

Correlation between the combinatory entropy of polymer and ideal liquid solutions

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A semiempirical equation of combinatory entropy in binary solutions of semiflexible or rod-like polymers in solvent has been derived, based on a correlation between the combinatory entropy in polymer solution derived by Flory, Huggins, Miller and Guggenheim and an ideal simple liquid solution. The expression for the partial entropy of mixing of solvent $\Delta S_{M,1}$ obtained in this work is given by:

$$\Delta S_{M,1}/k = -\ln \phi_1 - \phi_2(1-r^{-1}) + \alpha\phi_1\phi_2 + \ln\{[\phi_1 + (\phi_2/r)]/[\phi_1 + (\phi_2/r) + \alpha\phi_1\phi_2]\} \\ + \alpha\phi_2^2 \ln\{(r^{-1} + \alpha\phi_1)/[\phi_1 + (\phi_2/r) + \alpha\phi_1\phi_2]\}$$

where ϕ_i is the volume fraction of polymer ($i=2$) and solvent (1), r is the number of segments per polymer, k is the Boltzmann constant and α is a parameter characterizing the flexibility of polymer chain such that $\alpha=0$ for flexible polymers and $\alpha=(1-r^{-1})/\phi_1$ for rigid-rod polymers. The chemical potential of solvent in the polymer solution is given by:

$$\mu_1 - \mu_1^0 = RT[-\Delta S_{M,1}/k + \chi_1^0(1+\alpha)\phi_2^2]$$

where χ_1^0 is the polymer-solvent interaction parameter in the Flory-Huggins theory.

(Keywords: combinatory entropy; polymer solution; ideal simple liquid solution; Flory-Huggins theory; semiflexible polymer; rod polymer)

INTRODUCTION

The Flory-Huggins theory is the most simple and fundamental theory of flexible polymer solutions. The theory uses the mean field approximation that the concentration of solution is uniform over the entire range of solution, for calculating the number of configurations of polymer and solvent molecules and for evaluating the enthalpic term by a van Laar model¹. The division of the free energy into entropic and enthalpic terms made the Flory-Huggins theory even more simple and useful. Flory also stressed a division of the solution into intermolecular and intramolecular factors, and stated that thermodynamic properties of a flexible polymer solution are independent of the structure and flexibility of the macromolecules, and are dependent on only one parameter, the number of segments per polymer, r .

Guggenheim², Miller³, and Huggins⁴ derived essentially the same equations for the entropy of mixing in polymer solutions where a parameter Z coordination number is included in addition to the parameter r . Investigation of the combinatory entropy for non-flexible polymers such as semiflexible and rod-like polymer has been made by Flory^{5,6}, where new parameters are introduced: a fraction f of the bonds bent out of the co-linear direction of the preceding segment in the semiflexible polymer, and the angle of inclination of the particle to the domain axis in the rod-like polymer. Many different approaches to the calculation of combinatory entropy and free energy in polymer solutions have been made. The effects of orientation on combinatory entropy

are discussed by DiMarzio⁷, while the combinatorial entropy correction for imperfect randomness is calculated by Huggins⁸. More rigorous calculation of combinatory entropy based on the self-avoiding and mutually avoiding walk has been done by Kurata⁹ using the pseudoconfiguration method, and by Bawendi and Freed¹⁰⁻¹² in the lattice spin-field theory, and by Monte Carlo simulation^{13,14}.

This work discusses the correlation between the combinatory entropy in polymer solution and the ideal liquid mixture based on the lattice theories of Flory, Huggins, Guggenheim and Miller and a simple and useful equation is derived for the entropy of mixing and chemical potential in binary solutions of semiflexible and rod-like polymers in solvents. Division of the Gibbs free energy of mixing into the entropic and enthalpic term in polymer solution is also discussed.

