_{\alpha\beta}$ must be redefined, while the homopolymer quantities r_α and $\epsilon_{\alpha\alpha}$ remain unchanged. The entropic partial structure parameter r_β now depends[26] on the random copolymer composition x

$$r_\beta = \frac{[s_\mathrm{C} + s_\mathrm{C}^{(\mathrm{tri})} + 3s_\mathrm{C}^{(\mathrm{tetr})}]x + [s_\mathrm{D} + s_\mathrm{D}^{(\mathrm{tri})} + 3s_\mathrm{D}^{(\mathrm{tetr})}](1-x)}{s_\mathrm{C}x + s_\mathrm{D}(1-x)} \tag{9}$$

as do the energies $\epsilon_{\beta\beta}$ and $\epsilon_{\alpha\beta}$. When both monomers C and D contain, $n_{2,\mathrm{stiff}}^{(\mathrm{C})}$ and $n_{2,\mathrm{stiff}}^{(\mathrm{D})}$ pairs of stiff bonds, respectively, eq 9 takes the form

$$r_\beta = \frac{[s_\mathrm{C} + s_\mathrm{C}^{(\mathrm{tri})} + 3s_\mathrm{C}^{(\mathrm{tetr})} - n_{2,\mathrm{stiff}}^{(\mathrm{C})}]x + [s_\mathrm{C} + s_\mathrm{D}^{(\mathrm{tri})} + 3s_\mathrm{D}^{(\mathrm{tetr})} - n_{2,\mathrm{stiff}}^{(\mathrm{D})}](1-x)}{s_\mathrm{C}x + s_\mathrm{D}(1-x)} \tag{10}$$

For the most the general case, where each monomer of species C has s_{C_1}, s_{C_2}, ..., s_{C_p} united atom groups of type C_1, C_2, ..., C_p, respectively, ($s_{\mathrm{C}_1} + s_{\mathrm{C}_2} + ... + s_{\mathrm{C}_p} = s_\mathrm{C}$) and where each monomer of species D has s_{D_1}, s_{D_2}, ..., s_{D_q} united atom groups of type D_1, D_2, ..., D_q, respectively, ($s_{D_1} + s_{D_2} + ... + s_{D_q} = s_D$), the monomer–monomer interaction energies $\epsilon_{\beta\beta}$ and $\epsilon_{\alpha\beta}$ are given by

$$\epsilon_{\beta\beta} = \left[\frac{s_C x}{s_C x + s_D(1-x)}\right]^2 \times \left[\sum_{i=1}^{p} \epsilon_{C_iC_i}\left(\frac{s_{C_i}}{s_C}\right)^2 + 2\sum_{i=1}^{p}\sum_{j>i}^{p} \epsilon_{C_iC_j}\frac{s_{C_i}s_{C_j}}{s_C{}^2}\right] + \left[\frac{s_D(1-x)}{s_C x + s_D(1-x)}\right]^2 \times \left[\sum_{i=1}^{q} \epsilon_{D_iD_i}\left(\frac{s_{D_i}}{s_D}\right)^2 + 2\sum_{i=1}^{q}\sum_{j>i}^{q} \epsilon_{D_iD_j}\frac{s_{D_i}s_{D_j}}{s^2_D}\right] + \left[\frac{2s_C x s_D(1-x)}{[s_C x + s_D(1-x)]^2}\right]\sum_{i=1}^{p}\sum_{j=1}^{q} \epsilon_{C_iD_j}\frac{s_{C_i}s_{D_j}}{s_C s_D} \qquad (11)$$

and

$$\epsilon_{\alpha\beta} = \frac{s_C x}{s_C x + s_D(1-x)}\sum_{i=1}^{k}\sum_{j=1}^{p} \epsilon_{A_iC_j}\frac{s_{A_i}s_{C_j}}{s_A s_C} + \frac{s_D(1-x)}{s_C x + s_D(1-x)}\sum_{i=1}^{k}\sum_{j=1}^{q} \epsilon_{A_iD_j}\frac{s_{A_i}s_{D_j}}{s_A s_D} \qquad (12)$$

Equations 1–12 provide the general recipe for evaluating χ of A-*b*-B diblocks and A-*b*-C_xD_{1-x} random copolymers (and the corresponding binary blends, of course), with the $\{\epsilon_{\alpha_i\beta_i}\}$ as the only adjustable parameters.

