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Dimensions of a Polymer Chain in a Mixed Solvent

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ABSTRACT: The equilibrium behavior of a flexible polymer in a binary solvent mixture is investigated via Monte Carlo simulation. The mixed solvent is modeled as an Ising fluid occupying the sites of a simple cubic lattice, with the polymer described as a self-avoiding random walk on the same lattice. The solvent has a critical consolute point, and the polymer preferentially adsorbs the better solvent component. A coupling between preferential adsorption and the solvent correlations present near the consolute temperature of the solvent causes the chain to contract, as predicted by Brochard and de Gennes. However, preferential adsorption also causes chain contraction far from the critical temperature. At large values of preferential adsorption, the chain contracts below the dimensions it would have in either of the pure solvent components.

I. Introduction

Our understanding of the equilibrium properties of linear polymers in one-component solvents is very well developed. On the basis of mean field theories, such as the Flory–Huggins theory,[1] and more sophisticated renormalization group theories,[2,3] experiments on dilute polymer solutions can be quantitatively interpreted. As a consequence, recent theoretical efforts have been focused on less mature areas such as semidilute solution statics and dynamics, the dynamics of entanglements, and interfacial phenomena.

A problem that has received surprisingly little attention is the configurational statistics and thermodynamic properties of polymers in mixed solvents. Because a polymer chain may preferentially adsorb one of the solvent components, such systems can possess inhomogeneities not found in solutions of a polymer in a single-component solvent. Among the few theoretical treatments of this problem are the Shultz–Flory theory,[4] a type of mean field theory, and the Brochard–de Gennes theory,[5-7] which deals with the particular case of the solvent mixture being near a critical point. A related problem is the collapse of a large polymer in a good solvent upon the addition of smaller polymers incompatible with the longer chain.[8-13] The Brochard–de Gennes theory makes an interesting prediction for a polymer in a mixture of two good solvents, where the affinities of the macromolecule for the two solvent components differ substantially. The prediction is that the polymer will adopt collapsed configurations as the critical temperature T_c of the solvent mixture is approached, even though it would be swollen in either of the pure component solvents at the same temperature.

In contrast to the Flory–Huggins theory for one-component solvents, the theories for mixed solvents have not been subjected to extensive experimental tests. In part, this is due to the difficulty in independently varying a particular parameter such as the preferential affinity of the polymer for one of the solvent components, while holding other parameters of the system fixed. Yamakawa[14,15] has pointed out the complications introduced into the analysis of light scattering data by the presence of strong preferential adsorption. Because of such difficulties, experimental studies inconsistent with the Shultz–Flory theory are not particularly convincing.[16,17]

An alternative means of testing the analytical theories for polymers in mixed solvents is through computer simulation.[18] With simulation techniques there is no difficulty in independently varying solvent quality, preferential affinities, or temperature, while holding certain other parameters constant. Furthermore, because information on chain dimensions and correlations is readily accessible, computer simulation methods are ideal for detecting configurational changes, such as the collapse transition predicted by Brochard and de Gennes.

In the present paper we report Monte Carlo lattice simulations of a polymer in a two-component solvent mixture. Various predictions of the Shultz–Flory and Brochard–de Gennes theories are addressed. The organization of the manuscript is as follows. In section II we describe our modification of the conventional Monte Carlo technique to model ternary systems. The relevant theories are briefly reviewed in section III, and the simulation results are presented in section IV. Section V contains a discussion of these results and our conclusions.

II. Model Ternary System and the Simulation Technique

We consider a single polymer chain in a mixture of two solvents that will be denoted A and B. The state of the system is described by the occupancy of the sites of a simple cubic lattice in three dimensions by A molecules, B molecules, and "monomers" (i.e., the units linked in the polymer chain). The volumes of A, B, and monomer are assumed equal, hence volume fractions and mole fractions

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are identical in this model. The occupant of each lattice site interacts directly only with its six nearest neighbors and periodic boundary conditions are adopted. The polymer chain consists of $N - 1$ links, or equivalently N contiguous monomer sites. All remaining sites on the lattice are occupied by solvent molecules.

In our model ternary system there are six different nearest-neighbor interaction energies (ϵ_{ij}). However, the equilibrium properties of the model are completely determined by specifying any two composition variables (such as volume fractions of monomer and A, Φ_P, and Φ_A) and the three dimensionless interaction parameters (z is the lattice coordination number, i.e., $z = 6$):

$$\chi_{AP} = \frac{z}{k_b T}[\epsilon_{AP} - 0.5(\epsilon_{AA} + \epsilon_{PP})] \tag{II.1}$$

$$\chi_{BP} = \frac{z}{k_b T}[\epsilon_{BP} - 0.5(\epsilon_{BB} + \epsilon_{PP})] \tag{II.2}$$

$$\chi_{AB} = \frac{z}{k_b T}[\epsilon_{AB} - 0.5(\epsilon_{AA} + \epsilon_{BB})] \tag{II.3}$$

The nearest-neighbor energies ϵ_{ij} will be assumed temperature independent for a given solvent. It will prove convenient to use $\chi_{AP} k_b T$ as the energy scale to define two new independent variables:

$$\eta = \chi_{AB}/\chi_{AP} \tag{II.4}$$

$$\gamma = \frac{\chi_{AP} - \chi_{BP}}{\chi_{AP}} \tag{II.5}$$

γ, the "preferential affinity", is a measure of the energetic preference of the polymer for the better solvent component. η measures the strength of interactions between solvent components A and B.