FUNDAMENTAL RELATION IN THE CALCULATION OF COMBINATORY ENTROPY

It is well known that the configurational partition function of ideal, simple liquid mixtures (SM) of N_1 molecules of component 1 and N_2 molecules of component 2 is given by:

$$\Omega_{SM} = (N_1 + N_2)! / (N_1! N_2!) \quad (1)$$

$$\approx X_1^{-N_1} X_2^{-N_2} \quad (2)$$

where $X_i = N_i / (N_1 + N_2)$ is the mole fraction of i and the Stirling approximation that $N_1! \approx (N_1/e)^{N_1}$ is used. It is

interesting to calculate the number of configurations of the mixture under the condition that n_1 molecules of 1 are fixed at n_1 different positions in the lattice, which is designated as $\Omega_{n_1}^F$ and is given by:

$$\Omega_{n_1}^F = \Omega_{SM} X_1^{n_1} \quad (3)$$

where $X_1^{n_1}$ is the probability that n_1 different positions are occupied by n_1 molecules of 1 simultaneously, or in other words n_1 molecules are fixed at n_1 different positions in the lattice. It is obvious that if N_1 molecules of 1 and N_2 molecules of 2 are fixed at positions of $(N_1 + N_2)$, then the number of configuration is one, since $\Omega_{SM} X_1^{N_1} X_2^{N_2} = 1$, from equation (2). It is also interesting to calculate the number of configuration when n_1 molecules of 1 are removed or disappear from the mixture, which is designated as $\Omega_{n_1}^R$ and is given by:

$$\Omega_{n_1}^R = (N_1 + N_2 - n_1)! / [(N_1 - n_1)! N_2!] \quad (4)$$

$$= \Omega_{SM} [N_1(N_1 - 1) \dots (N_1 - n_1 + 1)] / [(N_1 + N_2)(N_1 + N_2 - 1) \dots (N_1 + N_2 - n_1 + 1)] \quad (5)$$

The value of $\Omega_{n_1}^R$ is equal to the number of configurations in which n_1 molecules of 1 are combined with the rest of the molecules $(N_1 - n_1)$ of 1 to make $(N_1 - n_1)$ big or long molecules.

CORRELATION BETWEEN THE COMBINATORY ENTROPY IN POLYMER AND IDEAL LIQUID SOLUTIONS

It is instructive to express the combinatory partition function in the Flory-Huggins theory by using the previous relation. The Flory-Huggins equation was originally expressed by¹:

$$\Omega_{F-H} = (N_2!)^{-1} [Z(Z-1)^{r-2}]^{N_2} [N_1^{(1-r)N_2}] \times r^{(N_2 r)} [(N_1/r)! (N_1/r - N_2)!]^r \quad (6)$$

where N_i is the number of solvent molecules ($i=1$) and polymer ($i=2$), r is the number of segments per polymer, Z is the coordination number and $N_t = N_1 + rN_2$ is the total number of lattices. Equation (6) reduces to:

$$\Omega_{F-H} = q_2^{N_2} \{N_t! / [N_1! (rN_2)!]\} \phi_2^{N_2(r-1)} \quad (7)$$

where

$$q_2 = Z(Z-1)^{r-2} r / e^{r-1} \quad (8)$$

and

$$\phi_2 = rN_2 / (N_1 + rN_2) \quad (9)$$

In the Flory-Huggins theory, Ω_{F-H} in equation (7) is divided into the intramolecular factor q_2 for polymer chain and the intermolecular factors, which are expressed by the ideal mixing term $N_t! / [N_1! (rN_2)!]$ for rN_2 disconnected and separated molecules of 2 from N_2 polymers with r segments per polymer and N_1 solvent molecules, and the probability term that $N_2(r-1)$ separated molecules are fixed at $N_2(r-1)$ positions in the lattice. In other words, equation (7) gives the number of configurations of ideal mixing of N_1 of 1 and rN_2 of 2 under the restriction that $(r-1)N_2$ separated molecules are fixed and only N_2 molecules of 2 and N_1 molecules of 1 are free to move in the lattice with $(r-1)N_2$ fixed points. If rN_2 of 2 are fixed, the configuration Ω_{rN_2} becomes:

$$\Omega_{rN_2} = q_2^{N_2} \phi_1^{-N_1} \quad (10)$$

and the partial entropy of solvent (1) $\Delta S_{M,1}$ defined by $\Delta S_{M,1} = k(\partial \Delta \ln \Omega / \partial N_1)_{T,P,N_2}$ and $\Delta \ln \Omega = \ln \Omega_M - \ln \Omega_{N_1=0} - \ln \Omega_{N_2=0}$ is given by:

$$\Delta S_{M,1}/k = -\ln \phi_1 - \phi_2 \quad (rN_2 \text{ fixed}) \quad (11)$$