The knowledge of both portions of χ enables the evaluation of the order–disorder transition temperature that is generally determined from the vanishing of the inverse structure factor $1/S(q^*)$. We use here a modified Leibler theory[27] in which χ and $S(q^*)$ are related by

$$\frac{1}{S(q^*)} = \frac{F(x_1, x_2, f)}{N} - 2\chi \qquad (13)$$

where N is the polymerization index of the diblock and where the function F is generalized[28] to account for unequal Kuhn lengths of the two segment types

$$F(x_1, x_2, f) = \frac{f^2\, g(x_1) + 2f(1-f)h(x_1)h(x_2) + (1-f)^2\, g(x_2)}{f^2(1-f)^2\,[g(x_1)g(x_2) - h^2(x_1)h^2(x_2)]} \qquad (14)$$

$$g(x_i) = 2x_i^{-2}(x_i + e^{-x_i} - 1), \quad i = 1, 2$$

$$h(x_i) = x_i^{-1}(1 - e^{-x_i}), \quad i = 1, 2$$

and

$$x_1 \equiv (q^*R_1)^2,\ x_2 \equiv (q^*R_2)^2$$

In the above expressions, $R_i = \sqrt{(^1/_6)N_i}a_i$ ($i = 1, 2$; $N_1 + N_2 = N$) are the blocks' radii of gyration [with a_i ($i = 1, 2$) being the Kuhn lengths], f is the volume fraction of block 1, and q^* is the wavevector q for which F attains a maximum. The volume fraction $f \equiv f_1$ is usually determined from the mole fraction $y \equiv y_1 = N_1/N$ as

$$f = \frac{yv_1}{yv_1 + (1-y)v_2}$$

where v_i ($i = 1, 2$) are the molar monomer volumes. For the A-*b*-C_xD_{1-x} systems, both v_2 and a_2 are approximated by the averages

$$v_2 \approx v'_2 x + v''_2(1-x) \text{ and } a_2 \approx a'_2 x + a''_2(1-x)$$

with the prime and double prime superscripts referring to monomers of species C and D, respectively. The quantity q^* is evaluated from the vanishing of the first derivative of F as a function of y, v_i, and a_i ($i = 1, 2$). The order–disorder transition temperature simply follows from eqs 13 and 8 as

$$T_{odt} = \frac{\chi'_h N}{(^1/_2)F(x_1, x_2, f) - \chi_s N} \qquad (15)$$

where χ_s and χ'_h are obtained from eqs 1–12. Equation 15 differs from the standard Leibler formula[27] by the presence of an entropic portion χ_s of χ and by a more general expression for F, as given by eq 14.

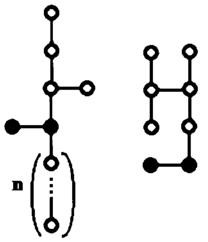

Figure 1. United atom structures for the *n*-alkyl methacrylate (*n*AMA) and styrene (S) monomers. Filled circles denote united atom groups belonging to the chain backbone, while open circles indicate the side groups.

III. Results

The formulas derived in section II for the interaction parameter χ are specialized below for a series of PS-*b*-poly(*n*-alkyl methacrylate) diblock copolymers and for a series of PS-*b*-poly(X_x-*co*-Y_{1-x}) systems, where X and Y denote, respectively, *n*-alkyl methacrylate with $n = p$ and $n' = q$ united atom groups in the alkyl chain. The monomer structures for both styrene and *n*-alkyl methacrylate monomers are depicted in Figure 1. Given these monomer structures, the monomer site occupancy indices are $s_\alpha \equiv s_S = 8$ and $s_\beta \equiv s_{n-\mathrm{AMA}} = 6 + n$. Stiffness in the actual styrene molecule is introduced into our model by taking the two pairs of side group bonds (see Figure 1) as completely rigid ($n^{(S)}_{2,\mathrm{stiff}} = 2$). As mentioned earlier, to minimize the number of adjustable parameters, we assume that the diblock copolymer monomers contain only three chemically distinct united atom groups: alkyl CH_n groups ($n = 0, 1, 2$ or 3), aromatic CH_n groups ($n = 0$ or 1), and oxygen atoms. This assumption appears to produce six different interaction energies $\epsilon_{\mathrm{Alk-Alk}}$, $\epsilon_{\mathrm{Ar-Ar}}$, $\epsilon_{\mathrm{O-O}}$, $\epsilon_{\mathrm{Alk-Ar}}$, $\epsilon_{\mathrm{Alk-O}}$, and $\epsilon_{\mathrm{Ar-O}}$, but only three combinations are found to be independent for the systems studied. In addition, no interaction is ascribed to the united atom group pairs involving the tetrafunctional carbon of the *n*-alkyl methacrylate monomer due to the obvious steric hindrances preventing nearest neighbor interactions for these carbons in the actual molecules.