Specification of $\{\eta,\gamma,\chi_{AP},\Phi_P,\Phi_A\}$ is equivalent to specification of $\{\chi_{AP},\chi_{BP},\chi_{AB},\Phi_P,\Phi_A\}$ and completely determines the thermodynamic state of the polymer/mixed solvent system. In the present simulations η and γ will be assumed temperature independent and held constant for a given mixed solvent, while χ_{AP} is varied. From eq II.1, this corresponds to changing the temperature of the system, in accord with the usual experimental situation. Monte Carlo simulations were performed for four different mixed solvent/polymer systems, labeled 1–4 in Table I. Each system is characterized by a unique $\{\eta,\gamma\}$ and was studied at the χ_{AP} values indicated. In all of the simulations reported, the overall fraction of monomer on the lattice is sufficiently low that we assume the results are independent of Φ_P. For computational reasons that will be discussed shortly, most of the results presented are for small chains of length N equal to 40. One consequence of this is that the coil size changes only modestly with changes in solvent quality: R_g^2 varies by $\sim$20% between athermal and Θ-like pure solvents.[19] Hence extreme χ values were necessary to affect measurable changes of coil dimension in this study. We find, as expected, that more reasonable χ values are possible with longer chains.

The Metropolis method[20] is employed to compute the configurational averages needed to determine the equilibrium properties of the ternary model. New configurations are generated by either a polymer move (reptation type[21]) or a solvent move. The Glauber algorithm[22] (open system at fixed chemical potentials) is used for the solvent dynamics, except where indicated otherwise.

The computational requirements for the present ternary simulations are unavoidably larger than for either a polymer in a single-component solvent or for a pure binary fluid mixture. Both the solvent and polymer must be equilibrated, yet polymer properties can only be averaged over the small fraction of sites occupied by monomers. (In the present simulations this fraction is approximately 0.1%). Hence, if polymer moves are attempted only on the occasions that randomly selected lattice sites happen to be occupied by monomer, then the computer time will be roughly 3 orders of magnitude longer than for simulations of the same chain in a pure solvent.

Table I
Mixed Solvent Parameters

solvent	γ	η	χ_{AP}
$\chi_{AB} = 0$; $\chi_{AP} = -\chi_{BP}$			
1	2.0	0.0	−0.45
1	2.0	0.0	−1.2
1	2.0	0.0	−2.4
1	2.0	0.0	−4.2
1	2.0	0.0	−6.0
$\chi_{AB} = 0$; $\chi_{BP} = 0$; χ_{AP} as given			
2	1.0	0.0	−1.2
2	1.0	0.0	−2.4
2	1.0	0.0	−4.8
2	1.0	0.0	−9.6
2	1.0	0.0	−12.0
$\chi_{AB} = \chi_{BP}$; $\chi_{AP} = -{}^1/_2\chi_{BP}$			
3	3.0	−2.0	−0.3
3	3.0	−2.0	−0.6
3	3.0	−2.0	−0.9
3	3.0	−2.0	−1.05
3	3.0	−2.0	−1.2
3	3.0	−2.0	−1.245
3	3.0	−2.0	−1.29
3	3.0	−2.0	−1.32
$\chi_{AB} = 4\chi_{AP}$; $\chi_{AP} = \chi_{BP}$			
4	0.0	4.0	0.3
4	0.0	4.0	0.525
4	0.0	4.0	0.645

The computational expense can be reduced substantially by biasing the site selection process to achieve a fixed ratio Q of attempted polymer moves to attempted moves of any type. The value of Q is chosen large enough to achieve rapid equilibration of the polymer, yet small enough to ensure equilibration of the solvent during the simulation. For typical runs Q is taken to be 0.3.

To further reduce the computational expense, it is desirable to minimize the lattice size L for a given chain length N. However, for $N > L$, the fully extended chain can interact directly with its own periodic image. Fortunately, the probability of an extended chain configuration is small. Assuming Gaussian statistics,[1] we choose the lattice size so that this probability is less than 10^{-6}. Furthermore, at each point during the course of a simulation when chain averages are computed, a check is made to make sure that the end-to-end distance, R, satisfies $R < L$. If this condition is not met, the simulation run is discarded. Finally, we note that, except where explicitly indicated, the correlation length of the binary solvent mixture is much less than L. We have performed extensive tests to verify that the results reported are independent of lattice size.

To further test our code, we have performed a number of simulations of a polymer in a one-component solvent. We find quantitative agreement with the results of ref 19. Of particular interest is that the scaling exponent ν for the radius of gyration ($R_g \sim N^\nu$) was observed to be very close to its asymptotic value for N as small as 40, both in an athermal (good) solvent with $\chi_{AP} = 0$ and in a Θ solvent with $\chi_{AP} = 0.825$.[19] Unless indicated otherwise, all simulation data in the present paper are for polymer chains with 40 links.

