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Chain Conformation in Ternary Polymer Solutions

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ABSTRACT: This paper presents a theoretical study on chain conformation of a solute polymer P in a mixture of different chemical species A and B, where A is a good solvent and B is a nonsolvent or an incompatible polymer. In the case of B being a nonsolvent, particular attention is drawn in the vicinity of the critical point of the A/B solvent mixture. On the basis of a lattice theory extended to inhomogeneous three-component polymer systems, it is found that the polymer chain P is swollen in the concentration region close to the critical demixing point. We present quantitative calculation and compare it with the experimental results obtained for the poly(tetrahydrofuran)/methanol/cyclohexane system. In the case of B being an incompatible polymer, polymer P collapses as the concentration of polymer B is increased. The nature of the transition is theoretically studied. We find that the transition is easier when the B chain becomes longer and is sharper when the length of the B chain relative to that of P becomes smaller.

1. Introduction

Recent experimental data[1] show that a polymer dissolved in a mixture of a good solvent and a poor one swells near its critical demixing point. On the other hand, theoretical analyses[2] of ternary polymer solutions suggested that effective interaction induced by critical fluctuation is, for most practical situations, attractive irrespective of the solvent nature. It was also theoretically claimed[3] that, in the case of a mixture of two good solvents, there is a collapse just above the critical point and a reswelling exactly at T_c. This poses a rather puzzling situation. As for single-polymer conformation in three-component solutions, coil-to-globule transition induced by the existence of incompatible polymers has recently received considerable attention.[4-11] Very little is known, however, about the influence of the concentration on the nature of the transition.

The present paper describes spatial dimensions of a polymer chain (P) dissolved in a mixture of a good solvent (A) and a nonsolvent (B). While A is always assumed to be a monomolecular solvent, B is allowed to be a polymer. We assume, however, that N, the degree of polymerization (DP) of P, is larger than n, that of B.

We study, from a unified point of view, the following two environments:

(i) In the case where B is a low molecular weight species we focus our attention to the region in the vicinity of the critical demixing point of an A/B mixture. We find that in the critical region, where the free energy of the mixed solvent is in a limit of stability, the P chain swells to nearly twice its size in the pure A solvent. This fact indicates that instability in the background medium induces effective repulsion between the polymer segments.

(ii) In the case where the DP of B is larger, we focus our attention on the concentration region where B polymers begin to overlap. It is shown that the P chain shrinks to a compact globule for sufficiently large B concentration. The transition from a swollen random coil to a compact globule due to the existence of B chains becomes easier as n becomes larger, while it becomes sharper as n/N becomes smaller.

For the first problem, de Gennes[2] predicted through certain intuitive arguments that the indirect interaction between two segments of a polymer chain, for most practical situations, results in an attractive and long-range interaction. Hence a polymer chain must contract in the critical region. The viscometric measurement by Dondos and Izumi,[1] however, showed quite opposite behavior of a polymer chain, poly(tetrahydrofuran) (PTHF), in the mixed solvent methanol/cyclohexane. Reduced viscosity of PTHF exhibited clear peaks at the critical concentration for temperatures near the critical value when methanol fraction was increased. We therefore examine this problem once again from a statistical–mechanical point of view. For

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polymeric networks instead of a single chain, the problem is of practical interest, relating to volume change of gels,[4] preferential adsorption of one component by gels,[5,6] freezing of AB patterns,[6] and so on.

For the second problem, we studied in a series of papers[7-9] the coil–globule transition induced by the existence of incompatible chains. The phenomena were first observed in a biological system where DNA at very low dilution in a buffer was contracted from an extended random coil to a high-density globule by addition of poly(oxyethylene) (POE) and small amount of NaCl. This internal condensation, called Ψ condensation, was later studied by Post and Zimm[11] and Frisch and Fesciyan[12] from molecular theoretical point of views. In ref 11 the analyses were confined to the dependence of chain conformation on the interaction parameter χ and the intramolecular ternary cluster integral. Effect of concentration was not considered. Reference 12, on the other hand, obtained the effective segment interaction as a function of POE concentration. The local modification of the solvent composition due to the variation of chain dimensions was not properly taken into consideration. Consequently the chain free energy was minimized with respect to a single variable α, the expansion factor of the chain. Nose[13] also studied essentially the same transition phenomena on the basis of the concentration blob picture for a guest polymer in a semidilute solution of incompatible polymers. Polymer-induced sudden collapse of a long chain was found to occur around the overlap concentration. Variation of the second virial coefficients was also discussed. Calculation of absolute amplitudes of physical quantities, however, was beyond the scope of the scaling theory.