On the other hand, $\Delta S_{M,1}$ for the Flory-Huggins theory is:

$$\Delta S_{M,1}/k = -\ln \phi_1 - \phi_2 + \phi_2/r \quad (12)$$

The term ϕ_2/r in equation (12) comes from the freedom with which N_2 separated molecules of 2 can move over the restricted lattice. A formulation of the combinatory entropy in polymer solutions for various theories has been done by the same procedure as mentioned above, which is given by:

$$\Omega_{\text{comb}} = q_2^{N_2} \Omega_{\text{ideal}} \phi_2^{(r-1)N_2} f(N_1, N_2, r, Z) \quad (13)$$

where f is a function of N_1 , N_2 , r and coordination number Z and is dependent on the model. It is derived that Ω_{rod} for a mixture of N_2 parallel oriented rigid-rod polymers with axis ratio r and N_1 solvent is equal to $\Omega_{\text{rod}} = (N_1 + N_2)! / (N_1! N_2!)$ and, using equation (4), is given by:

$$\Omega_{\text{rod}} = \Omega_{\text{ideal}} \{ [N_2 r (N_2 r - 1) \dots (N_2 + 1)] / [N_t (N_t - 1) \dots (N_1 + N_2 + 1)] \} \quad (14)$$

where

$$\Omega_{\text{ideal}} = N_t! / [N_1! (rN_2)!] \quad (15)$$

The Ω_{rod} corresponds to the number of configurations of ideal mixture under the restriction that $N_2(r-1)$ separated molecules of 2 are removed from the system or combined with the rest of 2 to make N_2 long rod molecules. The $\Delta S_{M,1}$ for the rod polymer solution is expressed using the volume fraction in equation (9) by:

$$\Delta S_{M,1}/k = -\ln \phi_1 + \ln [1 - (1 - r^{-1})\phi_2] \quad (16)$$

$$\approx -\ln \phi_1 - (1 - r^{-1})\phi_2 \quad \phi_2 \approx 0 \quad (17)$$

where equation (17) shows that $\Delta S_{M,1}$ for the rod mixture approaches that of the Flory-Huggins theory at the limit of $\phi_2 = 0$. The partial entropy of mixing of polymer in the Flory-Huggins theory is given by:

$$\Delta S_{M,2}/k = \phi_1(r-1) - \ln \phi_2 \quad (\text{F-H}) \quad (18)$$

and that for the rod polymer solution by:

$$\Delta S_{M,2}/k = -\ln \phi_2 + \ln [1 + \phi_1(r-1)] \quad (\text{Rod}) \quad (19)$$

$$\approx -\ln \phi_2 + \phi_1(r-1) \quad \phi_1(r-1) \approx 0 \quad (20)$$

Therefore $\Delta S_{M,2}$ for the rod polymer solution at the limit of $\phi_1 = 0$ is equal to that of the Flory-Huggins theory for a flexible polymer solution.

DERIVATION OF COMBINATORY ENTROPY IN SOLUTION OF SEMIFLEXIBLE AND ROD-LIKE POLYMERS IN SOLVENT

The configurational partition function Ω_{mix} for solutions of semiflexible and rod-like polymers in solvent which can predict cases of both flexible polymer solutions and parallel oriented rod solution is given by:

$$\Omega_{\text{mix}} = q_1^{N_1} q_2^{N_2} \Omega_{\text{ideal}} \phi_2^{N_2(r-1)-x} \times \{ [(N_2 + x)(N_2 + x - 1) \dots (N_2 + 1)] / [(N_1 + N_2 + x) \dots (N_1 + N_2 + 1)] \} \quad (21)$$

where q_i is the partition function for solvent (1) and polymer (2) in the pure state and x is a number