III. Theories for Mixed Solvent Systems

In the simplest theory for a ternary system, the mixed solvent is treated as a hypothetical single solvent, characterized by an effective Flory interaction parameter. R. L. Scott[23] derived the following expression for the effective χ parameter of a mixed solvent with components A and B at volume fractions Φ_A and Φ_B:

$$\chi^{SLA} = \Phi_A\chi_{AP} + \Phi_B\chi_{BP} - \Phi_A\Phi_B\chi_{AB} \tag{III.1}$$

In the alternate set of independent variables, this equation becomes

$$\chi^{SLA} = \Phi_A\chi_{AP} + \Phi_B(1 - \gamma)\chi_{AP} - \Phi_A\Phi_B\eta\chi_{AP} \tag{III.2}$$

Equation III.1, which is called the "single liquid approximation", makes an interesting prediction for the influence of A–B interactions upon chain dimensions. For $\chi_{AB} = \chi_{AP}\eta > 0$, the third term in eq III.1 increases the quality (reduces χ) of the mixed solvent, relative to the pure solvent qualities. In fact, eq III.1 predicts that a mixture of two solvents, each of which is a poor solvent for the polymer, can behave collectively as a good solvent. The physical explanation is simple. There is an energetic driving force to reduce the total number of solvent–solvent contacts when $\chi_{AP}\eta > 0$. This can be accomplished by chain expansion, which increases the number of monomer–solvent contacts at the expense of solvent–solvent contacts. Equation III.1 predicts the opposite trend for solvents with $\chi_{AP}\eta < 0$, i.e. solvent–solvent attractions reducing mixed solvent quality.

In the single liquid theory just described, no consideration is given to the possibility that the better solvent has a higher concentration near the polymer, i.e., there is "preferential adsorption" of the one solvent by the polymer. Such inhomogeneities in solvent composition were taken into account in an approximate fashion in the Shultz–Flory theory. In the Shultz–Flory theory,[4] the ternary system is viewed as two homogeneous phases, one within the polymer coil and one outside it. The free energy of the coil phase consists of the free energy of mixing three components (calculated with the mean field lattice theory) plus an elastic contribution opposing chain expansion. The total free energy is minimized with respect to the size of the coil phase and the amount of good solvent within that phase. Shultz and Flory derived the following expression for the effective χ parameter of the mixed solvent, χ^{SF}:

$$\chi^{SF} = \frac{1}{2} - \frac{1 - 2\Phi_A\chi_{AP} - 2\Phi_B\chi_{BP} + D\Phi_A\Phi_B}{2\Phi_A + 2\Phi_B - 4\Phi_A\Phi_B\chi_{AB}} \tag{III.3}$$

where

$$D = 2\chi_{AB}\chi_{AP} + 2\chi_{AB}\chi_{BP} + 2\chi_{AP}\chi_{BP} - \chi_{AB}^2 - \chi_{AP}^2 - \chi_{BP}^2 \tag{III.4}$$

An interesting simplification of eq III.3 occurs for the special case of an equimolar mixed solvent, in the limit that Φ_P is zero ($\Phi_A = \Phi_B = 0.5$):

$$\chi^{SF} = 0.5(\chi_{AP} + \chi_{BP}) - 0.25\chi_{AB} + \frac{(\chi_{AP} - \chi_{BP})^2}{4.0(2.0 - \chi_{AB})} \tag{III.5}$$

$$\chi^{SF} = \chi^{SLA} + \frac{\gamma^2\chi_{AP}^2}{4(2 - \eta\chi_{AP})} \tag{III.6}$$

$$\chi^{SF} = \chi_{AP}\left(1 - \frac{\gamma}{2} - \frac{\eta}{4}\right) + \frac{\gamma^2\chi_{AP}^2}{4(2 - \eta\chi_{AP})} \tag{III.7}$$

Hence, for zero preferential affinity, $\gamma = 0$, the single liquid approximation and the Shultz–Flory theory are identical for an equimolar mixed solvent. The term in eq III.6 associated with preferential affinity is positive and hence predicts a reduction in solvent quality over that predicted by the Scott single liquid approximation. Equation III.5 makes it clear that the Shultz–Flory theory predicts catastrophic behavior when χ_{AB} approaches 2.0 (the mean field critical value). This has not been generally realized, because Shultz and Flory presented their results in the form of eq III.3, from which the predicted behavior near T_c is not readily apparent.

In a much more recent study, Brochard and de Gennes[5-7] derived an expression for infinite chains that is similar to eq III.7 by considering the coupling of the local solvent composition field to the monomer density field of a single chain in a binary solvent:

$$\chi = \chi_{AP}\left(1 - \frac{\gamma}{2} - \frac{\eta}{4}\right) + \frac{\gamma^2\chi_{AP}^2}{\left[\dfrac{(\eta\chi_{AP})_{crit}}{\eta\chi_{AP}} - 1\right]^{1.25}} \tag{III.8}$$

In eq III.8 $(\eta\chi_{AP})_{crit}$ is the value of $\eta\chi_{AP}$ at the critical point (2.0 in the mean field theory, $\sim$2.66 in the Ising model). Brochard and de Gennes have also substituted the known value of the Ising exponent (1.25) for the mean field estimate of 1.0 in eq III.7. For temperatures near the critical point of the binary solvent mixture, long-wavelength composition fluctuations in the solvent are predicted to give rise to attractive pair interactions between monomers with a comparable long range. The predicted effect of these attractive interactions is to give a positive contribution to χ of the form of the second term on the right-hand side of eq III.8. Because the magnitude of this term increases without bound as the critical temperature of the solvent mixture is approached, Brochard and de Gennes predict that the solvent quality will decrease to the point of chain collapse near T_c. Defining τ as $(T - T_c)/T_c$, Brochard and de Gennes predict that the chain collapse occurs at a value of τ given by[6]

$$\tau_{min} = \left[\frac{\gamma^2\chi_{AP}^2}{0.5 - \chi^{SLA}}\right]^{0.8} \tag{III.9}$$

