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Importance of Chemical Mismatch in Tricritical Polymer Solutions

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ABSTRACT: Using a renormalization group analysis for the tricritical behavior of dilute polymer solutions with many chemically different polymers, we show that the chemical mismatch is indeed important. This is contrary to the irrelevance of chemical mismatch in good solutions. We find the second virial coefficients at the tricritical point to vanish with chain length L as $L^{-1/2}[\ln(L/a)]^{-9/11}$, where a is the small cut-off. This behavior is in a different universality class from the one for the tricritical solutions of polymers of the same chemical type. The generalization to block copolymers is also addressed.

I. Introduction

The equilibrium properties of dilute solutions of long polymers near the Flory temperature Θ have been studied both experimentally[1–7] and theoretically.[8–13] The renormalization group theory has clearly established that the behavior of a dilute polymer solution at the Θ temperature is a tricritical phenomenon.[9–13]

In this paper we study theoretically the problem of a dilute solution containing many chemically different polymers in a common Θ solvent. Using the renormalization group theory of tricritical phenomena, we demonstrate that the chemical mismatch is relevant and the tricritical behavior is in a universality class different from that observed for a dilute solution of polymers of only one chemical type at the Θ temperature. This conclusion is also different from the situation of polymer solutions in good solvents[14] where chemical mismatch is irrelevant in the asymptotic limit of large molecular weights. However our conclusion in Θ solutions is analogous to that of Schafer and Kappeler[15] for good solutions of polymers of finite molecular weights.

We find that the second virial coefficients for a dilute solution with two chemically different chains vanish at the common Θ temperature, according to $L^{-1/2}[\ln(L/a)]^{-9/11}$, where L is the chain length and a is the microscopic cutoff length comparable to monomer size. The exponent of the logarithmic correction is a new component. This result is actually valid for any number of chemically different polymers as long as the common Θ temperature is the same. For a system with three or more different chemical species, the chemical mismatch appears even for the third virial coefficient. The third virial coefficient is independent of chemical differences for a system with two chemically different polymers. We also studied the role of chemical mismatch in dilute solutions of A–B, A–B–A, and A–B–C block copolymers at the common Θ temperature.

The new universality class observed here for the tricritical phenomenon of a dilute polymer solution of many chemically different polymers at the common Θ temperature is the same as the one previously derived for the tricriticality of a dilute polymer solution in quenched random media at the Θ temperature.[17]

The remainder of the paper is organized as follows. In section II, we introduce the continuum model to study the relevance of chemical mismatch of the tricritical polymer solutions. The perturbation theory is presented in section III followed by a renormalization group analysis in section IV. The results of two and three chemically different tricritical polymers are discussed in sections V and VI, respectively. The major conclusions are presented in the final section.

II. Continuum Model

We assume that a polymer chain in a dilute solution at the Θ temperature is adequately described by a continuum chain with the generalized Edwards Hamiltonian

$$\beta\mathcal{H} = \frac{1}{2}\int_0^L \mathrm{d}s \left(\frac{\partial R(s)}{\partial s}\right)^2 + \frac{v}{2}\int_0^L \mathrm{d}s \int_0^L \mathrm{d}s'\, \delta(R(s) - R(s')) + \frac{w}{3!}\int_0^L \mathrm{d}s \int_0^L \mathrm{d}s' \int_0^L \mathrm{d}s''\, \delta(R(s) - R(s'))\delta(R(s') - R(s'')) \quad (2.1)$$

where the first term describes the connectivity of the polymer chain and the second and third terms describe the excluded volume interaction between two and three constituent monomers along the chain, respectively. The parameters v and w measure the effective psuedopotential interactions among two and three monmomers, respectively.

For the many chain system, the above model can be easily generalized. In this paper we consider systems containing two or three different types of monomers. In such cases we need to introduce various kinds of two-body interactions v_{ij} and three-body interactions w_{ijk} (with i, j, k = A, B, C and $v_{ij} = v_{ji}$; $w_{iij} = w_{iji} = w_{jii}$) for interaction between chemically different monomers, v_{ii} and w_{iii} for the two- and three-body interactions of same type of monomer. The parameters v_{AB}, w_{AAB}, and w_{ABB} describe the interactions between A polymer and B polymer, v_{CB}, w_{CCB}, and w_{CBB} describe the interactions between C polymer and B type polymer, and v_{AC}, w_{AAC}, and w_{ACC} describe the interactions between A and C type chains. When we consider the cases $w_{AAB} \neq w_{BBA}$, $w_{BBC} \neq w_{CCB}$, and $w_{AAC} \neq w_{CCA}$, we will treat them as independent parameters to study systematically the chemical mismatch at the three-body interaction level. w_{ABC}, corresponding to the interaction between three different polymers, is considered also as an independent parameter different from the above defined three-body parameters. The two- and three-body excluded volume interactions described in eq 2.1 can be generalized to the system which contains three chemically different polymer chains A, B, and C, and the generalized Hamiltonian is expressed compactly

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using the interaction parameters v_{ij} and w_{ijk} as follows

$$\beta\mathcal{H} = \sum_{i=A}^{C}\frac{1}{2}\int_0^{L_i}\mathrm{d}s\left(\frac{\partial R_i(s)}{\partial s}\right)^2 + \sum_{i,j=A}^{C}\frac{v_{ij}}{2}\int_0^{L_i}\mathrm{d}s\int_0^{L_j}\mathrm{d}s'\,\delta(R_i(s)-R_j(s')) + \sum_{i,j,k=A}^{C}\frac{w_{ijk}}{3!}\int_0^{L_i}\mathrm{d}s\int_0^{L_j}\mathrm{d}s'\int_0^{L_k}\mathrm{d}s''\,\delta(R_i(s)-R_j(s'))\delta(R_j(s')-R_k(s'')) \quad (2.2)$$

The partition function of the system can be written as

$$Z = \prod_{i=A,B,C}\int \mathrm{d}^d R_i(L_i)\int \mathrm{d}^d R_i(0)\int \mathrm{D}[R_i]\exp[-\beta\mathcal{H}] \quad (2.3)$$

The first two integrations in the above equation describe that the partition function of the system is independent of where the polymer ends are in a given volume, and the third integration is the sum of all different conformations of the polymer chains.

Instead of the parameters v_{ij} and w_{ijk} it is convenient to use the Fixman dimensionless expansion parameters in three dimensions, which are defined as

$$\tilde{v}_{ii} = \frac{v_{ii}L_i^{1/2}}{(2\pi)^{3/2}}$$

$$\tilde{v}_{ij} = \frac{v_{ij}L_i^{1/4}L_j^{1/4}}{(2\pi)^{3/2}}$$

$$\tilde{w}_{ijk} = \frac{w_{ijk}}{(2\pi)^3} \quad (2.4)$$

We study the above model using the direct renormalization group theory in three dimensions. The principle of the renormalization group methods involves the following steps. One makes a perturbation expansion for all the physical quantities of interest in terms of Fixman's dimensionless parameters $\tilde{v}$ and $\tilde{w}$. In the asymptotic limit of infinetely long polymers the bare parameters $\tilde{v}$ and $\tilde{w}$ diverge logarthmically in three dimensions. One eliminates then these bare parameters in favor of physical parameters and looks at the fixed point conditions to find the universal behavior.

III. Perturbation Expansion

We first assume for simplicity that all three chains A, B, and C have the same contour lengths $L_A = L_B = L_C = L$. The polydispersity will be discussed in the next section. If ρ_A, ρ_B, and ρ_C denote the concentrations of the chains A, B, and C, the virial expansion for the osmotic pressure Π is,

$$\frac{\Pi}{K_BT} = \sum_{i=A,B,C}\rho_i + \frac{1}{2}\sum_{i,j=A,B,C}\rho_i\rho_jA_2^{ij} + \frac{1}{3}\sum_{i,j,k=A,B,C}\rho_i\rho_j\rho_kA_3^{ijk} + \dots \quad (3.1)$$

where A_2^{ij} denotes the second virial coefficient between i and j chains and A_3^{ijk} the third virial coefficient between i, j, and k chains. The second virial coefficients A_2^{ij} have the dimension of a volume, and the third virial coefficients A_3^{ijk} have the dimension of volume squared.