of molecule 2 characterizing the flexibility of the polymer chain, with $x=0$ for flexible polymer or polymer chain in the Flory–Huggins theory and $x=N_2(r-1)$ for the rigid-rod polymer. The physical meaning of factors in equation (21) is as follows. The quantity $\phi_2^{N_2(r-1)-x}$ is the probability that $N_2(r-1)-x$ positions are occupied by $N_2(r-1)-x$ molecules of 2, and the last term corresponds to the decrease in number of configurations due to removal of x molecules of 2 from the total (N_1+N_2+x) to make N_2 free long or big molecules with x/N_2 molecules combined per molecule. The situation is shown schematically in Figure 1 where N_2 long chains with average length x/N_2 are wandering in the lattice with $N_2(r-1)-x$ fixed points of 2. Equation (21) gives the maximum number of configurations for any value of x , although Ω_{Mix} decreases with an increase of x . It is essential to determine the function of x with respect to N_1 and N_2 . The determination of function x was made based on the results of equations (17) and (20), which means that the Flory–Huggins theory of $x=0$ approaches the rod polymer theory at the limit of $\phi_2=0$ and $\phi_1=0$. It is assumed in this work that x is expressed by:

$$x = \alpha \phi_1 r N_2 \quad (22)$$

where α is a parameter characterizing the polymer chain. The partial entropy is given using equations (21) and (22) by:

$$\begin{aligned} \Delta S_{M,1}/k = & -\ln \phi_1 - \phi_2(1-r^{-1}) + \alpha \phi_1 \phi_2 \\ & + \ln \left\{ \frac{(\phi_1 + \phi_2/r)}{[\phi_1 + \phi_2/r + \alpha \phi_1 \phi_2]} \right\} \\ & + \alpha \phi_2^2 \ln \left\{ \frac{(r^{-1} + \alpha \phi_1)}{[\phi_1 + \phi_2/r + \alpha \phi_1 \phi_2]} \right\} \end{aligned} \quad (23)$$

and for polymer:

$$\begin{aligned} \Delta S_{M,2}/rk = & \phi_1(1-r^{-1}) - (\ln \phi_2)/r - \alpha \phi_1^2 \\ & + r^{-1} \ln \left[\frac{(\phi_1 + \phi_2/r)(1 + \alpha r \phi_1)}{(\phi_1 + \phi_2/r + \alpha \phi_1 \phi_2)} \right] \\ & + \alpha \phi_1^2 \ln \left\{ \frac{(r^{-1} + \alpha \phi_1)}{[\phi_1 + \phi_2/r + \alpha \phi_1 \phi_2]} \right\} \end{aligned} \quad (24)$$

The first three terms on the right-hand side of equations (23) and (24) come from $\Omega_{\text{ideal}} \phi_2^{N_2(r-1)-x}$ in equation (21) and the rest from the last factor in equation (21). The calculation is given in more detail in the Appendix.

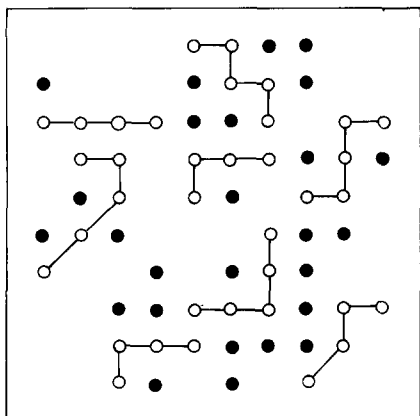


Figure 1 Schematic diagram of the configurations in polymer solution according to equation (21). The filled circles correspond to fixed points in the lattice and connected open circles are chains wandering in the lattice. An empty space is filled with solvent molecules

RESULTS AND DISCUSSION

The calculation for partial entropy of mixing for solvent and polymer has been carried out based on equations (23) and (24) for $r=100$ and various values of α , and is shown in Figures 2 and 3, where maximum and minimum points in $\Delta S_{M,1}/k$ versus ϕ_2 and $\Delta S_{M,2}/k$ versus ϕ_2 are observed over the concentration range of $\phi_2=0.0-0.2$ and $\alpha \geq 0.29$. This means that a phase separation occurs solely due to the entropy contribution to the chemical potential in the semiflexible polymer solution with $\alpha \geq 0.29$. It is important to point out that x in equation (22) expresses an excess number of solvent molecules surrounding the total polymer segments rN_2 from that in the random mixing model, because $x=0$ or $\alpha=0$ indicates the random mixing model. The quantity x is also related to the polymer flexibility. Figure 4 demonstrates schematically how $X=(x+x_0)/N_2$ decreases with increasing flexibility, where X means the number of solvent molecules surrounding the polymer and x_0 is that for N_2 polymers in the random mixing model. In the case of rod polymers, $X=r(Z-2)+2$, while in the flexible polymer many lattices of solvent surrounding the polymer