Brochard and de Gennes provide a simple physical explanation for the chain collapse.[5-7] The solvent correlation length ξ is large near T_c. The good solvent that is preferentially adsorbed to the polymer creates a region of good solvent around itself of spatial extent ξ that attracts other segments of the polymer, thereby constituting an indirect long-range attraction between monomers. However, if ξ greatly exceeds R_g, as is likely to be the case sufficiently close to T_c, the polymer chain will be completely immersed in the better solvent and reexpansion should occur.[5] Reexpansion will also occur if the buildup in monomer concentration within the collapsed coil displaces the critical temperature.[6,7] Hence on physical grounds, one expects first contraction and then reexpansion of the chain as T_c is approached from above. It is of interest to note that the problem of a polymer in a mixed solvent is a special case of the more general problem of a polymer in an environment with annealed impurities.[24] The configurational statistics of a polyelectrolyte chain wth counterion-screened Coulombic pair interactions belongs to this same class of problems and can be treated with methods similar to those used by Brochard and de Gennes.

IV. Results

As discussed in section III, the configuration of a chain in a two-component solvent is affected by preferential

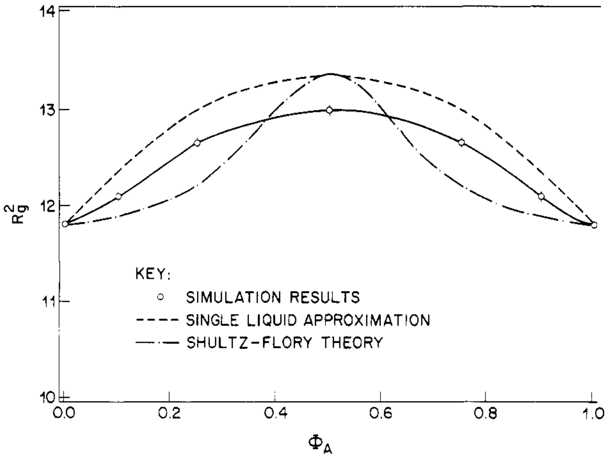

Figure 1. Concentration dependence of the radius of gyration in a solvent with no preferential affinity but with unfavorable solvent–solvent interactions.

affinity of the polymer for one of the solvents as well as by unfavorable solvent–solvent interactions ($\chi_{AB} = \eta\chi_{AP} > 0$). Both phenomena likely influence chain dimensions in real mixed solvents. To sort out their relative effects upon R_g, we first consider each phenomenon separately and then investigate the simultaneous presence of preferential affinity and solvent–solvent interactions.

A. Unfavorable Solvent–Solvent Interactions with No Preferential Affinity. Both the single liquid approximation (eq III.2) and the Shultz-Flory theory (eq III.3) with zero preferential affinity predict that R_g is increased by a demixing tendency on the part of the two solvent components. To test this we chose a mixed solvent with $\gamma = 0$, $\eta = 3$, and $\chi_{AP} = 0.6$ (recall that the pure solvent Θ condition on the cubic lattice is $\chi_{AP} = 0.825$[19]). Hence, there is no preferential affinity of the polymer for either solvent, but A–B solvent contacts are unfavorable. Figure 1 shows the concentration dependence of R_g in this mixed solvent. For $\Phi_A = 0$ or 1, R_g has the same pure solvent value since $\gamma = 0$. At intermediate values of Φ_A, the chain is expanded to minimize the unfavorable interactions between solvents A and B, in qualitative agreement with the theories.

We can quantitatively check the single liquid and Schultz-Flory theories by comparing the coil radii predicted by these theories with the simulated values. The values of R_g for the single liquid and Shultz–Flory theories are equal to the R_g values that would be obtained with $N = 40$ in a pure solvent with effective χ values given by eq III.2 and III.3, respectively. The relationship between R_g and χ for a pure solvent is established by simulations similar to those discussed in section II. Figure 1 compares the predictions of the two theories with the simulated results. The two theories agree with each other at $\Phi_A = 0.5$ (see eq III.6), but neither quantitatively predicts the simulation results for $N = 40$. In particular the theories overpredict the solvent quality at $\Phi_A = 0.5$.

B. Preferential Affinity with Zero Solvent–Solvent Interaction Energy. Here and throughout the rest of the paper, equimolar mixed solvents are considered. First suppose that the two solvent components have no attraction or repulsion toward each other; i.e., $\eta = 0$. Hence the solvent has no critical consolute point.

1. Preferential Adsorption. When $\gamma > 0$, the concentration of the better solvent component is always greater near the polymer than in the surrounding solvent. Experimental results[16,17,25] have been reported for this concentration difference, normalized by the chain length. In the spirit of these measurements, we define a quantity λ, the "preferential adsorption", which is a measure of the excess of the good solvent component in *direct* contact with the polymer:

$$\lambda = [N_A^{\mathrm{ads}} - \Phi_A(N_A^{\mathrm{ads}} + N_B^{\mathrm{ads}})]/N \qquad \text{(IV.1)}$$

In eq IV.1, N_A^{ads} is the number of solvent A nearest neighbors of the chain, and Φ_A is the overall volume fraction of A on the lattice. We emphasize that the terms *preferential adsorption* and *preferential affinity* are not equivalent. Preferential adsorption is a consequence of preferential affinity, in the sense that a concentration difference is a consequence of a chemical potential difference.

