

Correlation between the combinatorial entropy of polymer and ideal liquid solutions: 2. Ternary polymer–polymer–solvent and binary polymer–polymer systems

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A semiempirical equation of combinatorial entropy in ternary solutions containing two semiflexible polymers and flexible and semiflexible polymers in solvent has been derived, based on a previous equation for a binary polymer solution. The partial entropy of mixing for solvent, $\Delta S_{M,0}$, in the ternary system polymer (1)–polymer (2)–solvent (0) is expressed by:

$$\Delta S_{M,0}/k = -\ln \phi_0 + a - 1 + \ln[a/(a+b)] + b + k_1 \phi_1^2 \ln\{[r_1^{-1} + k_1(1-\phi_1)]/(a+b)\} \\ + k_2 \phi_2^2 \ln\{[r_2^{-1} + k_2(1-\phi_2)]/(a+b)\}$$

where $a = \phi_0 + (\phi_1/r_1) + (\phi_2/r_2)$, $b = k_1 \phi_1(1-\phi_1) + k_2 \phi_2(1-\phi_2)$, ϕ_i is the volume fraction of component i , and k_i is a constant characterizing the flexibility of polymer, for example $k_i = 0$ for a flexible polymer and $k_i > 0$ for a semiflexible polymer. Values of partial entropy of mixing for polymers, $\Delta S_{M,i}$, are evaluated in the ternary solution of two polymers with different flexibilities in solvent. The combinatorial entropy in a binary polymer–polymer system is also discussed.

(Keywords: combinatorial entropy; ternary solution; semiflexible polymer)

INTRODUCTION

The combinatorial entropy in ternary systems containing two polymers is very important in discussing thermodynamic properties of solutions such as phase equilibria. The Flory–Scott lattice theory^{1,2} is the most simple and useful theory for ternary systems containing two flexible polymers in solvent, where random mixing is assumed. Rubio and Renuncio³ have derived an approximate expression for the combinatorial entropy in a binary polymer–solvent system based on the concept of local composition in non-random mixing. The effects of orientation of polymer on the combinatorial term are discussed by DiMarzio⁴. Huggins⁵ has pointed out that the orientational randomness of segments of chain molecule and its concentration dependence also affect the combinatorial entropy. Silberberg⁶ has obtained the Flory–Huggins equation¹ by a different approach, and its extension to polymer mixtures has been discussed by Koningsveld and Stepto⁷. In a previous work⁸ a new parameter was introduced, reflecting the flexibility of polymer chain and predicting phase separation behaviour in a binary solution of semiflexible or rod-like polymer in solvent solely due to the combinatorial entropy term, which is consistent with the results of Onsager⁹ and Ishihara¹⁰.

This work presents an extension of the previous work to a ternary system containing two polymers with

different flexibilities, to find the basic properties of the ternary system and also a binary polymer–polymer system.

CORRELATION BETWEEN THE COMBINATORIAL ENTROPY IN TERNARY POLYMER SOLUTION AND TERNARY SIMPLE LIQUID SOLUTION

The number of configurations for a ternary simple liquid solution, Ω_{SM} , with molecules of nearly equal size or an ideal liquid solution is given by:

$$\Omega_{SM} = (N_0 + N_1 + N_2)! / (N_0! N_1! N_2!) \quad (1)$$

where N_i is the number of molecules of component i . On the other hand, the number of configurations in the ternary system containing N_1 molecules of polymer 1 with r_1 segments per polymer, N_2 molecules of polymer 2 with r_2 segments and N_0 molecules of solvent is given by the Scott theory² and is expressed in a more simple form by⁸:

$$\Omega_{P_1-P_2-S} = C \Omega_{ideal} \phi_1^{(r_1-1)N_1} \phi_2^{(r_2-1)N_2} \quad (2)$$

where C is the intramolecular factor for polymers 1 and 2 and does not affect the combinatorial entropy of mixing, and Ω_{ideal} is an ideal mixing term for the dismemberment of polymers to $r_1 N_1$ and $r_2 N_2$ segments, defined by:

$$\Omega_{ideal} = (N_0 + r_1 N_1 + r_2 N_2)! / [N_0! (r_1 N_1)! (r_2 N_2)!] \quad (3)$$