2. Free Energy of a Polymer Chain in a Mixed Solvent

Consider a single flexible P chain dissolved in a solution of total volume V. Let a be the size of its statistical unit. Let us assume that the size of a solvent molecule A and of the statistical unit of B is also the same and given by a. We divide the space into cubic cells of volume a^3. The total number of cells in the system is $\Omega \equiv V/a^3$. We apply to our problem the lattice theory of Flory–Huggins.[14] Let the center of mass of the P chain be the origin of the coordinate, and let $\phi(r)$ be the local volume fraction of its segment expressed as a function of distance r from the origin. The volume fraction of the B chain segment and A solvent is then given as $\phi_B(r) = (1 - \phi(r))v(r)$ and $\phi_A(r) = (1 - \phi(r))(1 - v(r))$, respectively, in terms of the solvent volume fraction $v(r)$. At a position away from the P chain, the boundary conditions

$$\phi(\infty) = 0, \qquad v(\infty) = x \tag{2.1}$$

must be fulfilled, where x is the bulk concentration of the B component in the A/B mixture.

The conformational free energy of the P chain is then expressed as

$$\beta F = A(\alpha) + \int_0^\infty \Delta f_{\text{mix}}(\phi,v) 4\pi r^2 \, \mathrm{d}r \, a^{-3} \tag{2.2}$$

where $\beta \equiv 1/k_BT$ is the inverse temperature and α the expansion factor $(\langle s^2\rangle/\langle s^2\rangle_0)^{1/2}$ for the gyration radius of the chain relative to the ideal state. The mean radius of gyration $\langle s^2\rangle_0$ for a Gaussian chain is given by $\langle s^2\rangle_0 = Na^2/6$. The first term of eq 2.2 is the elastic part of the free energy due to deformation of the segment distribution. It is explicitly given[14] by

$$A(\alpha) = 3\left(\frac{\alpha^2 - 1}{2} - \ln \alpha\right) \tag{2.3}$$

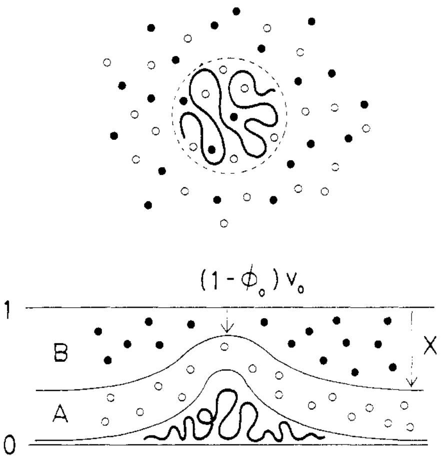

Figure 1. Single polymer P dissolved in a solvent mixture A/B (top). Spatial variation of the concentration of each component is also shown (bottom). The volume fraction of the B solvent takes a limiting value x well away from the polymer, while it is modified to $(1 - \phi_0)v_0$ at the center of the segment distribution. The polymer shrinks as x is increased.

The second term is the free energy change due to mixing the three components:

$$\Delta f_{\text{mix}}(\phi,v) = \frac{(1 - \phi)v}{n} \ln (1 - \phi)v + (1 - \phi)(1 - v) \ln (1 - \phi)(1 - v) + \chi_{AP}\phi(1 - \phi)(1 - v) + \chi_{BP}\phi(1 - \phi)v + \chi_{AB}(1 - \phi)^2 v(1 - v) \tag{2.4}$$

where χ_{ij} is the interaction parameter between the segments of i and j species. Functional minimization of (2.2) by varying $\phi(r)$ and $v(r)$ leads to equilibrium conformation of the chain. We carry forward this minimization by assuming the form of distribution $\phi(r)$ to be Gaussian with mean square radius of gyration $\langle s^2\rangle$:

$$\phi(r) = \phi_0 e^{-\beta_0(r/\alpha)^2} \tag{2.5}$$

where $\beta_0 \equiv 3/(2\langle s^2\rangle_0) = 9/Na^2$. Since $\phi(r)$ must satisfy normalization

$$\int_0^\infty \phi(r) 4\pi r^2 \, \mathrm{d}r \, a^{-3} = N \tag{2.6}$$

the constant ϕ_0 is given in terms of α by

$$\phi_0 = C/N^{1/2}\alpha^3; \qquad C \equiv (9/\pi)^{3/2} = 4.849 \tag{2.7}$$

Similarly we assume, considering the boundary condition (eq 2.1), $v(r)$ to be Gaussian:

$$v(r) = x(1 - \delta e^{-\beta_0(r/\alpha)^2}) \tag{2.8}$$

The parameter δ gives the magnitude of modification in local concentration of the A/B mixture by the presence of the P chain. At the center of the P chain the B fraction is given by $v(0) = x(1 - \delta)$. Hence B chains are excluded from the region when $0 < \delta < 1$, preferentially absorved when $\delta < 0$, and unphysical when $\delta > 1$. Figure 1 shows the cross sectional view of the segment volume fraction for each component.