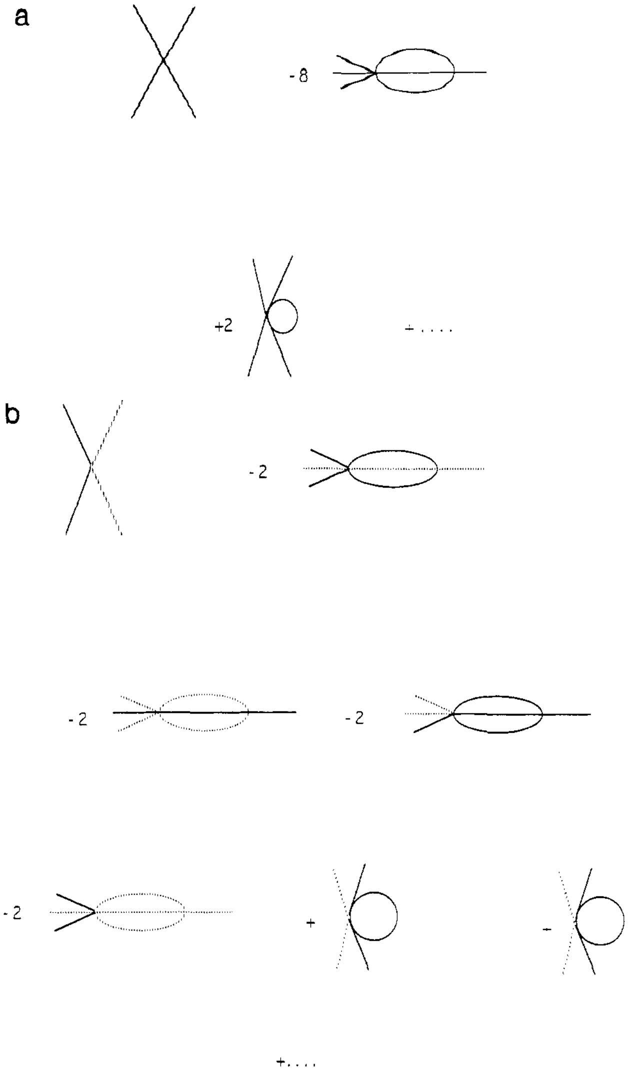

Figure 1. (a) Polymer diagrams for the second virial coefficient A_2^{ii}. (b) Diagrams for the mutual virial coefficient A_2^{ij}, where a solid line denotes a polymer of chemical type i and a dotted line denotes a polymer of type j.

The second and third virial coefficients can be written as

$$A_2^{ij} = \frac{Z_c^{ij}[L,L]}{(Z^i[L])^2} \quad i, j = A, B, C \quad (3.2)$$

$$A_3^{ijk} = \frac{Z_c^{ijk}[L,L,L]}{(Z^i[L])^3} \quad i, j, k = A, B, C \quad (3.3)$$

where $Z_c^{ij}[L,L]$ and $Z_c^{ijk}[L,L,L]$ are the connected two and three polymer chain partition functions of i, j, and k type chains. The diagrammatic rules for expanding virial coefficients and the renormalization procedures are described in detail in refs 10 and 12. The difference in our case is that we have three different kinds of lines in the diagrammatic description corresponding to polymers A, B, and C. In calculating the diagrams, we associate a factor $-v_{AA}(v_{BB},v_{cc})$ with the interaction between two A(B,C) type polymers, and $-v_{AB}(v_{BC},v_{CA})$ between polymers A(B,C) and B(C,A). Similarly, a factor of $-w_{AAA}(w_{BBB},w_{CCC})$ is associated with the interaction between three A(B,C) type monomers, and $-w_{AAB}(w_{BBA},w_{ACC},w_{AAC},w_{CCB},w_{BBC})$ with the interaction between two A(B,C,A,C,B) polymers and B(A,A,C,B,C) polymers. When three chemically different polymers interact, we give a weight $-w_{ABC}$. Figure 1 shows the diagrams corresponding to the second virial coef-

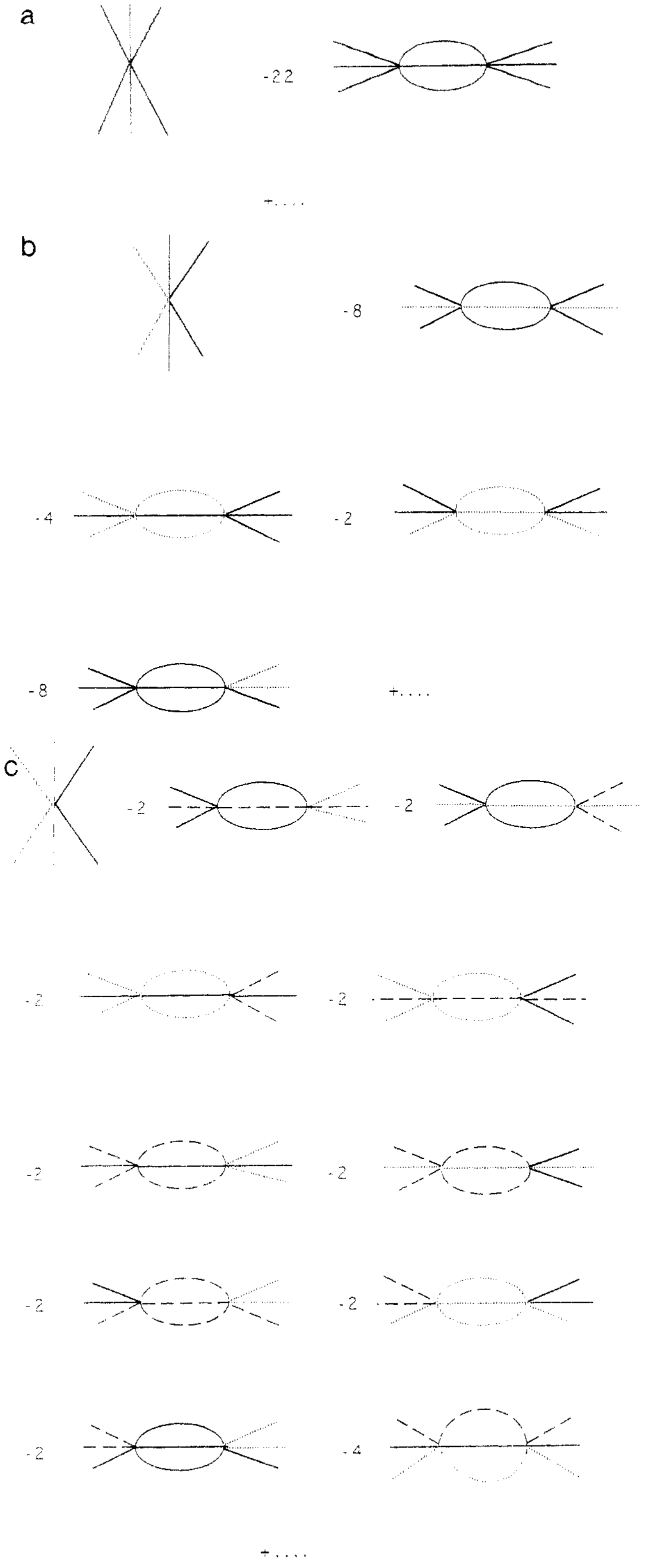

Figure 2. (a) Diagrams contributing to the third virial coefficient A_3^{iii}. (b) Diagrams for the third virial coefficient A_3^{iij}. The chemically different i and j polymers are represented by solid and dotted lines, respectively. (c) Diagrammatic representation of the perturbation expansion for the third virial coefficient A_3^{ijk}. The chemically different i, j, and k polymers are denoted by solid, dashed, and dotted lines, respectively.

ficients, and Figure 2 shows the polymer diagrams for third virial coefficients. Since we are working in three-dimensional space, the only relevant diagrams which diverge logarithmically in the asymptotic limit of infinite chains are the diagrams with three internal lines,[9,10] and to the leading order these diagrams are shown in Figure 1 and 2. The prefactor in front of every diagram describes the symmetry of the diagram (or number of ways one can make that diagram). Parts a and b of Figure 1 show the diagrams for A_2^{ii} and A_2^{ij}(i ≠ j), respectively. In Figure 1b there are more diagrams compared to Figure 1a because of the difference in the excluded volume parameters between different kinds of monomers. Notice that, when we take i and j polymers of the same type in Figure 1b, Figure 1b reduces to Figure 1a. The second virial coefficient corresponding to the like molecules are obviously independent of v_{ij}(i ≠ j), w_{iij}(i ≠ j), and w_{ijk}(i ≠ j ≠ k, i ≠ k) and it is equal to

$$A_2^{ii} = (2\pi L)^{3/2}[\tilde{v}_{ii}(1 - 16\pi\tilde{w}_{iii}\ln(L/a)) - 8\tilde{w}_{iii}] \quad (3.4)$$

The mutual second virial coefficient is given by

$$A_2^{ij} = (2\pi L)^{3/2}[\tilde{v}_{ij}[1 - 4\pi(\tilde{w}_{iij} + \tilde{w}_{ijj})\ln(L/a)] - 4\pi(\tilde{v}_{ii}\tilde{w}_{iij} + \tilde{v}_{jj}\tilde{w}_{jji})\ln(L/a) - 4(\tilde{w}_{iij} + \tilde{w}_{jji})] \quad (3.5)$$

with i ≠ j, i, j = A, B, C, where the terms having logarithmic divergence are from diagrams with three internal line and a is the cutoff parameter which is of the order of one monomer length.