and ϕ_i ($i = 1, 2$) is the volume fraction of i :

$$\phi_i = r_i N_i / N_t \quad (4)$$

where $N_t = N_0 + r_1 N_1 + r_2 N_2$. The procedure to obtain equation (2) is the same as that in the binary solution (equation (7) in ref. 8). The quantities $\phi_i^{(r_i-1)N_i}$ in equation (2) mean a probability that the $(r_i-1)N_i$ segments are fixed at certain $(r_i-1)N_i$ different positions in the lattice. Equation (2) expresses the number of configurations in an ideal ternary system with N_0 , $r_1 N_1$ and $r_2 N_2$ different molecules under the condition that $(r_1-1)N_1$ of 1 and $(r_2-1)N_2$ of 2 are fixed in different positions in the lattice⁸. If the polymers in the ternary system are N_1 rods with an axis ratio r_1 for polymer 1 and N_2 rods with the ratio r_2 for polymer 2, the number of configurations for the ternary rod system is equal to that of an ideal mixture of N_0 , N_1 and N_2 different molecules and is given using the same procedure as equation (14) in ref. 8:

$$\Omega_{\text{Rod}} = (N_0 + N_1 + N_2)! / (N_0! N_1! N_2!) \quad (5)$$

$$= \Omega_{\text{ideal}} \{ r_2 N_2 (r_2 N_2 - 1) \cdots (N_2 + 1) r_1 N_1 (r_1 N_1 - 1) \cdots \cdot (N_1 + 1) / [N_1 (N_1 - 1) \cdots (N_1 + N_2 + N_0 + 1)] \} \quad (6)$$

Equation (6) is derived by using Ω_{ideal} in equation (3).

It is found from equations (5) and (6) that Ω_{Rod} corresponds to Ω_{ideal} under a condition that $(r_i-1)N_i$ of molecule i are removed from the lattice or combined with the rest of N_i molecules to make N_i long or big molecules⁸.

DERIVATION OF THE COMBINATORY ENTROPY IN THE POLYMER-POLYMER-SOLVENT SYSTEM

It is important to discuss a correlation between the entropy of mixing in ternary systems with two types of rods of different axial ratios and with two flexible polymers of different molecular weights in deriving the combinatory entropy in a ternary system. The partial entropy in the ternary rod solution is given from equation (5) by:

$$\Delta S_{M,0}/k = -\ln \phi_0 + \ln [1 - \phi_1(1 - r_1^{-1}) - \phi_2(1 - r_2^{-1})] \quad (7)$$

$$\approx -\ln \phi_0 + a - 1 \quad \phi_1 \rightarrow 0, \phi_2 \rightarrow 0 \quad (8)$$

$$\Delta S_{M,1}/r_1 k = -r_1^{-1} \ln \phi_1 + r_1^{-1} \ln (r_1 \phi_0 + \phi_1 + r_1 r_2^{-1} \phi_2) \quad (9)$$

$$\approx -r_1^{-1} \ln \phi_1 + a - r_1^{-1} \quad \phi_0 \rightarrow 0, \phi_2 \rightarrow 0 \quad (10)$$

$$\Delta S_{M,2}/r_2 k = -r_2^{-1} \ln \phi_2 + r_2^{-1} \ln (r_2 \phi_0 + r_1^{-1} r_2 \phi_1 + \phi_2) \quad (11)$$

$$\approx -r_2^{-1} \ln \phi_2 + a - r_2^{-1} \quad \phi_0 \rightarrow 0, \phi_1 \rightarrow 0 \quad (12)$$

On the other hand, the partial entropy of mixing in the ternary system with two flexible polymers is derived by Scott² and is given by:

$$\Delta S_{M,0}/k = -\ln \phi_0 + a - 1 \quad (13)$$

$$\Delta S_{M,1}/r_1 k = -r_1^{-1} \ln \phi_1 + a - r_1^{-1} \quad (14)$$

$$\Delta S_{M,2}/r_2 k = -r_2^{-1} \ln \phi_2 + a - r_2^{-1} \quad (15)$$

where quantity a is defined by:

$$a = \phi_0 + \phi_1/r_1 + \phi_2/r_2 \quad (16)$$

It is obvious that $\Delta S_{M,i}/r_i k$ in the rod 1-rod 2-solvent system at the limit of $\phi_j \rightarrow 0$ and $\phi_k \rightarrow 0$, $i \neq j \neq k$, is equal to that for the system with two flexible polymers-solvent or that in the Flory-Scott theory.