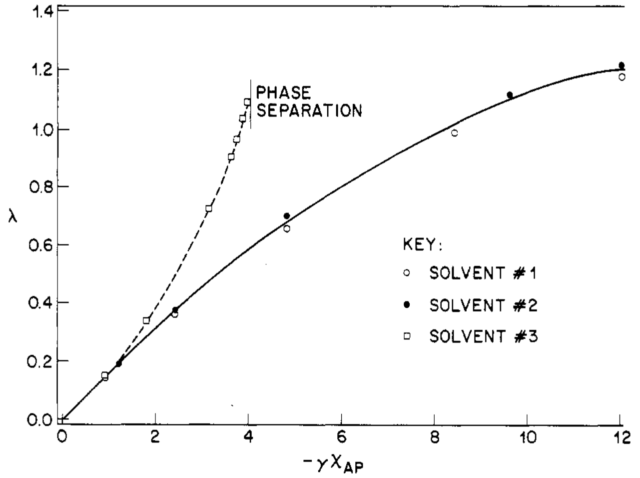

Figure 2. Amount of preferential adsorption as a function of $\gamma\chi_{AP}$, in solvents with and without a critical point.

For an equimolar mixed solvent, the preferential adsorption λ is in principle a function of the three χ_{ij} or equivalently η, γ, and χ_{AP}. Since we consider mixed solvents with $\eta = 0$ in this section, λ is at most a function of the two remaining variables. In fact, we find empirically that λ is approximately a function of only the single combination variable $\gamma\chi_{AP}$. The preferential affinity γ is constant for a given solvent, but the combination variable increases in magnitude as the temperature is lowered (see eq II.1 for χ_{AP}). Consequently the preferential adsorption λ monotonically approaches its theoretical maximum value of 2.0 (for a cubic lattice) as the temperature is lowered. For example, the solid curve in Figure 2 gives the dependence of λ on $\gamma\chi_{AP}$ for mixed solvents 1 and 2 of Table I, characterized by γ equal to 2.0 and 1.0, respectively.

2. Good Solvent/Poor Solvent Mixture. Suppose we choose the mixed solvent to be composed of a good solvent and a poor solvent, with $\eta = 0$ and $\gamma = 2.0$ (solvent 1, Table I). *Neglecting* the effect of preferential adsorption, Scott's single liquid approximation (eq III.2) predicts that $\chi^{\mathrm{SLA}} = 0$, i.e., that the solvent quality and the radius of gyration are independent of χ_{AP} or temperature. However, as we have already seen in Figure 2, the excess amount of the preferred solvent near the polymer (λ) increases as χ_{AP} becomes more negative. According to the argument of Dondos and Benoit,[16,17] the mixed solvent should become more "A-like" near the chain, and R_g should increase. The Shultz–Flory theory (eq III.7), on the other hand, predicts chain contraction as χ_{AP} becomes more negative. Figure 3 demonstrates that the Shultz–Flory theory qualitatively predicts the correct dependence of the radius of gyration upon χ_{AP}. The argument of Dondos and Benoit fails because it implies that a high values of λ, the chain may be regarded as residing in a pure solvent composed of the better component of the mixed solvent. However, as we show in section IV.B.4, the monomer–monomer correla-

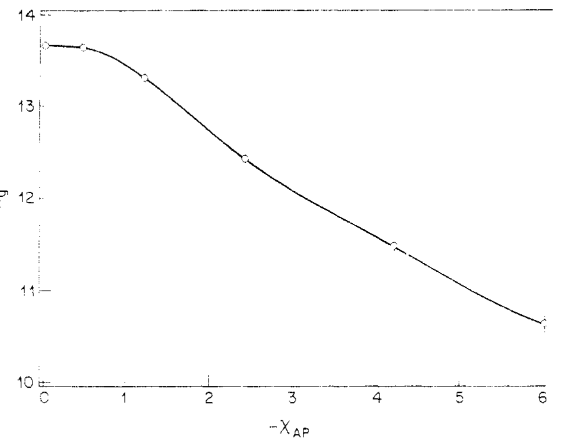

Figure 3. Radius of gyration as a function of χ_{AP} in solvent 1.

tions differ considerably on a short length scale from those present in a pure solvent of any quality.

Consider the following quantitative test of the Shultz–Flory predictions regarding the contracting effect of preferential affinity. We have simulation results for R_g as a function of χ_{AP} in a pure solvent for $N = 40$ and $N = 100$ and in various mixed solvents such as solvent 1. An effective interaction parameter for a mixed solvent (χ^{EFF}) can be defined as the value of χ_{AP} for a pure solvent in which R_g has the same value (for the same value of N). Following this procedure with the results for a chain of length $N = 40$ in mixed solvent 1 (Figure 3), we obtain $\chi^{EFF} \sim 0.44$ for the state $\chi_{AP} = -2.4$. The Shultz–Flory theory (eq III.7) predicts an effective χ value of 2.9, and thus greatly *overestimates* the influence of preferential affinity upon the coil size of finite length chains. However, for a chain of length $N = 100$ in the same mixed solvent, we find that χ^{EFF} has increased to $\sim$0.53. Thus finite size effects are significant in mixed solvent 1, with the coil sizes of longer chains more contracted and in better agreement with the Shultz–Flory theory. It appears unlikely, however, that the Shultz–Flory theory will become quantitative as the chain length is increased, even in the limit of infinite molecular weight.