Substituting (2.5) and (2.8) and (2.2) and carrying out the integral, we find

$$\beta F(\phi_0,\delta) = A(\alpha) + \frac{N}{\phi_0}[f(\phi_0,\delta) - f(0,0)] + \Omega f(0,0) \tag{2.9}$$

where a function $f(\phi_0,\delta)$ of two independent variables ϕ_0 and δ is explicitly defined in Appendix A. Specifically

$$f(0,0) \equiv f_{AB} = \frac{x}{n} \ln x + (1 - x) \ln (1 - x) + \chi_{AB}x(1 - x) \tag{2.10}$$

is the free energy per lattice cell for a uniform mixture of A solvent and B polymer. Similarly, we obtain the total number N_B of B chains in the solution as

$$N_B = \frac{1}{n}\int_0^\infty (1 - \phi(r))v(r)4\pi r^2 \, dr \, a^3 = \frac{x}{n}\left[\Omega - \frac{N}{\phi_0}(\phi_0 + \delta - C_2\phi_0\delta)\right] \quad (2.11)$$

where $C_m \equiv 1/m^{3/2}$ ($m = 2, 3, 4, ...$) are a set of numerical constants whose definitions are found also in Appendix A. The total number N_A of the solvent is given by $N_A = \Omega - N - nN_B$ by a space-filling condition.

We now minimize (2.9) with respect to ϕ_0 and δ under fixed number of N_A (and therefore N_B). This is equivalent to the minimization of a function $G(\phi_0,\delta)$ defined by $G(\phi_0,\delta) \equiv \beta F(\phi_0,\delta) + \mu_A N_A + \mu_B n N_B$, where μ_i is a Lagrange undetermined multiplier or, physically, the chemical potential of i species.

Simple manipulation leads to

$$G(\phi_0,\delta) = A(\alpha) + \frac{N}{\phi_0}[f(\phi_0,\delta) - f_{AB} - \mu x(\phi_0 + \delta - C_2\phi_0\delta)] + \text{const} \quad (2.12)$$

where const stands for the part independent of ϕ_0 and δ. The undetermined multipliers are combined to a single unknown $\mu \equiv \mu_B - \mu_A$. It is decided from (2.11) after minimization is performed. Variation with respect to ϕ_0 and δ leads to coupled equations:

$$A'(\alpha)\frac{d\alpha}{d\phi_0} + \frac{N}{\phi_0^2}\left(\phi_0\frac{\partial f}{\partial \phi_0} - f + f_{AB} + \mu x\delta\right) = 0 \quad (2.13a)$$

$$\frac{\partial f}{\partial \delta} - \mu x(1 - C_2\phi_0) = 0 \quad (2.13b)$$

3. Method for the Solution

We proceed to solve the coupled equations (2.13a) and (2.13b). Though they may be solved directly by numerical method, it is more instructive for getting a physical picture of the chain conformation to eliminate one of the unknowns (δ) and obtain a single equation for the expansion factor α. Since modification δ of the local concentration is due to the existence of the polymer chain, it is regarded as a function of the segment density ϕ_0. Let us expand it in powers of ϕ_0:

$$\delta = \sum_{n=1}^{\infty} a_n \phi_0^{\,n} \quad (3.1)$$

Similarly we expand the free energy as

$$f(\phi_0,\delta) = \sum_{n=0}^{\infty} G_n(\delta)\phi_0^{\,n} \quad (3.2)$$

Equation 2.13b is then transformed to

$$\sum_{n=0}^{\infty} G'_n(\delta)\phi_0^{\,n} = \mu x(1 - C_2\phi_0) \quad (3.3)$$

We determine the coefficients a_n by imposing a condition that δ satisfies eq 3.3 in each power of ϕ_0. To describe the results explicitly, we furthermore expand $G_n(\delta)$ as

$$G_n(\delta) = \sum_{m=0}^{\infty} g_{nm}(x)\delta^m \quad (3.4)$$

The coefficients g_{nm} are functions of the solvent composition x. They can be derived from the explicit form of $f(\phi_0,\delta)$. Some of them, which we need in the following analysis, are shown in Appendix B. Specifically we have $G_0(0) = g_{00} = f_{AB}(x)$. Term by term comparison leads to the result

$$\mu x = g_{01} \quad (3.5a)$$

$$a_1 = -(g_{11} + C_2 g_{01})/2g_{02} \quad (3.5b)$$

$$a_2 = -(3g_{03}a_1^{\,2} + 2g_{12}a_1 + g_{21})/2g_{02} \quad (3.5c)$$

and so on. The chemical potential difference has been decided by (3.5a).