It is assumed in this work that the number of configurations for a ternary system containing two polymers with different flexibilities, such as a rod-like polymer and a flexible polymer, in solvent is expressed based on equations (2) and (6) by

$$\Omega = \Omega_{\text{ideal}} \phi_2^{(r_2-1)N_2-x} \phi_1^{(r_1-1)N_2-y} \times \{ (N_0 + N_1 + N_2)! (N_2 + x)! (N_1 + y)! / [(N_0 + N_1 + N_2 + x + y)! N_2! N_1!] \} \quad (17)$$

The partial entropy of mixing calculated by equation (17) is given by:

$$\Delta S_{M,0} = -\ln \phi_0 + a - 1 + \ln [a/(a+b)] + b + k_1 \phi_1^2 \ln \{ [r_1^{-1} + k_1(1 - \phi_1)] / (a+b) \} + k_2 \phi_2^2 \ln \{ [r_2^{-1} + k_2(1 - \phi_2)] / (a+b) \} \quad (18)$$

$$\Delta S_{M,1}/r_1 k = -r_1^{-1} \ln \phi_1 + a - r_1^{-1} + r_1^{-1} \ln \{ a[1 + k_1 r_1(1 - \phi_1)] / (a+b) \} + b - k_1(1 - \phi_1) + k_1(1 - \phi_1)^2 \times \ln \{ [r_1^{-1} + k_1(1 - \phi_1)] / (a+b) \} + k_2 \phi_2^2 \ln \{ [r_2^{-1} + k_2(1 - \phi_2)] / (a+b) \} \quad (19)$$

$$\Delta S_{M,2}/r_2 k = -r_2^{-1} \ln \phi_2 + a - r_2^{-1} + r_2^{-1} \ln \{ a[1 + k_2 r_2(1 - \phi_2)] / (a+b) \} + b - k_2(1 - \phi_2) + k_2(1 - \phi_2)^2 \times \ln \{ [r_2^{-1} + k_2(1 - \phi_2)] / (a+b) \} + k_1 \phi_1^2 \ln \{ [r_1^{-1} + k_1(1 - \phi_1)] / (a+b) \} \quad (20)$$

where $b = k_1 \phi_1(1 - \phi_1) + k_2 \phi_2(1 - \phi_2)$ and it is assumed that x and y are given by:

$$x = k_2 r_2 N_2 (1 - \phi_2) \quad (21)$$

and

$$y = k_1 r_1 N_1 (1 - \phi_1) \quad (22)$$

where k_1 and k_2 are constants. Parameters x and y in equations (21) and (22) are determined as follows. It is demonstrated in the comparisons between equations (8), (10) and (12) and equations (13), (14) and (15) that the partial entropy of mixing in the ternary rod polymer solution approaches that for the ternary flexible polymer solutions corresponding to $x=0$ and $y=0$ at infinite dilution. One of the simple expressions satisfying a condition that both x and y approach zero in each of three cases — (i) $\phi_1 \rightarrow 0$ and $\phi_2 \rightarrow 0$; (ii) $\phi_0 \rightarrow 0$ and $\phi_1 \rightarrow 0$; and (iii) $\phi_0 \rightarrow 0$ and $\phi_2 \rightarrow 0$ — is given by equations (21) and (22). Equation (17) and parameters x and y in equations (21) and (22) in the ternary system are extensions of equations (21) and (22) in the binary system of ref. 8.