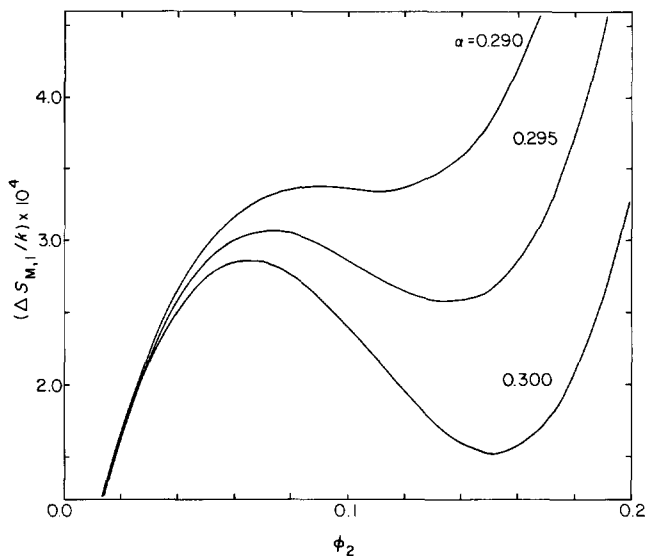


Figure 2 Plot of $\Delta S_{M,1}/k$ versus ϕ_2 calculated by equation (23) with $r=100$ for various values of α

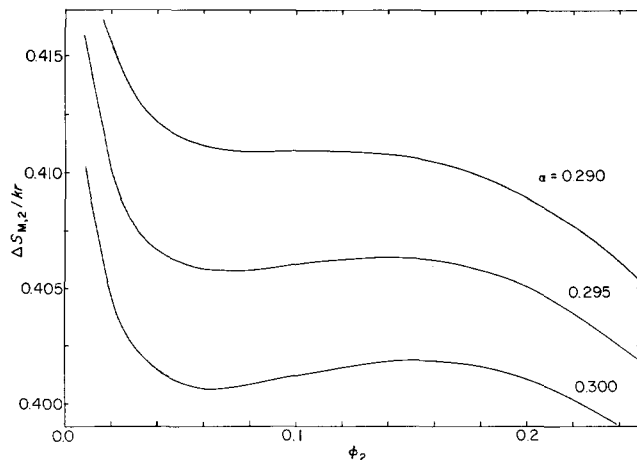


Figure 3 Plot of $\Delta S_{M,2}/kr$ versus ϕ_2 calculated by equation (24) with $r=100$ for various values of α

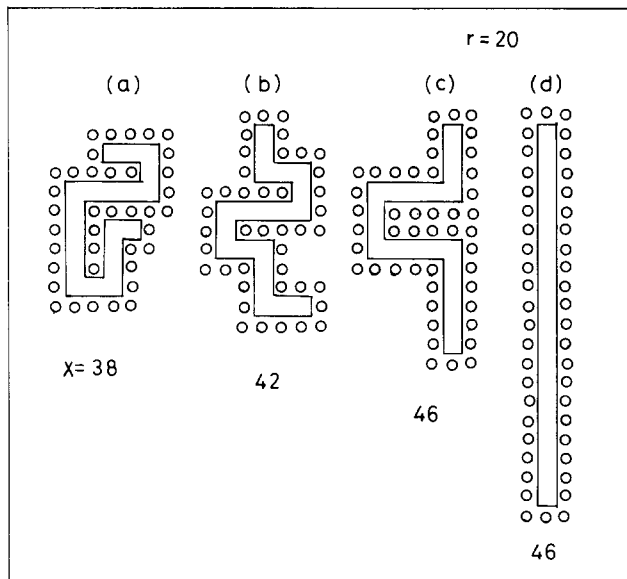


Figure 4 Schematic diagram of $X=(x+x_0)/N_2$ in various chains; (a) flexible chain; (b) and (c) semiflexible chain; (d) rigid-rod chain. The numbers represent the number of solvent molecules surrounding the chains in the plane of the diagram

segments are shared by two or more segments of polymer, and therefore X or x decreases considerably. It is of interest to examine a correlation between x and the enthalpy of mixing ΔH_M which is given in the Flory-Huggins theory by:

$$\Delta H_M = kT\chi_1^0\phi_1rN_2 \quad (25)$$

where χ_1^0 is the interaction parameter between polymer and solvent molecules. The functions of x in equation (22) and ΔH_m in equation (25) with respect to ϕ_1 and rN_2 are essentially the same. One can say that the enthalpic contribution is included in the expression of partial entropy of mixing in equations (23) and (24). This point is discussed in more detail. It is well known that a dissolution process of solvent into the polymer matrix is governed by the minimization process of the Gibbs free energy of mixing at constant temperature and pressure such that:

$$\Delta G_{M,\min} = \Delta H_M - T\Delta S_M \quad (26)$$

In mean field theories, such as the Flory-Huggins theory, ΔH_M and ΔS_M are evaluated by the random mixing model where the polymer segments are disconnected and distributed randomly to make a uniform concentration of polymer segments as an ideal solution. On the other hand, if there is a move towards a stable configuration in the dissolution process which accompanies the enthalpy change, the new configuration must have the most suitable ΔH_M to make ΔG_M a minimum. That means that ΔH_M and ΔS_M are cooperative. In other words, ΔS_M is expressed as a function of concentration and ΔH_M .

It is important to discuss theories of combinatory entropy in polymer solutions, which can predict the entropy in extreme cases of both flexible polymer and parallel oriented rigid-rod polymer. The partial entropy of mixing of solvent in the Guggenheim-Miller-Huggins theory is given by²⁻⁴:

$$\Delta S_{M,1}/k = -\ln\phi_1 + (Z/2)\ln[1 - 2\phi_2(r-1)/(Zr)] \quad (27)$$

and for $Z=2.0$ and $Z\rightarrow\infty$, respectively, by:

$$\Delta S_{M,1}/k = -\ln\phi_1 + \ln[1 - \phi_2(1-r^{-1})] \quad (28)$$

and

$$\Delta S_{M,1}/k = -\ln\phi_1 - \phi_2(1-r^{-1}) \quad (29)$$

It is obvious that equation (28) corresponds to the rigid-rod polymer equation (16) and equation (29) to the Flory-Huggins theory equation (12). The theory of rod-like particles is expressed by Flory as⁶:

$$\Omega_M = q_1^{N_1} q_2^{N_2} \left\{ \frac{(N_1 + yN_2)!}{[N_1!N_2!(N_1 + rN_2)^{(y-1)N_2}]} \right. \\ \left. \times (N_2! / \prod_k n_k!) \right\} \quad (30)$$

where $y = r \sin\psi$, ψ is the angle of inclination of a particle to the domain axis and n_k is the number of molecules whose directions occur within the elements⁶ of solid angle ω_k . Equation (30) reduces to:

$$\Omega_M = q_1^{N_1} q_2^{N_2} \left\{ \frac{(N_1 + yN_2)!}{[N_1!(yN_2)!]} \right. \\ \left. \times (yN_2/N_1)^{(y-1)N_2} [y^{N_2}/e^{(y-1)N_2}] (N_2! / \prod_k n_k!) \right\} \quad (31)$$

which is quite similar to the Flory-Huggins theory if $y=r$ and $(N_2! / \prod_k n_k!) \sim y^{N_2} = Z^{(r-1)N_2}$, except that yN_2/N_1 is used in equation (31) instead of $yN_2/(N_1 + yN_2)$ where $N_1 = N_1 + rN_2$. In the Flory rod particle theory, y is taken as a variable; $y=r$ gives the Flory-Huggins theory and $y=1$ gives that for parallel rigid-rod polymer or ideal mixtures of N_1 solvent molecules and N_2 polymers. However, the total number of lattices N_1 is unchanged in any value of y and therefore the probability that a submolecule occupies one lattice is given by yN_2/N_1 and not $yN_2/(N_1 + yN_2)$.