Substituting the power series for f in (2.13a), we obtain

$$A'(\alpha)\frac{d\alpha}{d\phi} + N\left[-\frac{1}{\phi_0^{\,2}}(G_0(\delta) - f_{AB}(x) - \mu x\delta) + \sum_{n=2}^{\infty}(n-1)G_n(\delta)\phi_0^{\,n-2}\right] = 0 \quad (3.6)$$

which is now an equation for a single unknown α. It determines the average dimensions of the segment distribution under a given external composition x of the solvent mixture. We use the relation between α and ϕ_0 (eq 2.7) and take into consideration the terms up to the second order of ϕ_0. The final equation we find is arranged into the form

$$\alpha^5 - \alpha^3 - \frac{q(x)}{\alpha^3} = N^{1/2}p(x) \quad (3.7)$$

where new functions are defined by

$$p(x) = C(-g_{02}a_1 + g_{20}) \quad (3.8a)$$

$$q(x) = C^2(-2g_{02}a_1a_2 - g_{03}a_1^{\,3} + g_{21}a_1 + 2g_{30}) \quad (3.8b)$$

An equation of the same type was first derived by Flory[14,15] in a study of the excluded-volume effect on chain dimensions, where there were no terms corresponding to q and, in the place of $p(x)$, the temperature deviation $\tau \equiv 1 - \theta/T$ from the θ point appeared. The method was later applied to systems of mixed solvents by Shultz and Flory.[16] In their analysis solvent concentration was assumed to be uniform inside the volume occupied by a polymer. Although an explicit form of the function $p(x)$ was obtained due to this assumption, the theory may predict a quite different behavior of α without the q/α^3 term. Deviation from our results is particularly enlarged for smaller values of α.

Ptitsyn[17] and de Gennes[18] later considered the q term in order to study thermally induced coil-to-globule transition of a polymer chain at low temperatures below the θ point. In these studies q was assumed to be temperature independent. The term originates in the intramolecular ternary cluster integral. In (3.7) these parameters are replaced by the functions of mixture composition. We can therefore easily be convinced that various conformational variations, including the coil–globule transition, are expected around the concentration where the function $p(x)$ changes its sign.

4. Results

Before presenting numerical solutions for the fundamental equation, eq 3.7, let us consider the two limiting cases where the solvent is either A or B. Several investigations on these special cases have been described in the literature. Setting $x = 0$ for a pure A solvent, we find

$$p(0) = CC_2(\tfrac{1}{2} - \chi_{AP}); \qquad q(0) = \tfrac{1}{3}C^2C_3 \quad (4.1)$$

The right-hand side of eq 3.7 turns out to be proportional to $\tau N^{1/2}$, where τ is the deviation of temperature from the θ point defined by $\tau \equiv {}^1/_2 - \chi$. The equation has