RESULTS

Calculation of $\Delta S_{M,i}/r_i k$ for various values of k_1 and k_2 has been carried out by using equations (18), (19) and

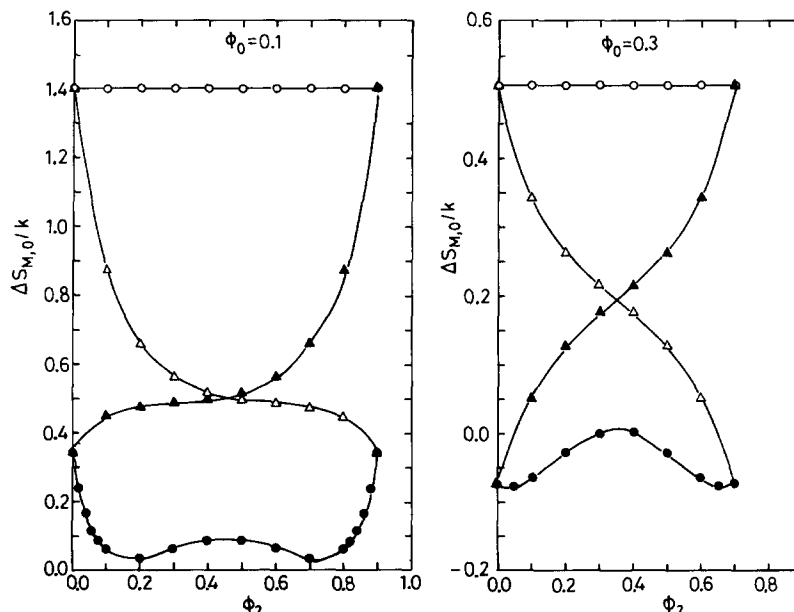


Figure 1 Plot of $\Delta S_{M,0}/k$ versus ϕ_2 in the ternary solution of polymer 1 with segments $r_1=1000$ and polymer 2 with $r_2=1000$ and constant concentration of solvent, $\phi_0=0.1$ and 0.3 , calculated by equation (18) for various polymer pairs: \circ , flexible polymer 1 with $k_1=0$ and flexible polymer 2 with $k_2=0$; \triangle , polymer pair of flexible polymer $k_1=0$ and semiflexible polymer $k_2=1$; \blacktriangle , polymers with $k_1=1$ and $k_2=0$; \bullet , polymers with $k_1=k_2=1$

(20) with $r_1=r_2=1000$; the results are plotted in Figures 1 and 2. The $\Delta S_{M,0}$ for the flexible polymer pair is independent of ϕ_2 due to $r_1=r_2=1000$ in this case. The $\Delta S_{M,0}$ for the ternary solution of flexible and semiflexible polymers in solvent, such as $k_1=1$ and $k_2=0$ or $k_1=0$ and $k_2=1$, increases with increasing concentration of flexible polymer in the solution; however, in the ternary solution of two semiflexible polymers in solvent, such as $k_1=k_2=1$, the $\Delta S_{M,0}$ has a maximum point in solutions with concentration $\phi_0>0.3$ and two minimum and one maximum points for $\phi_0<0.1$. In the cases of $\Delta S_{M,i}/r_i k$ for polymers, the value of $\Delta S_{M,1}/r_1 k$ is essentially the same as $\Delta S_{M,2}/r_2 k$, as expected from equation (17) if the subscripts 1 and 2 are exchanged.

There are four types of $\Delta S_{M,i}$, which are characterized by the entropy change when: (i) a flexible polymer is dissolved in the ternary solution of two flexible polymers in solvent ($k_1=k_2=0$); (ii) a flexible polymer is dissolved in the ternary solution of semiflexible and flexible polymers in solvent ($k_1=1$ and $k_2=0$ or $k_1=0$ and $k_2=1$); (iii) a semiflexible polymer is dissolved in the ternary solution of (ii); and (iv) a semiflexible polymer is dissolved in the ternary solution of two semiflexible polymers in solvent such as $k_1=k_2=1$. It is shown in Figure 2 that values of $\Delta S_{M,1}/r_1 k$ for the system $k_1=k_2=0$ increase linearly with increasing ϕ_0 at constant ϕ_1 . Values of $\Delta S_{M,1}/r_1 k$ for $k_1=0$ and $k_2=1$ increase with increasing ϕ_0 except for the low concentration region where a minimum point is observed at $\phi_1<0.3$. However, values of $\Delta S_{M,1}/r_1 k$ for $k_1=1$ and $k_2=0$ and for $k_1=k_2=1$ indicate quite different values and are dependent on ϕ_0 at the lower concentration range but approach a value corresponding to that of the binary solution of semiflexible polymer ($k_1=1$) in solvent at higher values of ϕ_0 . At very high concentrations of polymer 1, such as $\phi_1=0.9$, $\Delta S_{M,1}/r_1 k$ is almost constant in the systems $k_1=0$ and $k_2=1$ or $k_1=k_2=1$, while for $k_1=k_2=0$ or $k_1=1$ and $k_2=0$, $\Delta S_{M,1}/r_1 k$ increases with increasing ϕ_0 and the values approach each other.