It is interesting to determine the Gibbs free energy of mixing ΔG_M in binary solutions of semiflexible or rod-like polymer in solvent:

$$\Delta G_M = kT \{ N_1 \ln\phi_1 + N_2 \ln\phi_2 + (N_1 + N_2) \\ \times \ln[(\phi_1 + \phi_2/r + \alpha\phi_1\phi_2)/(\phi_1 + \phi_2/r)] \\ - N_2 \ln(1 + \alpha r\phi_1) \\ + \alpha r N_2 \phi_1 \ln[(\phi_1 + \phi_2/r + \alpha\phi_1\phi_2)/(r^{-1} + \alpha\phi_1)] \\ + \chi_1^0(1 + \alpha)\phi_1 r N_2 \} \quad (32)$$

where the enthalpy of mixing is assumed to be expressed by $\Delta H_M = kT\chi_1^0(1 + \alpha)\phi_1 r N_2$. Then the chemical potential of solvent and polymer is given by:

$$(\mu_1 - \mu_1^0)/RT = \ln\phi_1 + \phi_2(1-r^{-1}) - \alpha\phi_1\phi_2 \\ - \ln\{(\phi_1 + \phi_2/r)/[\phi_1 + \phi_2/r + \alpha\phi_1\phi_2]\} \\ - \alpha\phi_2^2 \ln\{(r^{-1} + \alpha\phi_1)/ \\ [\phi_1 + \phi_2/r + \alpha\phi_1\phi_2]\} + \chi_1^0(1 + \alpha)\phi_2^2 \quad (33)$$

and

$$(\mu_2 - \mu_2^0)/rRT = -\phi_1(1-r^{-1}) + \ln\phi_2/r + \alpha\phi_1^2 \\ - r^{-1} \ln[(\phi_1 + \phi_2/r)(1 + \alpha r\phi_1)/ \\ (\phi_1 + \phi_2/r + \alpha\phi_1\phi_2)] \\ - \alpha\phi_1^2 \ln\{(r^{-1} + \alpha\phi_1)/ \\ [\phi_1 + \phi_2/r + \alpha\phi_1\phi_2]\} + \chi_1^0(1 + \alpha)\phi_1^2 \quad (34)$$

Equations (33) and (34) indicate that the entropy and enthalpy terms in the chemical potential are cooperative through the parameter α which depends on the flexibility of polymer chain and $\alpha=0$ corresponds to the Flory-Huggins theory. As mentioned before, in the Flory-Huggins theory the $(r-1)N_2$ points in the lattice $N_1 = N_1 + rN_2$ are fixed or occupied by the separated segments of 2 and N_2 separated segments of 2, and N_1 solvents move around the lattice with $(r-1)N_2$ fixed points; therefore rN_2 separated segments are not allowed to overlap each other and therefore they are self- and mutually avoiding ones. The essential difference between the Flory-Huggins theory and the present one is the introduction of

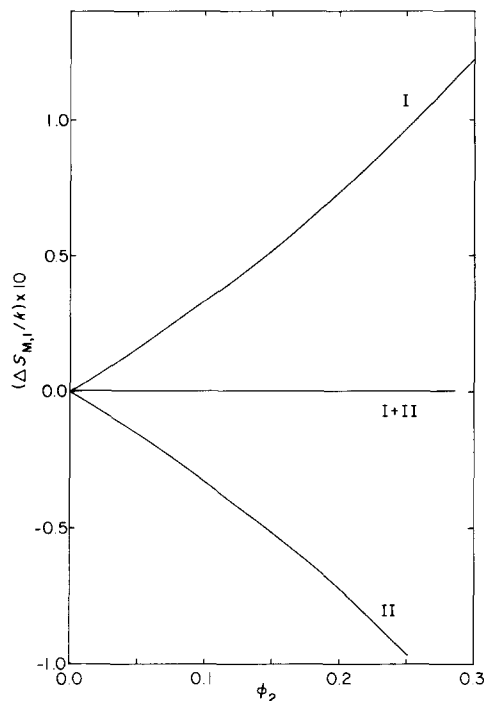


Figure 5 $\Delta S_{M,1}/k$ versus ϕ_2 plot for $\alpha=0.30$, where I corresponds to the first three terms on the right-hand side of equation (23) and II corresponds to the last two terms and therefore $\Delta S_{M,1}/k=I+II$