The perturbation results for the third virial coefficients A_3^{iii}, A_3^{iij}, and A_3^{ijk} can be obtained from eq 3.3. Each term in the perturbation expansion can be represented as a diagram. The leading diagrams are shown in Figure 2. The required polymer diagrams for the third virial coefficient between like molecules A_3^{iii} is given in Figure 2a, and as expected, A_3^{iii} is independent of $\tilde{w}_{iij}$ and $\tilde{w}_{ijk}$. The results for the mutual third virial coefficients A_3^{iij} and A_3^{ijk} are shown diagrammatically in Figure 2b,c, respectively. One can see clearly how the symmetry factor 22 is shared between different mutual three-body excluded volume parameters. The perturbative results for the third virial coefficients up to one loop level are listed as follows:

$$A_3^{iii} = (2\pi L)^3[\tilde{w}_{iii} - 44\pi\tilde{w}_{iii}^2\ln(L/a)] \qquad \text{i = A, B, C} \quad (3.6)$$

$$A_3^{iij} = (2\pi L)^3[\tilde{w}_{iij} - 2\pi(8\tilde{w}_{iij}^2 + 2\tilde{w}_{jji}^2 + 8\tilde{w}_{iii}\tilde{w}_{iij} + 4\tilde{w}_{ijj}\tilde{w}_{iij})\ln(L/a)] \qquad \text{i} \neq \text{j = A, B, C} \quad (3.7)$$

$$A_3^{ABC} = (2\pi L)^3[\tilde{w}_{ABC} + 4\pi(2\tilde{w}_{ABC}^2 + \tilde{w}_{ABC}\{\tilde{w}_{AAB} + \tilde{w}_{BBA} + \tilde{w}_{AAC} + \tilde{w}_{CCA} + \tilde{w}_{BBC} + \tilde{w}_{BCC}\} + \tilde{w}_{AAC}\tilde{w}_{AAB} + w_{BBA}\tilde{w}_{BBC} + \tilde{w}_{CCA}\tilde{w}_{CCB})\ln(L/a)] \quad (3.8)$$

The above results are for three chemially different polymer systems, but in principle, our perturbation results are very general and suited for any number of chemically different polymer systems. When we take the three-body parameters $\tilde{w}_{AAA} = \tilde{w}_{BBB} = \tilde{w}_{CCC} = \tilde{w}_{AAB} = \tilde{w}_{BBA} = \tilde{w}_{BBC} = \tilde{w}_{CCB} = \tilde{w}_{AAC} = \tilde{w}_{CCA} = \tilde{w}_{ABC}$, i.e., when the polymers are chemically identical, we find $A_3^{iii} = A_3^{iij} = A_3^{ABC}$, as should be expected.

The second and third virial coefficients have terms which are diverging logarithmically for very large molecular weights. These logarithic divergences can be removed by properly renormalizing the interaction parameters, $\tilde{v}_{ii}$ and $\tilde{v}_{ij}$(i ≠ j) and $\tilde{w}_{iii}$, $\tilde{w}_{iij}$(i ≠ j), and $\tilde{w}_{ABC}$, which is the objective of the next section.

IV. Renormalization Group Analysis

A. Third Virial Coefficient. Since we are interested in studying the relevance of chemical mismatch near the Θ temperature, we first consider the renormalization of third virial coefficients A_3^{iii}, A_3^{iij}(i ≠ j), and A_3^{ABC}. The three-body interaction parameters $\tilde{w}_{iii}$, $\tilde{w}_{iij}$, and $\tilde{w}_{ABC}$ are renormalized to $\tilde{w}^{R}_{iii}$, $\tilde{w}^{R}_{iij}$, and $\tilde{w}^{R}_{ABC}$, respectively. These renormalized parameters obey renormalization group equations in three dimensions, which are obtained from perturbation results of eqs 3.6–3.8 to be

$$L\frac{\partial \tilde{w}^{R}_{iii}}{\partial L} = -44\pi \tilde{w}^{R\,2}_{iii} \tag{4.1}$$

$$L\frac{\partial \tilde{w}^{R}_{iij}}{\partial L} = -16\pi \tilde{w}^{R\,2}_{iij} - 4\pi w^{\hat{R}\,2}_{ijj} - 8\pi \tilde{w}^{R}_{iij}\tilde{w}^{R}_{jji} - 16\pi \tilde{w}^{R}_{iii}\tilde{w}^{R}_{iij} \tag{4.2}$$

$$L\frac{\partial \tilde{w}^{R}_{ABC}}{\partial L} = -8\pi {\tilde{w}^{R}_{ABC}}^{2} - 4\pi \tilde{w}^{R}_{ABC} \sum_{i\neq j=A}^{C} \tilde{w}^{R}_{iij} - 4\pi(\tilde{w}^{R}_{AAB}\tilde{w}^{R}_{AAC} + \tilde{w}^{R}_{BBC}\tilde{w}^{R}_{BBA} + \tilde{w}^{R}_{CCA}\tilde{w}^{R}_{CCB}) \tag{4.3}$$

The asymptotic limit is given by one diverging quantity, which is the contour length of the chain L. When the chain becomes infinitely long, the w parameters tend to their fixed point[18] values, $\tilde{w}^{R}_{iii}{}^{*}$, $\tilde{w}^{R}_{iij}{}^{*}$, and $\tilde{w}^{R}_{ABC}{}^{*}$. These fixed point values can be obtained by solving the renormalization group equations (4.1)–(4.3). We take the solutions of the renormalization group equations in the following form:

$$\tilde{w}^{R}_{iii} = \frac{g_{iii}}{\ln(L/a)} \qquad i = A, B, C$$

$$\tilde{w}^{R}_{iij} = \frac{g_{iij}}{\ln(L/a)} \qquad i \neq j = A, B, C$$

$$\tilde{w}^{R}_{ABC} = \frac{g_{ABC}}{\ln(L/a)} \tag{4.4}$$

Substituting the above eq 4.4 into eqs 4.1–4.3, we obtain the set of equations for amplitudes (g_{iii}, g_{iij}, and g_{ABC})

$$g_{iii} = 44\pi g^{2}_{iii} \tag{4.5}$$

$$g_{iij} = 16\pi g^{2}_{iij} + 16\pi g_{iii}g_{iij} + 4\pi g^{2}_{iij} + 8\pi g_{iij}g_{ijj} \tag{4.6}$$

$$g_{ABC} = 8\pi g^{2}_{ABC} + 4\pi g_{ABC} \sum_{i\neq j=A}^{C} g_{iij} + 4\pi(g_{AAB}g_{AAC} + g_{BBA}g_{BBC} + g_{CCA}g_{CCB}) \tag{4.7}$$

The solutions of the above equations yield the following possible fixed points: (a) A Gaussian fixed point

$$g^{*}_{iii} = g^{*}_{iij} = g^{*}_{ABC} = 0 \tag{4.8}$$

(b) A fixed point at which all three chains are Gaussian but they interact

$$g^{*}_{AAA} = g^{*}_{BBB} = g^{*}_{CCC} = 0$$

$$g^{*}_{iij} = 1/28\pi \tag{4.9}$$

but we find a complex fixed point value for g^{*}_{ABC}, which is unphysical. Also unphysical fixed point values show up when one or two of the three chains are Gaussian but they interact mutually. (c) One fixed point where all chains are non-Gaussian and interacting

$$g^{*}_{AAA} = g^{*}_{BBB} = g^{*}_{CCC} = g^{*}_{AAB} = g^{*}_{ABB} = 1/44\pi$$

$$g^{*}_{CCA} = g^{*}_{AAC} = g^{*}_{BBC} = g^{*}_{CCB} = 1/44\pi$$

$$g^{*}_{ABC} = 3/88\pi,\ 1/44\pi \tag{4.10}$$

Among the various possible fixed points, the stable one can be obtained by stability analysis. The stability analysis we followed is similar to the one discussed in refs 16 and 17 for the case of tricritical systems in three dimensions. The details are given in the Appendix. We find none of the above fixed points to be stable.