After some algebra, the expressions from section II for the entropic and enthalpic portions of the effective interaction parameter χ for the PS-*b*-P(*n*-alkyl methacrylate) system reduce to the compact formulas

$$\chi_s = \sqrt{8(6+n)}\left[\frac{1}{z^2}\left(\frac{9}{8} - \frac{10+n}{6+n}\right)^2\right] \tag{16}$$

and

$$\chi'_h = \sqrt{8(6+n)}\left[\frac{z-2}{2k}\{9(2+n)^2\epsilon_1 + 12(2+n)\epsilon_2 + 16\epsilon_3\}\frac{1}{16(6+n)^2}\right] \tag{17}$$

with the three independent combinations of interaction energies

$$\epsilon_1 \equiv \epsilon_{\text{Alk-Alk}} + \epsilon_{\text{Ar-Ar}} - 2\epsilon_{\text{Alk-Ar}}$$

$$\epsilon_2 \equiv 6(\epsilon_{\text{Ar-Ar}} - \epsilon_{\text{Alk-Ar}}) + 4(\epsilon_{\text{Alk-O}} - \epsilon_{\text{Ar-O}})$$

$$\epsilon_3 \equiv 4\epsilon_{\text{O-O}} + 9\epsilon_{\text{Ar-Ar}} - 12\epsilon_{\text{Ar-O}}$$

as the adjustable parameters of the theory. The χ_s and χ'_h for the random copolymer PS-*b*-P(X_xY_{1-x}) diblock copolymers (in which $s_A \equiv s_S = 8$, $s_C \equiv s_X = 6 + p$, and $s_D \equiv s_Y = 6 + q$) are likewise obtained as

$$\chi_s = \sqrt{8[6+q+x(p-q)]}\left[\frac{1}{z^2}\left(\frac{9}{8} - \frac{10+q+x(p-q)}{6+q+x(p-q)}\right)^2\right] \tag{18}$$

and

$$\chi'_h = \sqrt{8[6+q+x(p-q)]}\left[\frac{z-2}{2k}\{9[2+q+x(p-q)]^2\epsilon_1 + 12[2+q+x(p-q)]\epsilon_2 + 16\epsilon_3\}\frac{1}{16[6+q+x(p-q)]^2}\right] \tag{19}$$

and χ'_h likewise depends on the same three independent combinations of interaction energies. Setting $x = 0$ (or $x = 1$) in eqs 18 and 19 recovers eqs 16 and 17, respectively. Specialization of eqs 18 and 19 to the PS-*b*-P($\text{MMA}_x\text{LMA}_{1-x}$) diblock copolymers studied by Mayes, Russell, and co-workers[11] yields

$$\chi_s = \sqrt{8(18-11x)}\left[\frac{1}{z^2}\left(\frac{9}{8} - \frac{22-11x}{18-11x}\right)^2\right] \tag{20}$$

and

$$\chi'_h = \sqrt{8(18-11x)}\left[\frac{z-2}{2k}\{9(14-11x)^2\,\epsilon_1 + 12\,(14-11x)\,\epsilon_2 + 16\epsilon_3\}\frac{1}{16(18-11x)^2}\right] \tag{21}$$