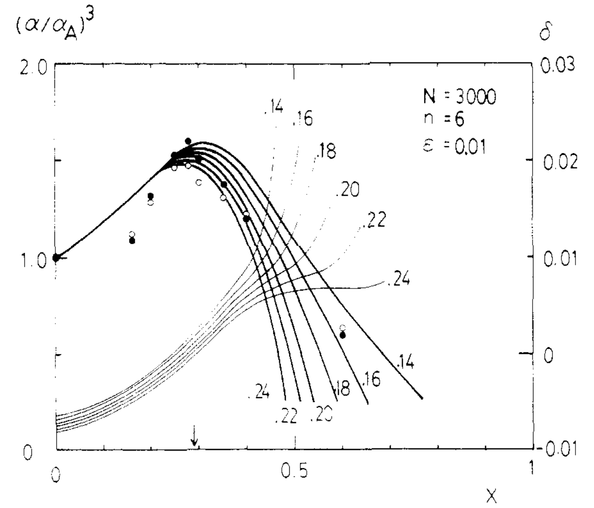

Figure 2. Expansion factor for a chain in an A/B mixture is shown against the bulk volume fraction x of the B component (thick lines). The local modification of the composition is also shown (thin lines). The parameter χ for A/B molecular contact is fixed to be near the critical value $(\chi_{AB}{}^c - \chi_{AB})/\chi_{AB}{}^c \equiv \epsilon = 0.01$). Near the critical demixing concentration x_c, which is shown by a vertical arrow, the expansion factor shows a broad maximum. The parameter χ_{BP} is varied from curve to curve for comparison with experimental data on PTHF in CH/M mixture. In the experiment the hydrodynamic radius was measured at two different temperatures (○ and ●) near the critical point. It is assumed to be proportional to the radius of gyration of the chain.

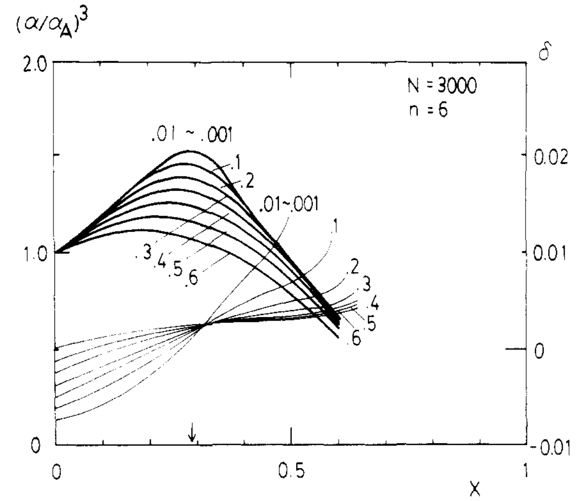

Figure 3. Same as in Figure 2. In this figure ϵ approaches zero while χ_{AP} and χ_{BP} are fixed. As soon as ϵ reaches 0.01 the chain seems to be in full extension.

reduced to be the one which was considered in ref 3.17, and 18, where it was found that the temperature variation of the chain conformation is very sharp when the numerical value of $q(0)$ is below a certain critical value (0.0228). Sudden collapse of a chain by the decrease of temperature was called the coil–globule transition.

In the case of pure B solvent, we set $x = 1$ to find

$$p(1) = CC_2\left(\frac{1}{2n} - \chi_{BP}\right); \qquad q(1) = \frac{1}{3n}C^2C_3 \quad (4.2)$$

Single-chain conformation in a melt of shorter incompatible chains was studied by Joanny et al.[19] They derived an equation of similar type. The absolute values of the numerical coefficients, however, were not examined in detail. Irrespective of these numerical values, the transition from a random coil to a collapsed globule was found to be more abrupt than for a chain in a poor solvent. This is simply due to the n dependence in the functions shown in (4.2).

We thus have confirmed that our theory covers the existing literature in the two-extreme limit. We next study the effects of concentration.

A. Chain Conformation Near the Critical Demixing Point of the Solvent Mixture. The critical point of the A/B mixture is determined by the conditions $f''_{AB}(x) = f'''_{AB}(x) = 0$. We thus have

$$x_c = 1/(1 + n^{1/2}); \qquad \chi_{AB}{}^c = (1 + n^{1/2})^2/2n \quad (4.3)$$

for the critical value of the concentration and χ parameter, respectively. We fix the temperature near above the critical value by setting

$$\chi_{AB}(T) = \chi_{AB}{}^c(1 - \epsilon) \quad (4.4)$$

where ϵ ($\ll 1$) is a dimensionless measure of the temperature deviation.

To explain the results of viscosity measurement obtained by Dondos et al.[3] for a poly(tetrahydrofuran) (PTHF) in a cyclohexane (CH)/methanol (M) mixture, we set $\epsilon = 0.01$ and $N = 3000$. To reproduce the observed value 0.28 of the critical concentration x_c for the CH/M mixture, we have set $n = 6$.

The parameter between PTHF and CH is chosen to be $\chi_{AP} = 0.45$. Figure 2 shows the variation of cubic power of the expansion factor against the methanol concentration. The parameter χ_{BP} is varied from curve to curve. Experimental data at two different temperatures are shown by ○ (51 °C) and ● (49 °C), for both of which ϵ is roughly given by 0.01. It was assumed[14] that the specific viscosity of a polymer chain is proportional to α^3. This is based on the idea of an equivalent sphere model. The hydrodynamic radius of the equivalent sphere is proportional to the radius of gyration. Quantitative agreement is attained for $\chi_{BP} = 0.20 \sim 0.22$. In the low-concentration region there is some discrepancy between theory and experiment. Figure 3 shows the same but for different temperatures. The parameter ϵ is changed while other χ parameters are fixed to be $\chi_{AP} = 0.45$ and $\chi_{BP} = 0.2$. The curves clearly show that the polymer chain is swollen to its extreme as soon as ϵ becomes smaller than about 0.01. The coil is essentially surrounded by a droplet of A, and this requires the expulsion of B. Close to the A/B critical point the derivative d^2f_{AB}/dx^2 of the free energy versus concentration is small, and the expulsion is easy.