When the three-body interaction parameters $\tilde{w}_{AAB} = \tilde{w}_{BBA}$, $\tilde{w}_{BBC} = \tilde{w}_{CCB}$, and $\tilde{w}_{ACC} = \tilde{w}_{AAC}$, then we have only seven independent three-body parameters, which are

$$\tilde{w}_{AAA}, \tilde{w}_{BBB}, \tilde{w}_{CCC}, \tilde{w}_{AAB}, \tilde{w}_{AAC}, \tilde{w}_{BBC}, \tilde{w}_{ABC} \tag{4.11}$$

The renormalized parameters corresponding to these seven $\tilde{w}$ parameters obey renormalization group equations, which can be obtained from eqs 4.1–4.3 using (4.11). Then one solves the amplitude equations (4.5)–(4.6) to find the following stable fixed point

$$g^{*}_{AAA} = g^{*}_{BBB} = g^{*}_{CCC} = 1/44\pi$$

$$g^{*}_{AAB} = g^{*}_{AAC} = g^{*}_{BBC} = 1/44\pi$$

$$g^{*}_{ABC} = 3/88\pi \tag{4.12}$$

Using this fixed point, we find near the tricritical point, the third virial coefficients for asymptotically large molecules as

$$A^{AAA}_{3} = A^{BBB}_{3} = A^{CCC}_{3} = \frac{(2\pi L)^{3}}{44\pi \ln(L/a)} \tag{4.13}$$

$$A^{AAB}_{3} = A^{BBC}_{3} = A^{CCA}_{3} = \frac{(2\pi L)^{3}}{44\pi \ln(L/a)} \tag{4.14}$$

$$A^{ABC}_{3} = \frac{3(2\pi L)^{3}}{88\pi \ln(L/a)} \tag{4.15}$$

Since not all the thirid virial coefficients of eqs 4.15–4.17 are equal near the tricritical point, there is a chemical mismatch at the level of three-body interactions. If we consider a system containing A and B type polymers alone in a common Θ solvent, then the third virial coefficients near the tricritical point turn out to be

$$A^{AAA}_{3} = A^{BBB}_{3} = A^{AAB}_{3} = \frac{(2\pi L)^{3}}{44\pi \ln(L/a)} \tag{4.16}$$

In this case since all the third virial coefficients in eq 4.15 are equal, at the level of three-body interaction, the chemical differences between A and B polymers are irrelevant. However, the chemical mismatch affects the behavior of the second virial coefficients dramatically, as shown in the next subsection.

So far we have studied monodisperse polymers of A, B, and C of same chain length L. The next step is to understand the effect of polydispersity between A, B, and C molecules on the renormalization group analysis. In doing the fixed point analysis for the monodisperse system, the chain length L is identified as the diverging length scale. For the polydisperse system containing chemically different polymers of various chain lengths, we can choose the longest chain length as the diverging length scale. Since the tricritical renormalization group equations (4.1)–(4.3) are scale invariant, the polydispersity effects do not change the fixed point values calculated above, given by eq 4.13. For example, if polymer A of chain length L_A is longer than B and C polymers with chain lengths, L_B and L_C, then L_A can be identified in the fixed point analysis as the logarithmically diverging length scale. In the case of copolymer solutions, we choose the chain length L of the copolymer as the logarithmically diverging length sale in our tricritical analysis. Even though polydispersity does not affect the universal tricritical logarithmic behaviors, the scaling functions are indeed influenced by polydispersity. The explicit forms of these functions are presented in the next section.

B. Second Virial Coefficients. The second virial coefficients in eq 3.1 are associated with the renormalization of two-body interaction parameters $\tilde{v}_{ii}$ (i = A, B, C) and $\tilde{v}_{ij}$ (i ≠ j). The renormalization group equations for the renormalized two-body interaction parameters, $\tilde{v}_{ii}^R$ and $\tilde{v}_{ij}^R$, in three dimensions are

$$L\frac{\partial \tilde{v}_{ii}^R}{\partial L} = -16\pi \tilde{v}_{ii}^R \tilde{w}_{iii}^R \qquad i = A, B, C \tag{4.17}$$

and

$$L\frac{\partial \tilde{v}_{ij}^R}{\partial L} = -8\pi \tilde{v}_{ij}^R \tilde{w}_{iij}^R - 4\pi \tilde{v}_{ii}^R \tilde{w}_{iij}^R - 4\pi \tilde{v}_{jj}^R \tilde{w}_{jji}^R \qquad i \neq j = A, B, C \tag{4.18}$$

In writing eqs 4.18 and 4.19, we have taken into account the following equalities:

$$\tilde{w}_{AAB} = \tilde{w}_{BBA} \qquad \tilde{w}_{BBC} = \tilde{w}_{CCB} \qquad \tilde{w}_{AAC} = \tilde{w}_{CCA} \tag{4.19}$$

Substituting the stable fixed point values of $\tilde{w}_{iii}^R$ and $\tilde{w}_{iij}^R$ from eq 4.13 into eqs 4.18 and 4.19 and looking for solutions of the form

$$\tilde{v}_{ii}^R = \tilde{v}_{ii}[\ln(L/a)]^{-\delta} \tag{4.20}$$

$$\tilde{v}_{ij}^R = \tilde{v}_{ij}[\ln(L/a)]^{-\delta} \tag{4.21}$$

we get

$$\delta \tilde{v}_{ii} = \frac{4}{11}\tilde{v}_{ii}$$

$$\delta \tilde{v}_{ij} = \frac{2}{11}\tilde{v}_{ij} + \frac{1}{11}\tilde{v}_{ii} + \frac{1}{11}\tilde{v}_{jj} \tag{4.22}$$

The eigenvalues δ_1 and δ_2 of these equations are $\delta_1 = 4/11$ and $\delta_2 = 2/11$. Since the smallest eigenvalue δ_2 dominates the thermodynamics near the tricritical point,

$$\tilde{v}_{ii}^R = \tilde{v}_{ii}[\ln(L/a)]^{-2/11}$$

$$\tilde{v}_{ij}^R = \tilde{v}_{ij}[\ln(L/a)]^{-2/11} \tag{4.23}$$

The two-body interactions renormalize with a different logarithmic power law compared to the case when all polymers are chemically the same.[10–12] The exponent 2/11 is characteristic of a new tricritical state.

V. Two Component Systems

In this section we discuss the conditions for the chemical mismatch between two different polymers near the tricritical point on the basis of the renormalization group equations derived above. We consider the cases of homopolymers of A and B in the dilute and semidilute solutions and A–B diblock and A–B–A triblock copolymers in dilute solutions.

A. Dilute Solutions Containing A,B Homopolymers. Consider two chemically different homopolymers A and B in a common Θ solvent. We study this system near the tricritical point to understand the role of the chemical difference between polymers on universal polymer properties in a common Θ solvent.

The results of renormalization group analysis for the monodisperse A, B homopolymer system can be obtained from the results of section IV. The stable tricritical fixed points for this system are same as in eq 4.13. Since the tricritical fixed point values are same for all the three-body interaction parameters, the chemical difference at the level of three-body interaction is irrelevant near the tricritical point for the A, B homopolymer system. But, the renormalized two-body interaction parameters are affected by chemical mismatch and they renormalize with a different logarithmic exponent, eq 4.23, compared to the exponent of the one component system derived in refs 10–12.