3. Mixture of Two Good Solvents. For the mixed solvent of Figure 3, at each temperature the preferred solvent component is better than athermal, while the poor solvent component is worse than a Θ solvent. This was a necessary consequence of choosing χ^{SLA} equal to zero. Suppose instead the mixed solvent is composed of two good components, one athermal, the other better than athermal. An example is solvent 2 of Table I, with $\gamma = 1.0$. Consider the behavior of the radius of gyration as the χ parameter of the preferred solvent component (χ_{AP}) becomes more negative. In Figure 2, we have already seen that the preferential adsorption λ increases monotonically with $|\chi_{AP}|$ in solvent 2. The Shultz–Flory theory predicts

$$\chi^{SF} = \left(1 - \frac{\gamma}{2}\right)\chi_{AP} + \frac{\gamma^2 \chi_{AP}{}^2}{8} \qquad \text{(IV.2)}$$

The first term of eq IV.2 is negative for mixed solvent 2 and dominates when χ_{AP} is close to zero. As χ_{AP} becomes more negative, the positive second term of eq IV.2 becomes increasingly important. Equation IV.2 predicts that if χ_{AP} is decreased from zero, the radius of gyration will exhibit a relative maximum at $\chi_{AP} \sim -6$. To test this prediction, R_g is plotted against $(1 - (\gamma/2))\chi_{AP}$ in Figure 4. We use this abscissa in order to facilitate comparison with another mixed solvent in Figure 4 (dashed curve). γ is zero for this latter solvent, and the Shultz–Flory theory predicts an effective χ parameter given by the first term of eq IV.2. For χ_{AP} near zero, the second term in eq IV.2 is negligible, thus the two mixed solvents yield similar values for R_g in Figure 4. A predicted by eq IV.2, R_g increases monotonically as χ_{AP} decreases from zero in the mixed solvent with no preferential affinity. The radius of gyration in mixed solvent 2, however, begins to contract as χ_{AP} becomes very negative. Thus the relative maximum that occurs in Figure 4 can be attributed to preferential affinity. The maximum occurs at $\chi_{AP} \sim -4$, which is less negative than predicted by the Shultz–Flory theory. When $\chi_{AP} \leq -12$, R_g in solvent 2 is less than it would be in *either* of the components of the mixed solvent at the same temperature.

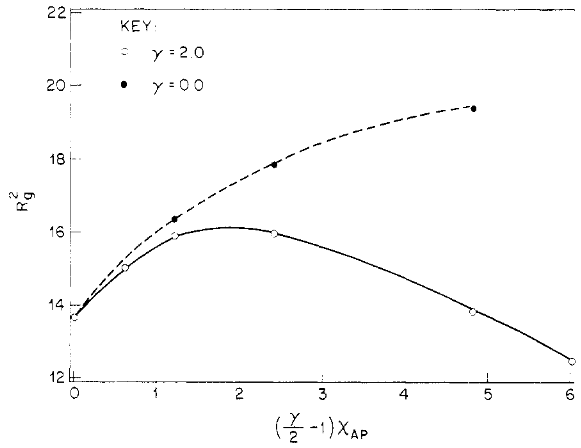

Figure 4. Radius of gyration as a function of $((\gamma/2) - 1)\chi_{AP}$ for mixed solvents with and without preferential affinity.

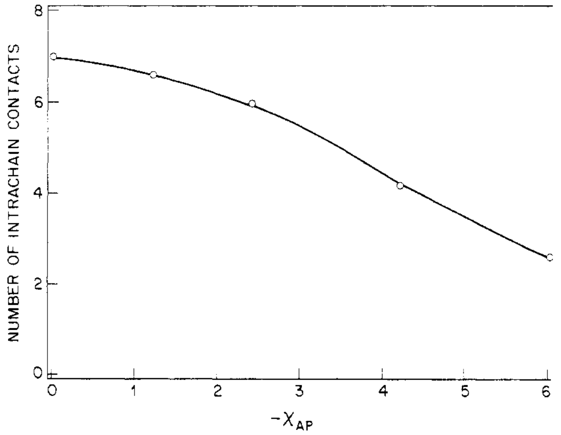

Figure 5. Average number of nearest-neighbor polymer–polymer contacts as a function of χ_{AP} in solvent 1.

4. Effect of Preferential Affinity on the Chain Configurations. We can use the simulations to determine how the chain that contracts as χ_{AP} becomes negative in Figure 3 differs on a molecular level from a chain in a solvent with no preferential affinity. In simulations of the chain collapse at the Θ temperature in a pure solvent, the average number of polymer–polymer contacts (nearest-neighbor type) increases as R_g decreases.[26] In Figure 5 we plot the average number of polymer–polymer contacts for a chain contracting as $-\chi_{AP}$ increases in solvent 1. As the coil contracts, polymer–polymer contacts *decrease* in likelihood. Though this trend differs from pure solvent behavior, it is understandable from energetic considerations. As χ_{AP} becomes more negative, the good solvent component increasingly coats the chain (see Figure 2), thereby preventing polymer–polymer contacts. However, as the chain contracts, it also tends to adopt configurations in which the preferred solvent component binds to the polymer at more than one site. We calculated the average number of polymer contacts with solvent component A,