Within our model, χ_s is always positive, while $\chi'_h \propto \epsilon = \epsilon_{\alpha\alpha} + \epsilon_{\beta\beta} - 2\epsilon_{\alpha\beta}$ can formally achieve both signs, depending on the three interaction energy combinations ϵ_1, ϵ_2, and ϵ_3 (and on the composition x when one of the two blocks is a random copolymer). We have found plethora of $\{\epsilon_i\}$ sets for which the enthalpic portion χ'_h of the interaction parameter χ is positive for PS−PMMA system ($n = 1$), negative for PS−PEMA, PS−PPMA, and PS−PBMA diblock copolymers ($n = 2$, 3, and 4), positive again for PS−PHMA, PS−POMA, and PS−PLMA melts ($n = 6$, 8, and 12), and finally negative for the block copolymer of styrene and a 53−47 wt % random copolymer of methyl ($n = 1$) and lauryl methacrylates ($n = 12$) [i.e., for PS-*b*-P($\text{MMA}_{0.74}\text{LMA}_{0.26}$)]. Systems with a positive χ'_h order on cooling, while systems with a negative χ'_h order on heating. The existence of numerous sets of energy parameters satisfies our primary goal of providing a mechanism for the variation of the order−disorder transition type with the length of the alkyl side group in the *n*-alkyl methacrylates. This remarkable behavior is explained in terms of different interactions between chemically different united atom groups (and the presence of the entropic χ_s) and does not require considering finite compressibility effects nor resorting to a sophisticated theory, although, as discussed below, finite compressibility, nonrandom mixing effects, etc. must affect the experimental χ parameters and, hence, the observed transition temperatures.

Table 1 summarizes the computed χ'_h that are generated using a typical set of ϵ_i values ($\epsilon_1 > 0$, $\epsilon_2 < 0$, and $\epsilon_3 > 0$), along with the computed entropic portions χ_s and the order−disorder transition temperatures T_{odt} for the eight PS-*b*-P*n*AMA systems studied. The monomer volumes v_1 and v_2 for each of these systems are treated as temperature-dependent quantities, and the values used in the calculation of T_{odt} are taken at the experimental order−disorder transition temperature (or at its lower or upper limit when the exact experimental T_{odt} is not available).[11] Because of the obvious simplification inherent in the use of a lattice model and, in particular, a cubic lattice ($z = 6$) and because of the simple monomer structures (see Figure 1), we ascribe an “uncertainty” of ±20% to the computed χ_s, and this yields the ranges for the transition temperatures T_{odt} presented in Table 1. Given this “uncertainty” in the χ_s, the agreement between theoretical and experimental transition temperatures T_{odt} appears satisfactory for all but the PS-*b*-PHMA system where the computed T_{odt} is probably too low. Using different sets of ϵ_i (for which $\epsilon_1 > 0$, $\epsilon_2 < 0$, and $\epsilon_3 > 0$) leads to a very similar pattern for the variation of T_{odt} with the length of the alkyl groups in the methacrylate block and to similar spreads of the calculated T_{odt} for the individual systems.

Considering the obvious simplifications inherent in the lattice model, the choice of cubic lattice, the assumption of incompressibility, and the simplified united atom structures for the monomers, it is inevitable that sufficient depth of probing must ultimately uncover limitations in the simple theory developed here. While some of the available small-angle neutron scattering data for the PS-*b*-P*n*AMA melts are regarded as approximate and only indicative of general trends,[29] upon taking the data for χ at face value some general agreement and departures from the theoretical predictions become apparent. The small-angle neutron scattering studies[11,12,30] exhibit a strong dominance of the entropic χ_s over the enthalpic portion χ_h of χ for all the PS-*b*-P*n*AMA systems considered ($n = 1$, 4, 6, 8, and 12). Our computed χ_s accord with this finding, except for the diblock copolymers with long alkyl side groups ($n = 8$ and 12). Several features may contribute to this discrepancy as follows:

Table 1. Comparison between Theory and Experiment[3,11,12] for the Order−Disorder Transition Temperature of Polystyrene-*b*-poly(*n*-alkyl methacrylate) Diblock Copolymers and for the Polystyrene-*b*-poly($MMA_{0.74}$-*co*-$LMA_{0.26}$) Random Copolymer System[a]