The renormalized second virial coefficients can be obtained from eqs 3.4 and 3.5 using eqs 4.13 and 4.23, and they are given as

$$A_2^{ii} = (2\pi L)^{3/2}[\tilde{v}_{ii}[\ln(L/a)]^{-2/11} - 8\tilde{w}_{iii}^{R}{}^*] \tag{5.1}$$

$$A_2^{AB} = (2\pi L)^{3/2}[\tilde{v}_{AB}[\ln(L/a)]^{-2/11} - 8\tilde{w}_{AAB}^{R}{}^*] \tag{5.2}$$

The above second virial coefficients of A, B homopolymers vanish at the tricritical point, which yields

$$v_{ii} \sim (2\pi)^{-3/2} 8 L^{-1/2} \frac{[\ln(L/a)]^{-9/11}}{44\pi} \tag{5.3}$$

$$v_{AB} \sim (2\pi)^{-3/2} 8 L^{-1/2} \frac{[\ln(L/a)]^{-9/11}}{44\pi} \tag{5.4}$$

For very long polymers the two-body excluded volume parameters vanish indentically at the tricritical point. The two-body excluded volume parameters for the finite chains are vanishing functions of molecular weight. The exponent 9/11 of the logarithmic correction in eqs 5.3–5.4 is different from exponent 7/11 of the single component system.[10–12] We determined from the tricritical theory of A, B homopolymers that the mutual excluded volume parameter v_{AB} vanishes as in eq 5.4. This agrees with the results of a scaling theory by de Gennes.[19]

When the monodisperse polymers A and B are of different lengths L_A and L_B, respectively, then we choose, as we discussed in the previous section, the longest chain length as the logarithmically diverging length scale. For the case when L_A is larger than L_B, we can write down the second virial coefficients using eq 5.4–5.2 as

$$A_2^{ii} = (2\pi L_i)^{3/2}\left[\tilde{v}_{ii}[\ln(L_A/a)]^{-2/11} - \frac{8[\ln(L_A/a)]^{-1}}{44\pi}\right] \qquad i = A, B \tag{5.5}$$

$$A_2^{AB} = (2\pi)^{3/2} L_A L_B \left[\frac{\tilde{v}_{AB}[\ln(L_A/a)]^{-2/11}}{{L_A}^{1/4}{L_B}^{1/4}} - \frac{4[\ln(L_A/a)]^{-1}}{44\pi}\left[\frac{1}{{L_A}^{1/2}} + \frac{1}{{L_B}^{1/2}}\right]\right] \tag{5.6}$$

At the tricritial point, the two-body excluded volume parameters for finite chain length L_A and $L_B (L_A > L_B)$ are given by

$$\upsilon_{ii} \sim (2\pi)^{-3/2} 8 L_i^{-1/2} \frac{[\ln(L_A/a)]^{-9/11}}{44\pi} \tag{5.7}$$

$$\upsilon_{AB} \sim (2\pi)^{-3/2} 4 \frac{[L_A^{1/2} + L_B^{1/2}]}{L_A^{1/2} L_B^{1/2}} \frac{[\ln(L_A/a)]^{-9/11}}{44\pi} \tag{5.8}$$

The results of eqs 5.5 and 5.8 are general, and they are independent of the chemically different number of polymer components in the system. Note that when $L_A = L_B = L$, eqs 5.7 and 5.8 reduce to eqs 5.3 and 5.4. If chain length L_A is very large compared to L_B, then from eq 5.8 we find

$$\upsilon_{AB} \sim \upsilon_B \sim L_B^{-1/2} [\ln(L_A/a)]^{-9/11} \tag{5.9}$$

When $L_B > L_A$, our results at the tricritical point eqs 5.7 and 5.8 are unchanged, except that the logarithmically divering length scale is L_B instead of L_A. If the polymer B of length L_B is longer than A polymer of length L_A, the mutually excluded volume parameters become

$$\upsilon_{AB} \sim \upsilon_A \sim L_A^{-1/2} [\ln(L_B/a)]^{-9/11} \tag{5.10}$$

This major conclusion is to be contrasted with the lack of chemical mismatch between A and B in a mutually good solvent in the asymptotic regime of infinite chain size.[14]

B. Semidilute Solutions of A, B Homopolymer Mixtures in a Θ Solvent. We study here the semidilute solution containing A chains and B chains in a Θ solvent. In order to study this, we generalize the formalism developed by Duplantier[10] for the case of semidilute polymer solutions near the Θ point. The details of this formalism and the results are given in ref 20. The tricritical laws in the semidilute regime are similar to the dilute case we discussed in the previous subsection. The monomer concentrations C_A and C_B of A and B polymers, respectively, are related to the chain lengths L_A and L_B and the chain concentrations as

$$C_A = \rho_A L_A \qquad C_B = \rho_B L_B \tag{5.11}$$

where ρ_A and ρ_B are the chain concentrations of A and B polymers. Instead of ρ_A and ρ_B one can use the total monomers x; $C_A = xC$ and $C_B = (1-x)C$. The semidilute regime is reached when the total monomer concentration is comparable to or larger than the overlap concentration C^* given by

$$C^* \sim \frac{1}{L_A^{1/2} x + L_B^{1/2}(1-x)} \tag{5.12}$$

For the monodisperse case $L_A = L_B = L$, and eq 5.12 reduces to

$$C^* \sim 1/L^{1/2} \tag{5.13}$$

Using the above equation, we can replace the chain length L in the logarithmic correction with $1/C^2$. The dimensionless third virial coefficients from eq 4.17 read at the semidilute regime

$$\frac{A_3^{AAA}}{(2\pi L)^3} = \frac{A_3^{BBB}}{(2\pi L)^3} = \frac{A_3^{AAB}}{(2\pi L)^3} = \frac{1}{44\pi \ln(1/C^2 a)} \tag{5.14}$$

The tricritical osmotic pressure in the semidilute regime is given by

$$\frac{\Pi}{K_B T} = \frac{C^2}{2}[x^2 \upsilon_{AA} + (1-x)^2 \upsilon_{BB} + 2(1-x)x\upsilon_{AB}]\{\ln(1/C^2 a)\}^{-2/11} + \frac{1}{3}\frac{C^3}{44\pi \ln(1/C^2 a)} \tag{5.15}$$

This expression for osmotic pressure can be taken as the starting point to study the thermodynamics of A, B homopolymer mixtures in a mutual Θ solvent.

C. Dilute Solutions Containing Diblock Copolymers near the Θ Point. In this section we study diblock copolymers in a solvent S near the tricritical point. Consider a diblock copolymer having a sequence of A of chain length L_A linked to the sequence of B of length L_B. The fractions of A and B blocks in the copolymer of length L are given by

$$L_A = fL \qquad L_B = (1-f)L \tag{5.16}$$

The tricritical fixed point analysis for the diblock copolymers are the same as that of the A, B homopolymer system. There exists a stable fixed point when the three-body parameters $w_{AAB} = w_{ABB}$, and the stable fixed point reads as

$$\tilde{w}^R_{AAA}{}^* = \tilde{w}^R_{BBB}{}^* = \tilde{w}^R_{AAB}{}^* = \frac{1}{44\pi \ln(L/a)} \tag{5.17}$$

The above fixed point is independent of the difference between lengths of A and B blocks, and we have identified the total chain length L of the copolymer as the diverging length scale. The third virial coefficient of the diblock copolymer near the tricritical point is given by

$$A_3^{A-B} = A_3^{AAA} + A_3^{BBB} + 3(A_3^{AAB} + A_3^{BBA})$$

$$= (2\pi L)^3 [f^2 \tilde{w}^R_{AAA}{}^* + (1-f)^2 \tilde{w}^R_{BBB}{}^* + ((1-f)f^2 + f(1-f)^2)\tilde{w}^R_{AAB}{}^*] \tag{5.18}$$

Combining eqs 5.17 and 5.18 yields

$$A_3^{A-B} = \frac{1}{44\pi \ln(L/a)} \tag{5.19}$$

From the above equation, we conclude that the third virial coefficient is independent of the chemical difference between A and B blocks near the tricritical point.