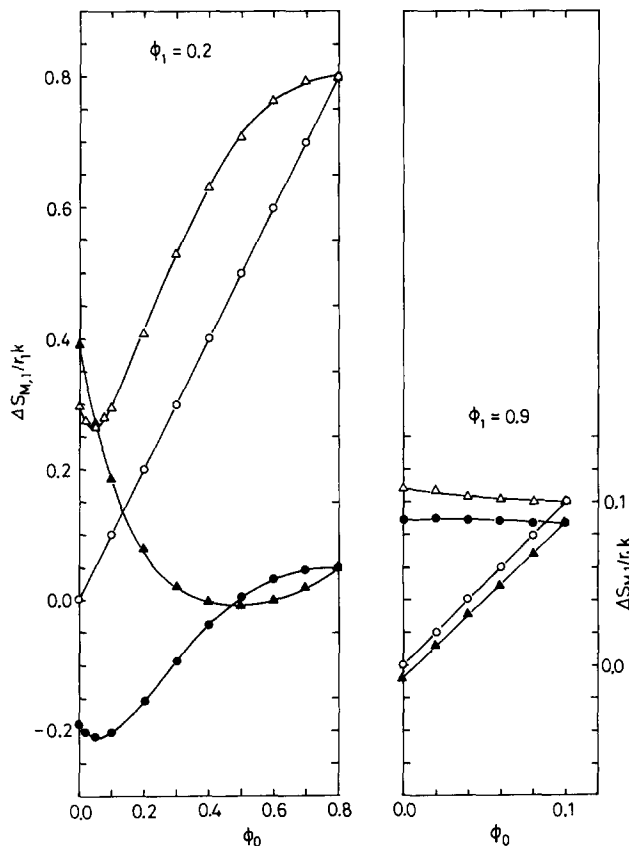


Figure 2 Plot of $\Delta S_{M,1}/r_1 k$ versus ϕ_0 in the ternary solution of polymers with the same segments as in Figure 1 and constant concentration of polymer 1, $\phi_1=0.2$ and 0.9 , calculated by equation (19) for various polymer pairs: symbols as in Figure 1

DISCUSSION

It is interesting to discuss the physical meaning of quantities x and y in equations (17), (21) and (22). The parameters x and y express numbers of segments for

polymer 2 and 1, respectively, that exhibit rod-like properties in all the segments of semiflexible polymer chain; $x = y = 0$ therefore corresponds to flexible polymers with no rod-like character and the largest values of $x = (r_2 - 1)N_2$ for polymer 2 and $y = (r_1 - 1)N_1$ for polymer 1 correspond to the rod polymer with an axial ratio of r_2 for polymer 2 and r_1 for polymer 1. There is a basic relation for the combinatory entropy in the ternary solution that when the solution approaches the pure state, such as $\phi_0 \rightarrow 0$ and $\phi_1 \rightarrow 0$, the number of configurations approaches that of the Flory-Huggins theory and then approaches configurations of the pure state irrespective of the properties of pure components such as flexibility, as is demonstrated in equations (7) to (15). In other words, values of x and y approach zero when ϕ_i and ϕ_j ($i \neq j$) approach zero. The expressions of x and y in equations (21) and (22) satisfy the above conditions and also relate to the amount of solvent and segments of polymer j around polymer i , which increases with increasing rod-like properties of polymer chain i . A detailed discussion is given in ref. 8.