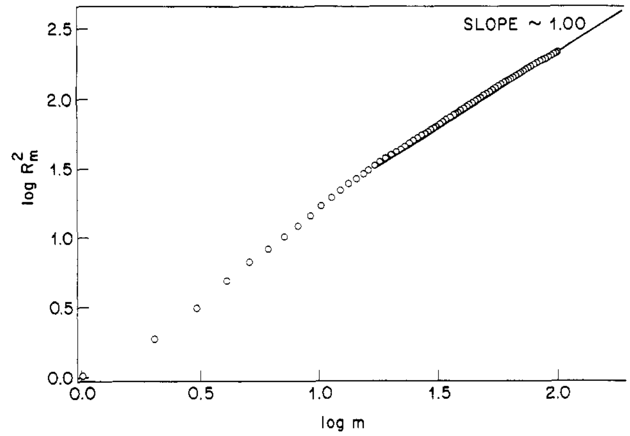

Figure 6. Mean-square distance between monomers separated by m polymer segments, in a solvent with preferential affinity (solvent 1).

per adsorbed A molecule, and this quantity increases monotonically as $-\chi_{AP}$ increases. Possibly the number of polymer contacts per adsorbed A increases in order to minimize the preferential adsorption λ (and hence the excess amount of component A on the lattice) for a given preferential affinity γ. This has implications for the amount of chain folding, since gauche configurations (i.e., adjacent chain links differing in direction by 90° on the cubic lattice[27]) allow adsorbed solvent molecules to bind at more than one polymer site, while trans configurations do not. We determined that the gauche probability increases monotonically as $-\chi_{AP}$ increases in solvent 1. It may be that this increase in the amount of chain folding is responsible for the contraction in R_g which also occurs.

To determine the effect of preferential affinity on the exponent ν, we simulated chains of length N in the range 40–100 in solvent 1 at $\chi_{AP} = -2.4$. We found the scaling exponent of R_g^2 to be 1.06 over this range of N. This value of 2ν is of course not asymptotic but is subject to the finite size effects in solvent 1 discussed earlier. Nonetheless, its low value may be compared to the well-known value of 1.20 for a pure solvent with χ^{SLA} also equal to zero (athermal solvent). The exponent 2ν can also be determined from the internal expansion of the chain,[28] that is, the mean square distance (R_m^2) between monomers separated by m links along the chain. In Figure 6, we plot R_m^2 against m for a chain of length 100 in solvent 1. In this figure the slope exhibits two distinct values, with the lower value occurring for $m > 20$. This behavior is not seen in the pure solvent with the same χ^{SLA}. Furthermore, the slope for $m > 20$ in Figure 6 is lower than in the pure solvent, reflecting the reduction in solvent quality because of preferential affinity.

C. Preferential Affinity with Unfavorable Solvent–Solvent Interactions. We now consider mixed solvents with unfavorable solvent–solvent interactions, $\chi_{AB} = \eta\chi_{AP} > 0$. From eq II.1, $\eta\chi_{AP}$ is zero at very high temperature but increases in magnitude as the temperature is lowered. We investigate the polymer behavior as the critical value of $\eta\chi_{AP}$ (−2.66 for the Ising fluid[29]) is approached on lowering the temperature.

1. Preferential Adsorption. In section IV.B we demonstrated that the preferential adsorption is a function only of $\gamma\chi_{AP}$ when $\eta = 0$ (solid curve, figure 2). However, Brochard and de Gennes[6] predict that when η is nonzero, the preferential adsorption will diverge at the critical point. This critical point occurs at the same value of $\chi_{AB} = \eta\chi_{AP}$ in each mixed solvent. However, η has a different, constant value for each mixed solvent in Figure 2, hence the critical point occurs at a different value of the abscissa: $(\gamma\chi_{AP})_{crit} \sim 2.66\gamma/\eta$. For mixed solvent 3 ($\gamma = 3.0$, $\eta = -2.0$), the critical value of $\gamma\chi_{AP}$ is ≈ -4. In Figure 2, λ in mixed solvent 3 exhibits a strong rise near this value of $\gamma\chi_{AP}$, which is consistent with the prediction of Brochard and de Gennes.

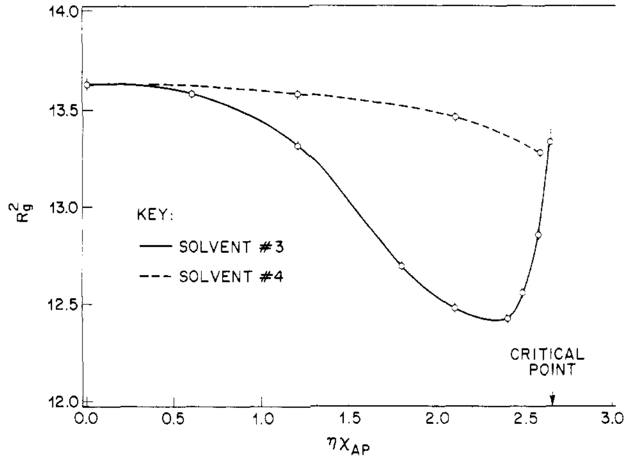

Figure 7. Behavior of the radius of gyration as the consolute point is approached, for solvents with and without preferential affinity (solvents 3 and 4, respectively).