The renormalized second virial coefficient of the diblock copolymer can be obtained by substituting eqs 5.17 and 4.23 into eqs 3.4 and 3.5, as

$$A_2 = A_2^{AA} + A_2^{BB} + 2A_2^{AB} = (2\pi L)^{3/2}[f^{3/2}(\tilde{\upsilon}^R_{AA} - 8\tilde{w}^R_{AAA}{}^*) + (1-f)^{3/2}(\tilde{\upsilon}^R_{BB} - 8\tilde{w}^R_{BBB}{}^*) + 2(f(1-f))^{3/4}(\tilde{\upsilon}^R_{AB} - 4\tilde{w}^R_{AAB}{}^*((f/(1-f))^{1/4} + ((1-f)/f)^{1/4}))] \tag{5.20}$$

where $\tilde{\upsilon}^R_{AA}$, $\tilde{\upsilon}^R_{BB}$, and $\tilde{\upsilon}^R_{AB}$ are the renormalized two-body interaction parameters given in eq 4.23.

The tricritical theory of diblock copolymers shows that at the tricritical point the second virial coefficients A_2^{AA}, A_2^{BB}, and A_2^{AB} vanish. Near the tricritical point the excluded volume parameters are vanishing functions of chain length, and they read as follows,

$$v_{\mathrm{AA}} \sim (2\pi)^{-3/2} 8 (Lf)^{-1/2} \frac{[\ln(L/a)]^{-9/11}}{44\pi} \tag{5.21}$$

$$v_{\mathrm{BB}} \sim (2\pi)^{-3/2} 8 L^{-1/2} (1-f)^{-1/2} \frac{[\ln(L/a)]^{-9/11}}{44\pi} \tag{5.22}$$

$$v_{\mathrm{AB}} \sim (2\pi)^{-3/2} L^{-1/2} 4 \frac{[f^{1/2} + (1-f)^{1/2}]}{f^{1/2}(1-f)^{1/2}} \frac{[\ln(L/a)]^{-9/11}}{44\pi} \tag{5.23}$$

D. Dilute Solutions of A–B–A Triblock Copolymer in a Θ Solvent. Consider an A–B–A triblock copolymer of total length L in a Θ solvent. The fraction of B block in the triblock copolymer is given by

$$L_{\mathrm{B}} = f_2 L \tag{5.24}$$

and the fraction of A monomers in the first and third blocks are respectively given by

$$L_{\mathrm{A1}} = f_1 L \qquad L_{\mathrm{A2}} = (1 - f_1 - f_2)L \tag{5.25}$$

The perturbation theory and renormalization group analysis for the problem is similar to the A, B homopolymer and A–B diblock copolymer systems discussed above.

The third virial coefficient for the A–B–A triblock copolymer is given by

$$A_3^{\mathrm{A-B-A}} = A_3^{\mathrm{A_1A_1A_1}} + A_3^{\mathrm{A_2A_2A_2}} + A_3^{\mathrm{BBB}} + 3(A_3^{\mathrm{A_1A_1B}} + A_3^{\mathrm{BBA_1}}) + 3(A_3^{\mathrm{A_2A_2B}} + A_3^{\mathrm{A_2BB}}) + 3(A_3^{\mathrm{A_1A_1A_2}} + A_3^{\mathrm{A_2A_2A_1}}) + 6A_3^{\mathrm{A_1A_2B}} \tag{5.26}$$

$$A_3^{\mathrm{A-B-A}} = (2\pi L)^3[\tilde{w}_{\mathrm{AAA}}^{\mathrm{R}}{}^*(f_1{}^3 + (1-f_1-f_2)^3 + 3(1-f_1-f_2)^2 f_1 + (1-f_1-f_2)f_1{}^2) + \tilde{w}_{\mathrm{BBB}}^{\mathrm{R}}{}^* f_2{}^2 + \tilde{w}_{\mathrm{AAB}}^{\mathrm{R}}{}^*(f_2(1-f_1-f_2)^2 + f_2{}^2(1-f_1-f_2) + f_1{}^2 f_2 + f_1 f_2{}^2)] \tag{5.27a}$$

$$= \frac{(2\pi L)^3}{44\pi \ln(L/a)} \tag{5.27b}$$

As in the case of A–B diblock polymers, the chemical difference between the blocks thus becomes irrelevant near the tricritical point at the level of three-body interactions even for the A–B–A triblock polymers.

The renormalized second virial coefficient of the A–B–A triblock copolymer is given by

$$A_2^{\mathrm{A-B-A}} = A_2^{\mathrm{A_1A_1}} + A_2^{\mathrm{A_2A_2}} + 2A_2^{\mathrm{A_1A_2}} + 2(A_2^{\mathrm{A_1B}} + A_2^{\mathrm{A_2B}}) + A_2^{\mathrm{BB}} \tag{5.28}$$

where

$$A_2^{\mathrm{A_1A_1}} + 2A_2^{\mathrm{A_1A_2}} + A_2^{\mathrm{A_2A_2}} = A_2^{\mathrm{AA}} = (2\pi L)^{3/2}\left[\frac{(1-f_2)^2 L^{1/2} v_{\mathrm{AA}} [\ln(L/a)]^{-2/11}}{(2\pi)^{3/2}} - 8\tilde{w}_{\mathrm{AAA}}^{\mathrm{R}}{}^*\{(1-f_1-f_2)^{1/2}(1-f_2) + f_1{}^{1/2}(1-f_2)\}\right] \tag{5.29}$$

$$A_2^{\mathrm{AB}} = A_2^{\mathrm{A_1B}} + A_2^{\mathrm{BA_2}} = (2\pi L)^{3/2}\left[\frac{f_2(1-f_2)L^{1/2} v_{\mathrm{AB}} [\ln(L/a)]^{-2/11}}{(2\pi)^{3/2}} - 4\tilde{w}_{\mathrm{AAB}}^{\mathrm{R}}{}^*\{f_1{}^{1/2} f_2 + f_2(1-f_1-f_2)^{1/2} + f_2{}^{1/2}(1-f_2)\}\right] \tag{5.30}$$

and

$$A_2^{\mathrm{BB}} = (2\pi L)^{3/2}[\tilde{v}_{\mathrm{BB}}^{\mathrm{R}} - 8\tilde{w}_{\mathrm{BBB}}^{\mathrm{R}}{}^*] \tag{5.31}$$

At the tricritical point the virial coefficients A_2^{AA}, A_2^{BB}, and A_2^{AB} vanish identically. The excluded volume parameters v_{AA}, v_{BB}, and v_{AB} near the tricritical point can be calculated by equating eqs 5.29–5.31 to zero, which yields

$$v_{\mathrm{AA}} \sim (2\pi)^{-3/2} L^{-1/2} 8 \frac{[f_1{}^{1/2} + (1-f_1-f_2)^{1/2}]}{(1-f_2)} \frac{[\ln(L/a)]^{-9/11}}{44\pi} \tag{5.32}$$

$$v_{\mathrm{BB}} \sim (2\pi)^{-3/2} 8 (f_2 L)^{-1/2} \frac{[\ln(L/a)]^{-9/11}}{44\pi} \tag{5.33}$$

and

$$v_{\mathrm{AB}} \sim (2\pi)^{-3/2} 4 L^{-1/2} \times \frac{[f_1{}^{1/2} f_2 + f_2(1-f_1-f_2)^{1/2} + f_2{}^{1/2}(1-f_2)]}{f_2(1-f_2)} \frac{[\ln(L/a)]^{-9/11}}{44\pi} \tag{5.34}$$

VI. Three Component Systems

We now consider polymer solutions containing three chemically different types of polymers in a common solvent S. We shall discuss the role of chemical mismatch in two types of three component systems. First, a system containing A, B, C homopolymers in a Θ solvent. The second type of system is A–B–C triblock copolymer solutions. In both cases, chemical mismatch plays a crucial role.

A. Dilute Solutions of A, B, C Homopolymers. The results of renormalization group analysis for the A, B, C homopolymers are given in section IV. The third virial coefficients near the tricritical point are given by eqs 4.14–4.16. The renormalized second virial coefficients are obtained using eqs 4.14–4.16 and eq 4.23 in eqs 3.4 and 3.5. At the tricritical point the second virial coefficients vanish, giving the results of eqs 5.7 and 5.8. Obviously, the third component C does not affect the tricritical values of the two-body excluded volume parameters. As demonstrated in section IV, the third virial coefficients are given by eqs 4.14–4.16. All these third virial coefficients are not equal near the tricritical point and hence there is a chemical mismatch in A, B, C homopolymer systems at the three-body interaction level.