It is also interesting to discuss the combinatory entropy in a binary polymer 1-polymer 2 system with various flexibilities of polymers. The partial entropy of mixing for polymers in the binary solution is calculated from that in the ternary system polymer-polymer-solvent in equation (19) with $\phi_0 \rightarrow 0$:

$$\begin{aligned} \Delta S_{M,1}/r_1 k &= (-r_1^{-1} \ln \phi_1 + a^* - r_1^{-1}) \\ &+ \{r_1^{-1} \ln[a^*(1 + k_1 r_1 \phi_2)/(a^* + c)] + c \\ &- k_1 \phi_2\} + \{k_1 \phi_2^2 \ln[(r_1^{-1} + k_1 \phi_2)/(a^* + c)] \\ &+ k_2 \phi_2^2 \ln[(r_2^{-1} + k_2 \phi_1)/(a^* + c)]\} \quad (23) \end{aligned}$$

where $a^* = \phi_1/r_1 + \phi_2/r_2$ and $c = (k_1 + k_2)\phi_1\phi_2$. Two types of behaviours are observed in Figures 3 to 5, which show plots of $\Delta S_{M,1}/r_1 k$ against ϕ_2 . The first type is observed in the systems with $k_1 = k_2 = 0$ and with $k_1 = 1$ and $k_2 = 0$ which correspond to cases where a flexible polymer and semiflexible polymer are dissolved in a matrix of two flexible polymers and a matrix of a semiflexible and flexible polymer pair, respectively, and is characterized by the fact that there is no maximum point in the plot of Figure 3. The second type is observed in the systems of $k_1 = 0$ and $k_2 = 1$ and of $k_1 = k_2 = 1$ where a flexible and semiflexible polymer are dissolved in a matrix of a flexible and semiflexible polymer pair and two semiflexible polymers, respectively, and is characterized by a maximum and a minimum point in the plots of Figures 4 and 5.

A basic explanation of these behaviours is that the number of configurations in a binary solution of two flexible polymers is much larger than that in semiflexible polymers with the same molecular weights. There is therefore a possibility of a greater increase in the number of configurations in the semiflexible polymers than in the flexible polymers or there is a possibility of a greater decrease in the number of configurations in the flexible polymers than in the semiflexible polymers when a polymer chain is introduced into these binary polymer systems. In the case of a matrix containing flexible and semiflexible polymers, the tendency for variation in the number of configurations in the solution rich in flexible polymer is different from that in the solution rich in semiflexible polymer. In other words, when a polymer chain with a certain flexibility is introduced into the

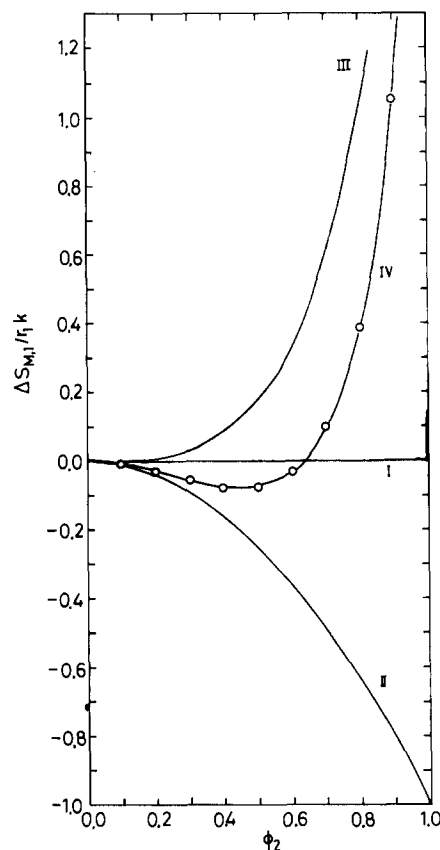


Figure 3 Plot of $\Delta S_{M,1}/r_1 k$ versus ϕ_2 in the binary solution of polymer 1 with $r_1 = 1000$ and polymer 2 with $r_2 = 1000$ calculated by equation (23) for the semiflexible polymer $k_1 = 1$ and flexible polymer $k_2 = 0$ pair; the lines I, II and III correspond to the first, second and third terms in equation (23) and $\Delta S_{M,1}/r_1 k = IV = I + II + III$. The values of I correspond to $\Delta S_{M,1}/r_1 k$ for a binary solution of two flexible polymers or the Flory-Huggins theory for polymer blends, and increase rapidly with the approach of $\phi_2 = 1.0$ or $\phi_1 = 0$