2. Behavior of R_g near the Consolute Point. Equation III.8 summarizes Brochard and de Gennes's analysis for mixed solvent quality near the consolute point. As the consolute point is approached, chain dimensions are predicted to depend crucially upon the presence of preferential affinity. For example, suppose we have two mixed solvents for which the first term of eq III.8 is zero, but only one of the solvents has preferential affinity. If we increase $|\eta\chi_{AP}|$ toward the critical value, eq III.8 predicts that chain dimensions will be constant in the solvent with $\gamma = 0$, but chain collapse will occur in the solvent with preferential affinity. The parameters of solvent 3 in Table I were chosen to best test this prediction. To facilitate simulation, a large value for γ was chosen. Hence the consolute point does not need to be approached extremely closely in order for significant coil contraction to occur (see eq III.9). The radius of gyration in solvent 3 is plotted against $\eta\chi_{AP}$ in Figure 7. The dashed curve in Figure 7 is the observed behavior of R_g in mixed solvent 4 with $\gamma = 0$. The first term in eq III.8 is zero for both of these mixed solvents, and the critical value of $-\eta\chi_{AP}$ is also the same (~2.66). In the solvent with $\gamma = 0$, R_g is relatively constant as predicted, while the presence of preferential affinity in solvent 3 results in first a strong contraction then a reexpansion as the critical point is approached.

The relative minimum of R_g in Figure 7 occurs at $\eta\chi_{AP} \sim 2.40$ ($\tau = 0.1$), which is surprisingly distant from the critical point. The reason for the reexpansion in R_g at this value of χ_{AP} is not obvious from the simulation results. One possible cause is the buildup of monomer concentration within the polymer coil, as discussed by Brochard and de Gennes.[6,7] Alternatively, the range of the attractive force causing the contraction may have exceeded the size of the finite chain at this value of χ_{AP}.

The minimum value of R_g in Figure 7 for a chain of length $N = 40$ implies that mixed solvent 3 has a maximum effective χ value of ~0.44. Both the Shultz–Flory theory (eq III.7) and the Brochard–de Gennes theory (eq III.8) predict much greater contraction. However, one might expect large finite chain effects near T_c, and this is borne out by simulations of longer chains. We find that a chain of length $N = 100$ is contracted almost to its Θ dimensions at the same mixed-solvent state, implying that the effective χ value has increased to ~0.72. Thus increasing N shifts

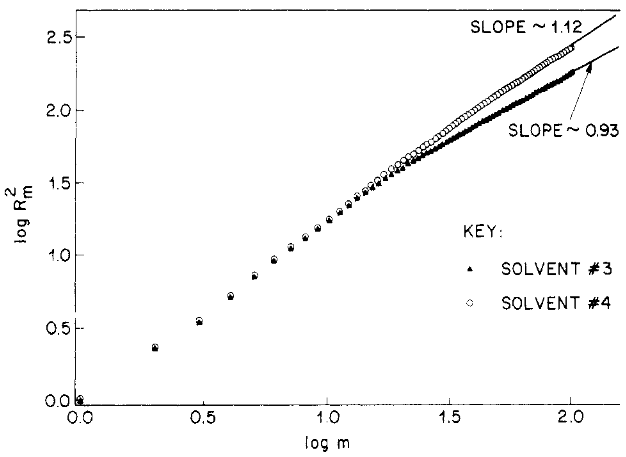

Figure 8. Mean-square distance between monomers separated by m polymer segments, in solvents with and without preferential affinity (solvents 3 and 4, respectively).

the results in the direction of better agreement with the theory. For N in the range 40–100, the scaling exponent 2ν (subject to finite size effects) is ~0.95 in this solvent. Figure 8 displays the internal polymer dimensions (R_m^2 versus m) in solvents 3 and 4 at $\eta\chi_{AP} = -2.40$. The limiting slope in Figure 8 for solvent 3 is 0.93, which is less than that observed for solvent 4 with $\gamma = 0$. This reduction in slope is indicative of the reduction in solvent quality attributable to preferential affinity. Note in Figure 8 that internal polymer dimensions are identical at low m in solvents with and without preferential affinity. We believe this is a reflection of the long range of the force causing the critical collapse. In contrast, the forces causing chain contraction are short ranged when $\eta = 0$, hence in solvent 1 we observed internal polymer dimensions to be affected by γ for all values of m. In solvent 1, we also determined that the probability of multiple polymer contacts per adsorbed solvent molecule increases as the chain contracts (see section IV.B); no such increase is observed as the chain contracts in solvent 3.

V. Summary

The simulation results for the effect of preferential affinity are consistent with the Shultz–Flory and Brochard–de Gennes theories. Preferential affinity causes both chain contraction and a buildup in concentration of the better solvent component near the polymer. As predicted by Brochard and de Gennes, a chain first contracts dramatically then reexpands as the consolute temperature is approached from above. However, preferential affinity also causes chain contraction far away from the critical point, as predicted by the Shultz–Flory theory. The effective range of the attractive force causing chain contraction is larger for the near-critical collapse. At large values of preferential affinity, the chain may contract below its dimensions in either of the pure solvent components. Also indicative of the decrease in solvent quality attributable to preferential affinity is the reduction of the Flory exponent ν.

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Molecular Weight Distribution and Moments for Condensation Polymerization with Variant Reaction Rate Constant Depending on Chain Lengths

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ABSTRACT: A new model for the chain length dependence of the reaction rate constant is proposed for the molecular weight distribution and averaged molecular weights obtained in linear condensation polymerization. An infinite molecular weight for a finite time is predicted if the reaction rate constant is increasing with chain length. The moments method is used and Gupta's model is reconsidered for analytic solutions. Both models are compared with available experimental data.

Introduction

The theory of molecular weight distribution of linear condensation polymers is well established on the principle of equal reactivity of Flory.[1] Even though experimental evidence seems to be generally in favor of this principle, it still seems to be interesting to investigate the systematic

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