B. Semidilute Solutions of A, B, C Homopolymer Mixtures in a Common Θ Solvent. Since the tricritical laws in the semidilute regime are similar to those in dilute solutions, we can propose a universal form for the osmotic pressure of A, B, C homopolymer systems. The monomer concentrations C_{A}, C_{B}, and C_{C} of A, B, and C polymers are related to the chain lengths L_{A}, L_{B}, and L_{C} and chain concentration ρ_{i} as

$$C_{\mathrm{i}} = \rho_{\mathrm{i}} L_{\mathrm{i}} \qquad \mathrm{i} = \mathrm{A, B, C} \tag{6.1}$$

We can use the total monomer concentration $C = C_{\mathrm{A}} +$

$C_B + C_C$ instead of ρ_i's. Consider x fraction of A type monomers and y fraction of B type monomers. Then the total concentration can be written as

$$C = C_A + C_B + C_C = xC + yC + (1 - x - y)C \qquad (6.2)$$

In the semidilute regime there exists a relation between total monomer concentration and chain lengths L_A, L_B, and L_C,

$$C \sim \frac{1}{L_A^{1/2}x + L_B^{1/2}y + L_C^{1/2}(1 - x - y)} \qquad (6.3)$$

For the monodisperse case $L_A = L_B = L_C = L$ eq 6.3 becomes

$$C \sim L^{-1/2} \qquad (6.4)$$

as expected. Using the above equations in eqs 4.14–4.16 and eq 2.7 the universal osmotic pressure near the tricritical point turns out to be

$$\begin{aligned}\frac{\Pi}{K_BT} = \frac{C^2}{2}[\ln(1/C^2a)]^{-2/11}[x^2v_{AA} + y^2v_{BB} + {}\\ (1 - x - y)^2v_{CC} + 2(1 - x - y)xv_{AC} + 2(1 - x - y)yv_{BC} + {}\\ 2xyv_{AB}] + \frac{C^3}{3}\frac{[3xy(1 - x - y) + 1]}{44\pi\ln(1/C^2a)} \qquad (6.5)\end{aligned}$$

Notice the explicit chemical mismatch at the level of second and third virial coefficients. If one of th three components vanishes, then there is no mismatch at the third virial coefficient level which is the result of two component systems, eq 5.15.

C. Dilute Solutions of A–B–C Triblock Copolymers in a Common Θ Solvent. Consider an A–B–C triblock copolymer of a sequence of monomers of length L_A linked to a sequence of A monomers of length L_A at one end and linked to a sequence of C monomers of length L_C at its other end. The fractions of A, B, and C blocks in the copolymer of length L are given by

$$L_A = f_1L \qquad L_B = f_2L \qquad L_C = (1 - f_1 - f_2)L \qquad (6.6)$$

The tricritical fixed point of A–B–C block copolymers is the same as that for the A, B, C homopolymer system, since the polydispersity among the blocks does not affect the fixed point. The third virial coefficient of an A–B–C triblock copolymer is given by

$$A_3^{\text{A–B–C}} = \sum_{\text{i=A}}^{\text{C}} A_3^{\text{iii}} + 3\sum_{\text{i}\neq\text{j=A}}^{\text{C}} A_3^{\text{iij}} + 6A_3^{\text{ABC}} \qquad (6.7)$$

Substituting the results of eqs 4.14–4.16 into eq 6.7

$$\begin{aligned}A_3^{\text{A–B–C}} = (2\pi L)^3\Big[{f_1}^3 + {f_2}^3 + (1 - f_1 - f_2)^3 + 3(f_1{f_2}^2 + {}\\ f_2{f_1}^2) + 3((1 - f_1 - f_2){f_2}^2 + (1 - f_1 - f_2)^2f_2) + 3((1 - f_1 - {}\\ f_2){f_1}^2 + (1 - f_1 - f_2)^2f_1) + \frac{18}{2}f_1f_2(1 - f_1 - f_2)\Big]\frac{1}{44\pi\ln(L/a)}\\ (6.8)\end{aligned}$$

The above equation can be written in a simplified form as

$$A_3^{\text{A–B–C}} = (2\pi L)^3\frac{[3f_1f_2(1 - f_1 - f_2) + 1]}{44\pi\ln(L/a)} \qquad (6.9)$$

This equation clearly shows the chemical mismatch in the third virial coefficient. If the fraction of one of the blocks goes to zero, then the first term on the right hand side of the above equation vanishes and hence there is no chemical mismatch at the third virial coefficient level, which is the result for diblock copolymers, eq 5.19.

The renormalized second virial coefficients are given for a triblock copolymer as follows

$$A_2^{\text{A–B–C}} = \sum_{\text{i=A}}^{\text{C}} A_2^{\text{ii}} + \sum_{\text{i}\neq\text{j=A}}^{\text{C}} A_2^{\text{ij}} \qquad (6.10)$$

where

$$\begin{aligned}A_2^{\text{AA}} &= (2\pi Lf_1)^{3/2}[\tilde{v}_{\text{AA}}^{\text{R}} - 8\tilde{w}_{\text{AAA}}^{\text{R}}{}^*]\\ A_2^{\text{BB}} &= (2\pi Lf_2)^{3/2}[\tilde{v}_{\text{BB}}^{\text{R}} - 8\tilde{w}_{\text{BBB}}^{\text{R}}{}^*]\\ A_2^{\text{CC}} &= (2\pi L(1 - f_2 - f_1))^{3/2}[\tilde{v}_{\text{CC}}^{\text{R}} - 8\tilde{w}_{\text{CCC}}^{\text{R}}{}^*]\\ A_2^{\text{AB}} &= (2\pi L)^{3/2}(f_2f_1)^{3/4}[\tilde{v}_{\text{AB}}^{\text{R}} - 4[(f_1/f_2)^{1/4} + {}\\ &\qquad (f_1/f_2)^{1/4}]\tilde{w}_{\text{AAB}}^{\text{R}}{}^*]\\ A_2^{\text{AC}} &= (2\pi L)^{3/2}((1 - f_1 - f_2)f_1)^{3/4}[\tilde{v}_{\text{AC}}^{\text{R}} - 4((f_1/(1 - f_1 - {}\\ &\qquad f_2))^{1/4} + ((1 - f_1 - f_2)/f_1))^{1/4}\tilde{w}_{\text{AAC}}^{\text{R}}{}^*]\\ A_2^{\text{BC}} &= (2\pi L)^{3/2}((1 - f_1 - f_2)f_2)^{3/4}[\tilde{v}_{\text{BC}}^{\text{R}} - 4((f_2/(1 - f_1 - {}\\ &\qquad f_2))^{1/4} + ((1 - f_1 - f_2)/f_2))^{1/4}\tilde{w}_{\text{BBC}}^{\text{R}}{}^*] \qquad (6.11)\end{aligned}$$

The second virial coefficients A_2^{ii}(i = A, B, C) and A_2^{ij}(i ≠ j = A, B, C) vanish at the tricritical point, which yields for chains with finite chain length

$$\begin{aligned}v_{\text{AA}} &\sim (2\pi)^{-3/2}L^{-1/2}f_1^{-1/2}8\frac{[\ln(L/a)]^{-9/11}}{44\pi}\\ v_{\text{BB}} &\sim (2\pi)^{-3/2}L^{-1/2}f_2^{-1/2}8\frac{[\ln(L/a)]^{-9/11}}{44\pi}\\ v_{\text{CC}} &\sim (2\pi)^{-3/2}L^{-1/2}(1 - f_1 - f_2)^{-1/2}8\frac{[\ln(L/a)]^{-9/11}}{44\pi}\\ v_{\text{AB}} &\sim (2\pi)^{-3/2}L^{-1/2}[(1/f_1)^{1/2} + (1/f_2)^{1/2}]4\frac{[\ln(L/a)]^{-9/11}}{44\pi}\\ v_{\text{BC}} &\sim (2\pi)^{-3/2}L^{-1/2}[(1/f_2)^{1/2} + {}\\ &\qquad (1/(1 - f_1 - f_2))^{1/2}]4\frac{[\ln(L/a)]^{-9/11}}{44\pi}\\ v_{\text{AC}} &\sim (2\pi)^{-3/2}L^{-1/2}[(1/f_1)^{1/2} + {}\\ &\qquad (1/(1 - f_1 - f_2))^{1/2}]4\frac{[\ln(L/a)]^{-9/11}}{44\pi} \qquad (6.12)\end{aligned}$$

VII. Conclusions

We have studied polymer solutions containing chemically different polymers in a common Θ solvent using direct renormalization group theory. The role of specific short ranged interactions between polymers of different chemical natures present in a common Θ solvent is analyzed beyond the mean field description. In contrast to the case of two chemically different polymers in a common good solvent, where the chemical mismatch is irrelevant for asymptotically large chain length, we find here that the chemical mismatch plays a crucial role near the tricritical point.