B. Polymer-Induced Coil–Globule Transition. A polymer chain is compacted in a solution by the existence of incompatible polymers. The transition from random coil state to a highly packed globule[7,8] is expected to be sharp when the chain is sufficiently long compared to the surrounding polymers and to be easily induced when they become longer. For this reason we set $N = 10000$. In the case of polystyrene this corresponds to a molecular weight as high as 10^7 since a statistical unit on a chain consists of several monomers. We dissolve such a long chain in a good solvent ($\chi_{AP} = 0.3$ for example). We then add B chains to the solution whose DP is given by n. They are compatible with P chain when $\chi_{BP} < 1/(2n)$ and incompatible when $\chi_{BP} > 1/(2n)$. The boundary is obtained by the condition that $p(1)$ in eq 4.2 vanishes. For a numerical calculation we set $\chi_{BP} = 0.1$ and vary n over the range from 50 to 200. Figure 4 shows the expansion factor α of a P chain against the volume fraction of B polymers in a bulk A/B mixture. As we remarked before, our approximation becomes unphysical as soon as the chain volume fraction ϕ_0 at the center of the segment distribution exceeds unity. The situation corresponds to complete exclusion of A solvent and also B polymers from the core of P segment

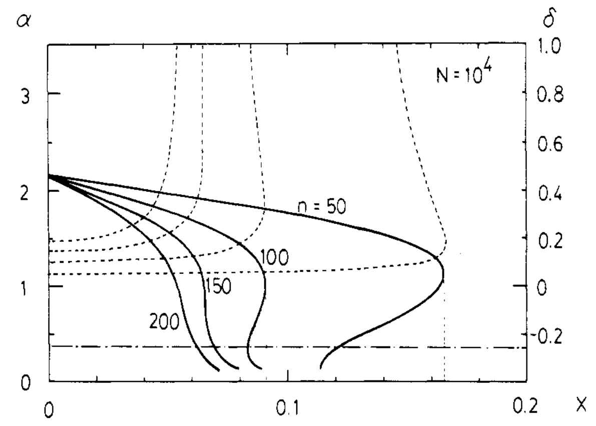

Figure 4. Expansion factor α and concentration modification δ are shown against the volume fraction x of B polymers. χ parameters are fixed to be $\chi_{AP} = 0.3$, $\chi_{BP} = 0.1$, and $\chi_{AB} = 0.4$. As x increases the giant polymer collapses to a compact globule from the core of which solvent molecules are completely excluded. The lower critical value α_c is shown by a broken line. As the DP of the B polymer, n, becomes larger, the transition is smeared from a first-order type to a gradual crossover.

distribution. When the P polymer shrinks below this limit, Gaussian form is not appropriate for the description of the collapsed globule. We show in Figure 4 the lower limit α_c by a horizontal line below which our method is not sufficient. Local modification δ of the A/B concentration also exceeds unity and hence becomes unphysical as soon as α reaches this lower limit.

In addition to this limitation, we have discarded the higher order terms of the form

$$\sum_{m=2}^{\infty} \frac{q_m(x)}{\alpha^{3m}} \tag{4.5}$$

on the right-hand side of eq 3.7. When α becomes as small as α_c, each term in eq 4.5 grows to the same order of magnitude, which is comparable to $q(x)/\alpha^3$. The method of expansion in powers of ϕ_0 itself therefore breaks down in such a low α region.

For those χ parameters fixed in our calculation, variation in the expansion factor α changes from discontinuous to continuous as the DP of B polymer is increased. The concentration at which change of α is remarkable decreases as n is increased. All these characteristics of the transition are in agreement with our previous study.[7-9] To obtain a sudden collapse, small χ_{BP} (which must of course satisfy $\chi_{BP} > 1/(2n)$) and large χ_{AB} are preferable.