sample	N_S	N_{MA}	f	a_{MA} (Å)	theory $\chi_s \times 10^2$	 χ'_h (K)	 T_{odt} (K)	exp T_{odt} (K)
28K PS_{d8}-*b*-PMMA	115	147	0.4778	7.4	4.14	2.14	303 to ∞	<373
50K PS-*b*-PEMA	237	223	0.5026	8.1	3.12	−3.11	214−1501	>463
110K PS-*b*-PPMA	434	507	0.4072	8.8	2.41	−3.75	220−505	473
75K PS_{d8}-*b*-PBMA	333	264	0.4717	9.5	1.88	−1.67	0 to ∞	473
27K PS-*b*-PHMA	127	81	0.4585	10.8	1.18	6.78	163−184	<373
23K PS-*b*-POMA	123	51	0.5050	12.3	0.759	17.8	327−346	<373
19K PS_{d8}-*b*-PLMA	85	37	0.3745	15.0	0.315	41.7	446−452	408
80K PS-*b*-P($MMA_{0.74}LMA_{0.26}$)	385	212, 74	0.4449	9.4	1.95	−2.12	248 to ∞	441

[a] The adjustable parameters of the theory are chosen as $\epsilon_1 = 12.45$ K, $\epsilon_2 = -91.33$ K, and $\epsilon_3 = 149.45$ K and are assumed to be independent of the deuterium content of the PS blocks. The Kuhn length a_S for the styrene monomers is taken as $a_S = 6.7$ Å.[12]

(a) First of all, the united atom models are designed to satisfy the important physical constraint[31] that the ratio of lattice sites occupied by different monomer species well aproximates the ratio of their specific volumes. While this constraint is adequately satisfied for the *n*-alkyl methacrylate monomers with smaller *n*, it ceases to be a good representation for the ratios of monomer specific volumes when *n* becomes large. This departure for larger *n* might arise from variations in the amount of excess free volume with *n*, thereby suggesting the potential importance of compressibility effects, especially for the higher *n* PS-*b*-POMA ($n = 8$) and PS-*b*-PLMA ($n = 12$) systems.

(b) The styrene monomer structure clearly is also oversimplified (see Figure 1) due to the inability of the available LCT to describe flexible chains with extended rigid side groups. Use of an alternative monomer structure[32] for styrene molecule leads to a large computed entropic χ_s for diblock copolymers with $n = 12$ and $n = 8$. Hovever, the χ_s for PS-*b*-PMMA systems is then much too small. Thus, we can develop versions of the theory that provide important agreement with experiments for low and high *n* separately.

(c) Another limitation of the present simplified theory stems from the neglect of $1/N$ corrections for these diblock systems that have rather low polymerization indices *N*. Our prior LCT theory[33] demonstrates that the junction between the two blocks yields $1/N$ corrections to the free energy that are an order of magnitude larger than the corrections due to chain ends in the case of homopolymers.

(d) The observed pressure sensitivity of the LDOT and its corresponding blend LCST indicates the obvious need for a theory capable of incorporating compressibility effects in order to describe quantitatively the full range of experimental phenomena. We are gratified to see our earlier predictions[1,2,20] of the pressure sensitivity borne out by the subsequent experimental studies.[21−23] Thus, to obtain better quantitative agreement with the whole set of experimental data for χ_s, χ'_h, and T_{odt}, it is necessary to introduce various physical features omitted in the present simplified theory. On the other hand, the present formulation is a sufficient tool for modeling purposes, i.e., for providing a general overall understanding for many of the remarkable experimental observations.[11]

(e) The extended Leibler theory omits important contributions from fluctuations that affect the predicted transition temperatures. Because the experimental T_{ODT} are rather rough, fluctuation corrections are not included.

IV. Discussion

Our simple theoretical approach distinguishes between specific interactions of different united atom groups and between the temperature independent and temperature-dependent portions of the Flory effective interaction parameter χ. The theory reproduces semiquantitatively the experimental data of Mayes, Russells, and co-workers[11] in the sense that we describe well the variation in the nature (lower vs upper temperature phase diagram) of the disorder−order transition with the length of the *n*-alkyl side group in PS-*b*-P*n*AMA diblock copolymers by using only three adjustable parameters. Ruzette et al.[11] provide an alternative thermodynamic analysis in which a LDOT is favored when both block components have matched densities and solubility parameters. Our molecular approach is quite distinct from that of Ruzette et al.[11] and establishing a relation between these two approaches is rendered difficult because of the thermodynamic inconsistency in the use of solubility parameter theory to describe a system for which the experimental χ parameter contains[11] a substantial entropic component.[15,16] Our theory is also extended to A-*b*-C_x-*co*-D_{1-x} diblock copolymers in which one block is a random copolymer, and this extension is likewise simple enough for easy usage by experimentalists. One benefit of this theory lies in the opportunity of making predictions for systems which have not been analyzed experimentally.