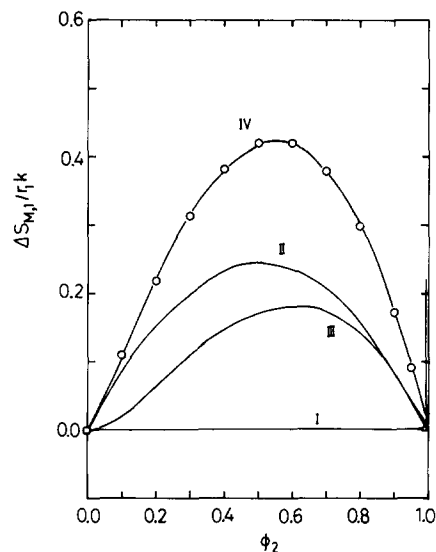


Figure 4 Plots of $\Delta S_{M,1}/r_1 k$ versus ϕ_2 in the binary solution of flexible polymer $k_1 = 0$, $r_1 = 1000$ and semiflexible polymer $k_2 = 1$, $r_2 = 1000$; description of lines is the same as in Figure 3, where $\Delta S_{M,1}/r_1 k$ increases with the approach of $\phi_2 = 1.0$ due to the I term

matrix of a binary polymer system, an entropy change due to (i) an increase of free space shared by molecules in the system and (ii) the formation of ordered or disordered regions may occur over the entire system; the change

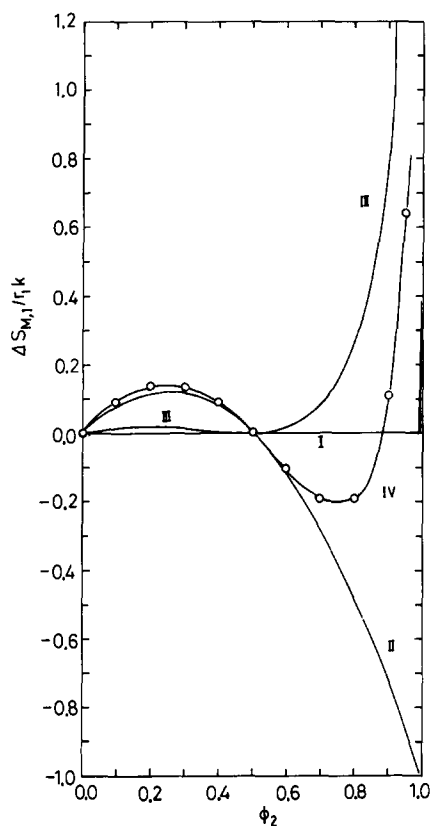


Figure 5 Plots of $\Delta S_{M,1}/r_1k$ versus ϕ_2 in the binary solution of semiflexible polymer $k_1=1$, $r_1=1000$ and semiflexible polymer $k_2=1$, $r_2=1000$; description of lines is the same as in Figure 3

depends strongly not only on the concentration but also on the packing state of the polymer chains in the matrix.

An analysis of $\Delta S_{M,1}/r_1k$ in the binary polymer system has been made based on equation (23) and is shown in

Figures 3 to 5, where $\Delta S_{M,1}/r_1k$ consists of three terms derived from: (i) the flexible polymer system in the Flory-Huggins theory; (ii) the semiflexibility of polymer chains through x and y ; (iii) variation of x and y with respect to N_1 or dx/dN_1 and dy/dN_1 . The contribution of (i) is very small and (ii) is negative except in the system with $k_1=0$ and $k_2=1$ and $k_1=k_2=1$ over low concentration of ϕ_2 , while that of (iii) is positive. The negative contribution in $\Delta S_{M,1}/r_1k$ indicates a formation of ordered regions in the system and the positive contribution indicates an increase of disordered regions over the entire system, although the individual changes of the entropy for polymers are not known in Figures 3-5. The miscibility of a binary polymer system with various flexibilities may be discussed fully if the enthalpy of mixing in the system is evaluated.

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