5. Discussion

We have studied conformational transition of a polymer molecule dissolved in various mixed solvents consisting of species which have opposite characters. It was shown that mixing of two solvents leads to completely new phenomena that do not exist if the two solvents are used separately. We have focused our attention mainly on two phenomena: swelling of a chain near the critical solution point of the solvent mixture and coil-to-globule transition induced by environmental polymers of incompatible nature.

To obtain explicit results our calculations have been based on several rather stringent approximations:

(i) It has been assumed that spatial variation of concentration distributions $\phi(r)$ and $v(r)$ are Gaussian. For an expanded polymer chain, however, it is known from both numerical work and renormalization group studies that this is not true. The segment distribution function is very complicated in such a way as characterized by several exponents. Incorporation of such parameters may lead to a refined equation for α which, instead, will be intractable. As the mixing free energy obtained has been based on the lattice theory of Flory–Huggins, which itself is a product of the mean field idea, amendment of the theory along this line will not be fruitful.

(ii) In the treatment of the thermodynamics for the A/B solvent mixture, whole analysis has been confined to the scope of the simplest mean-field approximation (i.e., regular solution). In the region near the critical point, where the correlation length of the concentration fluctuation grows as long as the polymer dimensions, effect of spatial fluctuation is expected to be significant. Proper consideration of the critial fluctuations may lead to a quite different nature of the indirect interaction between the polymer segments. It was shown in ref 2 and 3 that the lowest order concentration correlation can give rise to an attractive interaction rather than a repulsive one. The conclusion, however, should readily be changed once we proceed to consider the effects of higher order correlation functions (or multiple scattering terms in field-theoretical terminology). Every higher correlation of A/B concentration fluctuations gives opposite sign alternately to the effective interaction between polymer segments, and there is no reason for the lowest term to be dominant. Their conclusion is clearly not applicable to the case of the viscosity experiment made by Dondos and Izumi,[1] since a collapsed chain can never cause larger intrinsic viscosity, irrespective of the solvent. Regular solution approximation is the first necessary step for the quantitative analysis of this problem.

There are some other interesting phenomena which we can analyze by the method presented in the present paper. If we set $N = n$ and all χ parameters to be identical, we have a two-component solution. Chain dimensions of a single polymer in a solution is obtained as a function of the concentration. Flory's theorem, which states that a chain approaches the ideal state as the concentration is increased, can be quantitatively confirmed. If we consider a polymer network instead of a chain, we can study the volume transition of a gel in a mixed solvent. The elastic energy in eq 2.3 is multiplied by ν, the number of elastically effective chains in the network. The solvent composition will be modified inside the network.

It must be noticed that our method is not sufficient when the segment volume fraction in the core of a chain approaches unity. The chain completely excludes both solvents from the central region of the segment distribution. It takes a random walk in the space where there is neither a vacancy nor a solvent molecule. The number of configurations in the core region equals the number of Hamilton walks employed for the packing of a polymer chain.[21] For such a highly packed globule the lattice theory of Flory–Huggins itself does not give a proper description, and a new approach will be required.

Appendix A. Explicit Form of the Function $f(\phi_0,\delta)$

We first expand the logarithms in eq 2.2 in powers of ϕ_0 and δ and then carry out the integral term by term. After a straightforward but lengthy calculation we arrive at the result

$$\begin{aligned} f(\phi_0,\delta) = {} & \frac{x}{n}[-(\ln x)\delta + C_2(\ln x)\phi_0\delta - x(\zeta_0(\phi_0) + \zeta_0(\delta)) + \\ & (\phi_0 + \delta)(\zeta_1(\phi_0) + \zeta_1(\delta)) - \phi_0\delta(\zeta_2(\phi_0) + \zeta_2(\delta))] + \\ & (x \ln (1 - x))\delta - C_2(x \ln (1 - x))\phi_0\delta - (1 - x)(\zeta_0(-y\delta) + \\ & \zeta_0(\phi_0)) - [x\delta - (1 - x)\phi_0](\zeta_1(-y\delta) + \zeta_1(\phi_0)) + \\ & x\phi_0\delta(\zeta_2(-y\delta) + \zeta_2(\phi_0)) + h_0(\delta) + h_1(\delta)\phi_0 + h_2(\delta)\phi_0^2 \end{aligned} \tag{A.1}$$

where a parameter y is defined by $y \equiv x/(1 - x)$. Definitions of the functions which have newly appeared in eq A.1 are required. A set of functions $\zeta_m(x)$ ($m = 0, 1, 2, ...$) is defined by

$$\zeta_m(x) \equiv \sum_{n=1}^{\infty} \frac{x^n}{n(n+m)^{3/2}} \qquad \text{(A.2)}$$

in the form of a power series in x.