For instance, eq 19 enables predicting the nature (lower vs upper temperature) of the order−disorder transition for the whole family of PS-*b*-P(*n*AMA_x-*co*-*n*′AMA_{1-x}) diblock copolymers as a function of the random copolymer composition *x*. The predictions for 21 families of systems specified by different pairs of *n* and *n*′ ($n' > n = 1, 2, 3, 4, 6, 8, 12$) and variable *x* are generated by using a typical set of interaction energies ϵ_i ($\epsilon_1 > 0$, $\epsilon_2 < 0$, and $\epsilon_3 > 0$) and are collected in Table 2. With the exception of copolymers containing methyl methacrylate, there is a general pattern to the phase behavior of these systems, as follows:

(a) If both PS-*b*-P*n*AMA and PS-*b*-P*n*′AMA diblock copolymers order on cooling, the random copolymer PS-*b*-P(*n*AMA_x-*co*-*n*′AMA_{1-x}) systems likewise order on cooling over the whole range of compositions *x*.

(b) If both PS-*b*-P*n*AMA and PS-*b*-P*n*′AMA diblock copolymers order on heating, the random copolymer PS-*b*-P(*n*AMA_x -*co*-*n*′AMA_{1-x}) systems similarly order also on heating for $0 \leq x \leq 1$.

(c) If the PS-*b*-P*n*AMA melt orders on cooling, while the PS-*b*-P*n*′AMA melt orders upon heating, the PS-*b*-P(*n*AMA_x-*co*-*n*′AMA_{1-x}) systems order on heating when

Table 2. Order−Disorder Transition Type for a Series of PS-*b*-P(*n*AMA$_x$-*co*-*n*′AMA$_{1-x}$) Diblock Copolymers As Predicted from Eq 19 by Using the Same Set of Interaction Energies $\{\epsilon_i\}$ As Employed in the Calculations Summarized in Table 1

			type of order−disorder transition	
n	n'	diblock copolymer	UODT	LDOT
1	2	PS-*b*-P(MMA$_x$EMA$_{1-x}$)	$0.72 \le x \le 1$	$0 \le x \le 0.71$
1	3	PS-*b*-P(MMA$_x$PMA$_{1-x}$)	$0.86 \le x \le 1$	$0 \le x \le 0.85$
1	4	PS-*b*-P(MMA$_x$BMA$_{1-x}$)	$0.91 \le x \le 1$	$0 \le x \le 0.90$
1	6	PS-*b*-P(MMA$_x$HMA$_{1-x}$)	$0 \le x \le 0.30$; $0.95 \le x \le 1$	$0.31 \le x \le 0.94$
1	8	PS-*b*-P(MMA$_x$OMA$_{1-x}$)	$0 \le x \le 0.50$; $0.96 \le x \le 1$	$0.51 \le x \le 0.95$
1	12	PS-*b*-P(MMA$_x$LMA$_{1-x}$)	$0 \le x \le 0.68$; $0.98 \le x \le 1$	$0.69 \le x \le 0.97$
2	3	PS-*b*-P(EMA$_x$PMA$_{1-x}$)		$0 \le x \le 1$
2	4	PS-*b*-P(EMA$_x$BMA$_{1-x}$)		$0 \le x \le 1$
2	6	PS-*b*-P(EMA$_x$HMA$_{1-x}$)	$0 \le x \le 0.37$	$0.38 \le x \le 1$
2	8	PS-*b*-P(EMA$_x$OMA$_{1-x}$)	$0 \le x \le 0.58$	$0.59 \le x \le 1$
2	12	PS-*b*-P(EMA$_x$LMA$_{1-x}$)	$0 \le x \le 0.75$	$0.76 \le x \le 1$
3	4	PS-*b*-P(PMA$_x$BMA$_{1-x}$)		$0 \le x \le 1$
3	6	PS-*b*-P(PMA$_x$HMA$_{1-x}$)	$0 \le x \le 0.50$	$0.51 \le x \le 1$
3	8	PS-*b*-P(PMA$_x$OMA$_{1-x}$)	$0 \le x \le 0.70$	$0.71 \le x \le 1$
3	12	PS-*b*-P(PMA$_x$LMA$_{1-x}$)	$0 \le x \le 0.83$	$0.84 \le x \le 1$
4	6	PS-*b*-P(BMA$_x$HMA$_{1-x}$)	$0 \le x \le 0.75$	$0.76 \le x \le 1$
4	8	PS-*b*-P(BMA$_x$OMA$_{1-x}$)	$0 \le x \le 0.87$	$0.88 \le x \le 1$
4	12	PS-*b*-P(BMA$_x$LMA$_{1-x}$)	$0 \le x \le 0.93$	$0.94 \le x \le 1$
6	8	PS-*b*-P(HMA$_x$OMA$_{1-x}$)	$0 \le x \le 1$	
6	12	PS-*b*-P(HMA$_x$LMA$_{1-x}$)	$0 \le x \le 1$	
8	12	PS-*b*-P(OMA$_x$LMA$_{1-x}$)	$0 \le x \le 1$	