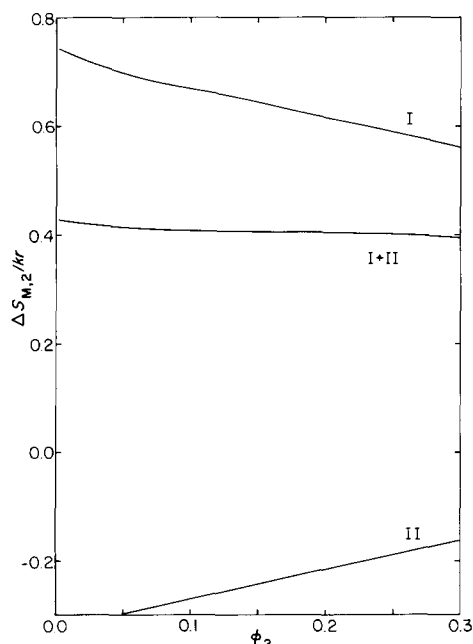


Figure 6 $\Delta S_{M,2}/kr$ versus ϕ_2 plot for $\alpha=0.30$, where I corresponds to the first three terms on the right-hand side of equation (24) and II corresponds to the last two terms and therefore $\Delta S_{M,2}/kr=I+II$

parameter x , reflecting the contribution of local motion of polymer chain and semiflexibility or rod-like character of local chain to the combinatory entropy, which are neglected in the Flory–Huggins theory. The parameter x also gives a measure of the number of contacts between the polymer segments and solvent in excess of that in the random mixing model.

The contributions to the partial entropy of mixing in the semiflexible polymer solution are examined by dividing $\Delta S_{M,i}$ into two factors: factor I related to the Ω_{ideal} and the probability term $\phi_2^{(r-1)N_2-x}$ in equation (21); and factor II related to the decrease in the number of configuration due to the formation of long chains. This

is shown in *Figures 5 and 6* where I is positive and II is negative. In $\Delta S_{M,1}$ I increases and II decreases with increasing ϕ_2 , and $\Delta S_{M,1}$ itself is small due to cancellation of the two terms. However, in the case of $\Delta S_{M,2}$, I decreases and II increases with increasing ϕ_2 , and $\Delta S_{M,2}$ decreases slightly with ϕ_2 and is dominated by I. It is shown that the phase separation behaviour in *Figures 2 and 3* is attributed mainly to factor II, related to the formation of long chains in solution. This is consistent with the conclusions reached by Onsager¹⁵ and Ishihara¹⁶, that solutions of sufficiently asymmetric long rods show phase separation.

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APPENDIX

The number of configurations for equation (21) is expressed by:

$$\Omega_{\text{Mix}} = q_1^{N_1} q_2^{N_2} \Omega_{\text{ideal}} \phi_2^{N_2(r-1)-x} (N_1 + N_2)! (N_2 + x)! / [(N_1 + N_2 + x)! N_2!] \quad (\text{A1})$$

The entropy of mixing ΔS_{Mix} for equation (A1) is:

$$\begin{aligned} \Delta S_{\text{Mix}}/k = & -N_1 \ln \phi_1 - N_2 \ln \phi_2 \\ & - (N_1 + N_2) \ln [(N_1 + N_2 + x)/(N_1 + N_2)] \\ & - x \ln \{ [(N_1 + N_2 + x)/(N_2 + x)] \phi_2 \} \\ & + N_2 \ln [(N_2 + x)/N_2] \end{aligned} \quad (\text{A2})$$

The partial entropy of mixing is calculated from equation (A2); that for solvent $\Delta S_{M,1}$ is:

$$\begin{aligned} \Delta S_{M,1}/k = & -\ln \phi_1 - \phi_2(1-r^{-1}) + x/N_1 \\ & + \ln [(N_1 + N_2)/(N_1 + N_2 + x)] + (dx/dN_1) \\ & \times \{ -\ln \phi_2 + \ln [(N_2 + x)/(N_1 + N_2 + x)] \} \end{aligned} \quad (\text{A3})$$

and that for polymer:

$$\begin{aligned} \Delta S_{M,2}/k = & r\phi_1 - \ln \phi_2 - \phi_1 - x\phi_1/N_2 \\ & + \ln [(N_1 + N_2)(N_2 + x)/(N_1 + N_2 + x)N_2] \\ & + (dx/dN_2) \{ \ln [(N_2 + x)/(N_1 + N_2 + x)] - \ln \phi_2 \} \end{aligned} \quad (\text{A4})$$

Equations (23) and (24) are derived from equations (A3) and (A4) with equation (22).