Another set of functions $h_m(x)$ ($m = 0, 1, 2$) is defined as

$$h_0(\delta) \equiv -\chi_{AB}x(1 - 2x + C_2x\delta)\delta \qquad \text{(A.3a)}$$

$$h_1(\delta) \equiv \chi(x) + C_2x\delta(-\chi'(x) + \chi_{AB}(1 - 2x)) + 2C_3\chi_{AB}x^2\delta^2 \qquad \text{(A.3b)}$$

$$h_2(\delta) \equiv -C_2\chi(x) + C_3\chi'(x)x\delta - C_4\chi_{AB}x^2\delta^2 \qquad \text{(A.3c)}$$

where

$$\chi(x) \equiv \chi_{AP}(1 - x) + \chi_{BP}x - \chi_{AB}x(1 - x) \qquad \text{(A.4)}$$

and $\chi'(x)$ is the derivative of $\chi(x)$. Numerical constants C_m ($m = 2, 3, 4, ...$) are defined by $C_m \equiv 1/m^{3/2}$.

Appendix B. Explicit Forms of the Functions $g_{nm}(x)$

Expanding eq A.1 in double powers of ϕ_0 and δ and comparing it with the definitions of eq 3.2 and 3.4, we obtain the following functions:

$$g_{01}(x) = -(x + \ln x)/n + \ln(1 - x) + 1 - \chi_{AB}(1 - 2x)$$

$$g_{02}(x) = C_2[(2 - x)/n + x/(1 - x) - 2\chi_{AB}x]/2$$

$$g_{03}(x) = C_3[(3 - 2x)/n + (x/(1 - x))^2]/6$$

$$g_{11}(x) = C_2[-2(1 - 1/n) + (\ln x)/n - \ln(1 - x) + \chi_{AP} - \chi_{BP} + 2\chi_{AB}(1 - 2x)]$$

$$g_{12}(x) = C_3[(1 - 1/n) - 1/(1 - x) + 4\chi_{AB}x]/2$$

$$g_{20}(x) = C_2[x(2 - x)/2n + (1 - x)/2 - \chi_{AP}(1 - x) - \chi_{BP}x + \chi_{AB}x(1 - x)]$$

$$g_{21}(x) = C_3[(1 - 1/n)/2 - \chi_{AP} + \chi_{BP} - \chi_{AB}(1 - 2x)]$$

$$g_{30}(x) = C_3[x(3 - 2x)/n + 1 - x]/6$$

Registry No. PTHF (homopolymer), 24979-97-3; PTHF (SRU), 25190-06-1; CH_3OH, 67-56-1; cyclohexane, 110-82-7.

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How Does the Polymer Main Chain Influence the Side-Chain Mobility? A Fluorescence Probe Study by Means of Twisted Intramolecular Charge-Transfer Phenomena

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ABSTRACT: ω-[[4-(*N,N*-Dimethylamino)benzoyl]oxy]alkyl methacrylates where alkyl is dodecyl, octyl, butyl, and ethyl were prepared and copolymerized with a large excess of methyl methacrylate. The content of the 4-(dimethylamino)benzoate (DMAB) as a fluorescence probe is less than 0.04 wt %. Fluorescence spectra of the samples were studied in dilute ethyl acetate (a good solvent) or *n*-butyl chloride (a poor solvent) solution. When rotation of the dimethylamino group is possible within the excited state lifetime, fluorescence from DMAB group is in part converted to twisted intramolecular charge-transfer (TICT) fluorescence. This fluorophore can therefore probe local segment mobility in the polymer. It was found that the ratio (*R*) of TICT emission intensity to the emission intensity from the local excited state of DMAB decreased with decreasing the alkyl spacer length. Together with the results of red edge excitation effects it was concluded that the local segment motion of side group was subjected to restriction by the polymer main chain as a function of separation from the main chain. Solvent and molecular weight effects were also discussed.

Introduction

The fluorescence method in polymer science is becoming increasingly popular because of its handiness and the possibility of obtaining detailed molecular information on the local environment.[2] When a small molecular fluorescence probe is simply mixed with a polymer to study averaged bulk properties of the polymer, one has to worry about the binding site or the position where the probe locates.[3] The demerit of probing a particular site could turn out to be a merit when one intends to study the distribution of the molecular environment in a polymer. We are now reporting a novel example providing the information on the distribution of segment mobility in a polymer side chain in dilute solution.

In view of recent advancement in time-resolved measurements of various rate constants, evidence is being

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