Table 3. Range of Calculated Order−Disorder Transition Temperature T_{odt} as a Function of the Polymerization Index *N* for PS-*b*-PMMA and PS-*b*-PEMA Diblock Copolymers Which Exhibit UODT and LDOT, Respectively[a]

diblock copolymer	N	T_{odt} (K)
PS$_{d8}$-*b*-PMMA, f = 0.4778	262	303 to −∞
	200	110−273
	180	84−243
PS-*b*-PEMA, f = 0.5036	460	214−1501
	530	177−610
	600	156−420

[a] The interaction energies $\{\epsilon_i\}$ are taken to be the same as those employed in the calculations summarized in Table 1.

$0 \le x \le a$ and on cooling when $a < x \le 1$, with the limiting mole fraction a (that separates these two regions of x) growing with n' for n fixed and growing with n for n' kept constant.

The PS-*b*-P(MMA$_x$-*co*-n'AMA$_{1-x}$) systems with methyl methacrylate in the random copolymer block undergo both UODT and LDOT for all $n' > 1$. If the PS-*b*-Pn'AMA diblocks order on cooling, the PS-*b*-P(MMA$_x n'$AMA$_{1-x}$) systems order on cooling for $0 \le x \le b$ and on heating for higher x, i.e., for $b < x \le 1$, but when PS-*b*-Pn'AMA diblocks order on heating, the PS-*b*-P(MMA$_x n'$AMA$_{1-x}$) systems order on heating for small and high x, i.e., for $0 \le x < c$ and $d < x \le 1$, and on cooling in the intermediate region of x, i.e., for $c \le x \le d$. Our calculations suggest, for instance, that LDOT behavior would not appear for PS-*b*-P(MMA$_x$-*co*-LMA$_{1-x}$) if the composition x of the P(MMA$_x$-*co*-LMA$_{1-x}$) were chosen less than 0.68. Using different sets of interaction ϵ_i ($\epsilon_1 > 0$, $\epsilon_2 < 0$, and $\epsilon_3 > 0$) does not change the overall structure of our predictions, but yields slightly different values of a, b, c, and d than those presented in Table 2.

Another interesting feature that emerges from our calculations concerns the sensitivity of the computed order−disorder transition temperature to the value of the entropic portion of χ_s of the interaction parameter χ. The simplest way of minimizing this sensitivity is to change the diblock polymerization index N. Table 3 illustrates this variation for the examples of PS-*b*-PMMA and PS-*b*-PEMA diblock copolymers which order upon heating and cooling, respectively. For the former system, a decrease in N leads to a narrower range of T_{odt} when the “uncertainty” of the computed χ_s is taken as ±20%. For the PS-*b*-PEMA systems, an increase in N is the appriopriate remedy for determining T_{odt} more accurately. The formulas in the preceding section also enable computing the variation of T_{odt} with the diblock composition f.

The obvious simplifications inherent in the present theory limit its ability to quantitatively describe all systems simultaneously. Improved fits are possible when the theory is restricted to narrower ranges of the alkyl chain length, while extensions of the theory to include compressibility, nonrandom mixing effects (i.e., a more precise computation of surface fractions), $1/N$ corrections, etc., can improve the accuracy of the theory at expense of analytical complexity. The present version, however, strikes a useful balance between simplicity of usage and overall quantitative description.

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