We have demonstrated that this presence of chemical mismatch leads to a new tricritical universality class. This is exactly the same universality class as the one we recently derived for a polymer solution at the Θ temperature in a quenched random medium.

For dilute solutions containing chemically different A, B homopolymers, we found that the dimensionless third virial coefficients near the tricritical point are all the same and hence chemical mismatch is not important at the level of three-body interaction among the monomers. But, the second virial coefficients of A, B homopolymers are affected by the chemical difference between A and B polymers and they renormalize with a different logarithimic exponent. Using this tricritical theory we have found that the mutual virial coefficient of the A, B homopolymers in a common solvent is a vanishing function of chain length, i.e., $\tilde{v}_{AB} \sim L^{-1/2}[\ln(L/a)]^{-9/11}$. Without the logarithmic correction, this reproduces the scaling results of de Gennes.[19] It must be pointed out that our results are different from those of Schafer and Kappeler[15] who have considered the effet of corrections to scaling on chemical mismatch effects in good solvents. We also studied the semidilute solutions of A, B homopolymer systems in a Θ solvent, and we propose a universal form for the osmotic pressure. The effect of chemical mismatch is explicit in the osmotic pressure at the level of two-body interaction among the monomers. This expression for the osmotic pressure may be used to study further phase separation in A, B homopolymer solutions in a θ solvent.

The two component block copolymers like A–B diblock and A–B–A triblock copolymers in a common Θ solvent are studied using tricritical renormalization group theory. We found that th third virial coefficient of the block copolymers is independent of the chemical difference between the A and B blocks. But, because of the second virial coefficient between A and B, the second virial coefficients renormalize differently. According to the tricritical theory of copolymer solutions, the mutual virial coefficient of (a) an A–B diblock copolymer with a fraction f of A polymer and of total length L has been found to be

$$v_{AB} \sim L^{-1/2}[\ln(L/a)]^{-9/11}[(1/f)^{1/2} + (1/(1-f))^{1/2}]$$

and (b) an A–B–A triblock copolymer of f_1 fraction of A polymer block and f_2 fraction of B block is found to be

$$v_{AB} \sim$$

$$L^{-1/2}[\ln(L/a)]^{-9/11}\frac{[f_1^{1/2}f_2 + f_2(1-f_1-f_2)^{1/2} + f_2^{1/2}(1-f_2)]}{f_2(1-f_2)}$$

We investigated the three component polymer systems like A, B, C homopolymers and A–B–C triblock copolymers, in their common Θ solvent. In the three component systems the effect of chemical differences among the polymers is felt at the levels of both third and second virial coefficients. We also calculated all of the second and third virial coefficients for the above mentioned systems. A universal form for the osmotic pressure is derived for A, B, C homopolymer mixtures in a common Θ solvent at semidilute concentrations.

Although the theory considered here is restrictive in terms of the requirement of a common Θ solvent for chemically different polymers, the full analysis is much more complicated for the more general, but experimentally easier, systems. It is, however, hoped that this will stimulate more interest in both experimental and theoretical investigations to fully understand the role of chemical mismatch and the modification of Θ temperature for a polymer solution by the presence of other chemically different polymers.

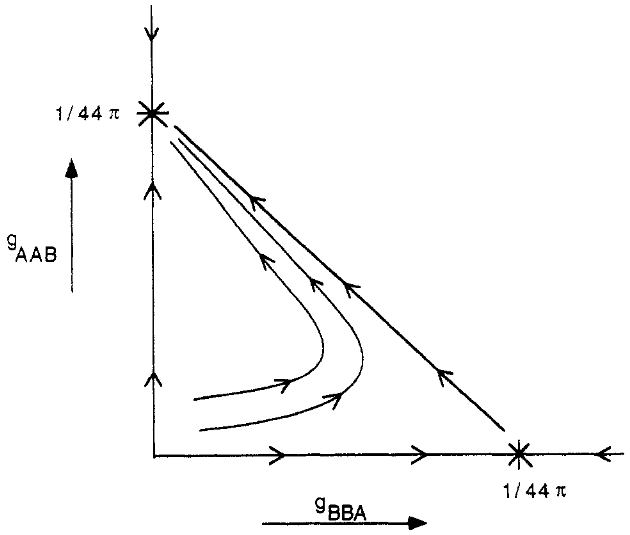

Figure 3. Flow diagram of the $g_{AAB} - g_{BBA}$ plane. g_{AAB} is taken to be the stable direction.

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Appendix

Here we give the details of the stability analysis used in section IV. We illustrate the stability analysis for the chemically different A and B polymer system. A generalization to more than two chemically different polymers is straightforward.

The most stable fixed point is determined by the procedure of linearizing eqs 4.1–4.2 about the fixed point,

$$\tilde{w}^{R}_{iii} = \frac{g^{*}_{iii}}{\ln(L/a)} + g_{iii1} \qquad i = A, B \qquad (A.1)$$

$$\tilde{w}^{R}_{iij} = \frac{g^{*}_{iij}}{\ln(L/a)} + g_{iij1} \qquad i \neq j = A, B \qquad (A.2)$$

where g_{iii1} and g_{iij1} are taken to be of the form

$$g_{iii1} = c_{iii}[\ln(L/a)]^{-\lambda} \qquad (A.3)$$

$$g_{iij1} = c_{iij}[\ln(L/a)]^{-\lambda} \qquad (A.4)$$

with c_{iii} and c_{iij} being the coefficients and λ being the eigenvalues to be determined now. Substituting eqs 4.1–4.2 yields

$$\lambda c_{iii} = 88\pi c_{iii} g^{*}_{iii} \qquad i = A, B \qquad (A.5)$$

$$\lambda c_{AAB} = 16\pi c_{AAA} g^{*}_{AAB} + \pi c_{AAB}(32 g^{*}_{AAB} + 16 g^{*}_{AAA} + 8 g^{*}_{BBA}) + \pi c_{BBA}(g^{*}_{AAB} + g^{*}_{BBA}) \qquad (A.6)$$

$$\lambda c_{BBA} = 16\pi c_{BBB} g^{*}_{BBA} + \pi c_{BBA}(32 g^{*}_{BBA} + 16 g^{*}_{BBB} + 8 g^{*}_{ABB}) + \pi c_{AAB}(g^{*}_{AAB} + g^{*}_{BBA}) \qquad (A.7)$$

For a locally stable fixed point, $\lambda > 1$ and $\tilde{w}_{iii}$ and $\tilde{w}_{iij}$ reduce to their fixed point values as we approach the tricritical point and $\ln(L/a) \rightarrow \infty$. If λ is less than unity, the renormalization group flow will be away from the fixed point, making that fixed point unstable. This analysis shows that for a physically relevant fixed point,

$$g^*_{\mathrm{iii}} = g^*_{\mathrm{AAB}} = g^*_{\mathrm{BBA}} = 1/44\pi \tag{A.8}$$

the eigenvalues are

$$\lambda_1 = \lambda_2 = 2 \qquad \lambda_3 = 72/44 \qquad \lambda_4 = 40/44 \tag{A.9}$$

Since λ_4 is less than unity, this fixed point becomes unstable. In Figure 3 we indicate the flow lines in the g_{AAB} and g_{BBA} plane and we have chosen g_{AAB} as the stable direction, but in general it could be either g_{AAB} or g_{BBA}. Once we assume $g_{\mathrm{AAB}} = g_{\mathrm{BBA}}$, there is a stable fixed point,

$$g^*_{\mathrm{iii}} = g^*_{\mathrm{AAB}} = 1/44\pi \tag{A.10}$$

with the eigenvalues as

$$\lambda_1 = \lambda_2 = 2 \qquad \lambda_3 = 18/11 \tag{A.11}$$

References and Notes

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