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Combinatory entropy in complex polymer solutions

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Abstract

The combinatory entropy S_{comb} in complex polymer solution has been calculated based on a lattice model. An inter-molecular part of S_{comb} in solution of polymer consisting of rod and flexible parts $S_{\text{inter,r–f}}$ is given by $S_{\text{inter,r–f}}/R = S_{\text{inter,F–H}}/R + (1 - mc\phi_2/r)\ln(1 - mc\phi_2/r) - \phi_2(1 - mc/r)\ln(1 - mc/r)$ where $S_{\text{inter,F–H}}/R = -(1 - \phi_2)\ln(1 - \phi_2) - (\phi_2/r)\ln\phi_2$ is that in the Flory–Huggins theory,ϕ_2 is the volume fraction of the polymer and m the number of repeated units in a polymer chain. The repeated unit consists of a rod part and a flexible part and c and a are the number of segments in the rod part and flexible part, respectively, and the total number of segments per polymer chain is r. The $S_{\text{inter,r–f}}$ in this work is essentially the same as that in the solution of rod-like particles derived by Flory except for the last term in $S_{\text{inter,r–f}}$. The combinatory entropy in the solution of star polymer $S_{\text{inter,star}}$ calculated in this work is given by $S_{\text{inter,star}}/R = S_{\text{inter,F–H}}/R - \phi_2\{(n-1)/r\}\ln\phi_2$ where n is the number of branches per star polymer. The critical concentration $\phi_{2,c}$ in solution of the star polymer calculated in this work is given by $\phi_{2,c} = 1/[1 + (r/n)^{1/2}]$ which is larger than that in solution of linear polymer of the same molecular weight of the polymer. An effect of chain stiffness on the critical concentration is also discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Combinatory entropy; Complex polymer solution; Flory–Huggins theory

1. Introduction

It is well known that the combinatory entropy in solution of flexible polymer in solvent is given by the Flory–Huggins theory [1]. After the basic theory, many theories have been derived. Guggenheim [2], Miller [3], Huggins [4] and Kurata [5] have derived the combinatory entropy of polymer solution by using higher order approximations for chain connectivity than that in the original Flory–Huggins theory. These modified theories give essentially the same expression of combinatory entropy in polymer solution and approach to that in the Flory–Huggins theory at the limit of $z \to \infty$ where z is the coordination number of the lattice. In 1956, the combinatory entropy in solution of semi-flexible chain molecules and of rod-like particles has been derived based on the lattice model [6,7] by Flory and the theories have been applied to solutions of liquid crystalline polymers [8–14] and semi-rigid macromolecules such as polypeptide [15–18] extensively.

In a previous work [19] we have derived the combinatory entropy S_{comb} in polymer solutions where polymer chains consist of rod and flexible parts. The S_{comb} in solutions of polymer with rod and flexible parts has been found to give the same function as those derived by Guggenheim [2], Miller [3], Huggins [4] and Kurata [5]. We have also calculated the S_{comb} in a solvated polymer solution where a strong interaction between polymer segments and solvent molecules occurs. The S_{comb} in the solvated polymer solution [19] gives a good prediction to the experimental data of negative partial molar entropy of dilution over low polymer concentration [20].

In this work we have proposed a general and simple method for the calculation of combinatory entropy in a complex polymer solution such as star polymers. We have also examined whether it is possible to reproduce the same S_{comb} as the Flory rod theory by using our method. The critical concentration of complex polymer solution calculated in this work has been examined through the experimental data.

The general method for calculation of combinatory entropy in complex polymer solution is given in the following sections.

1.1. Inter-molecular contribution in combinatory entropy

We use the lattice model in the calculation of combinatory entropy in polymer solution. The N_2 polymers with r segments per polymer and N_1 solvent molecules are inserted sequentially to the lattice sites where the number of total lattice sites is $N = N_1 + rN_2$. If all polymer chains are disconnected into rN_2 monomers, the number of configurations for

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the solution is given by

$$\Omega_0 = N!/\{N_1!(rN_2)!\} \tag{1}$$

$$= \phi_1^{-N_1}\phi_2^{-rN_2} \tag{2}$$

where the solution consists of rN_2 molecules of monomer (species 2), N_1 molecules of solvent (species 1) and the volume fraction of monomers is given by $\phi_2 = rN_2/(N_1 + rN_2) = 1 - \phi_1$. Some configurations in Eq. (1) satisfy a condition of the polymer solution that r segments or monomers are connected. Then the number of configurations for an inter-molecular part $\Omega_{\text{inter,PS}}$ in polymer solution is given by

$$\Omega_{\text{inter,PS}} = \Omega_0 P \tag{3}$$

where P is a probability to pick up the configurations relevant to the polymer solution from the extremely large number of configurations of Ω_0.

In the original Flory–Huggins theory $P_{\text{F–H}}$ is given by

$$P_{\text{inter,F–H}} = \phi_2^{(r-1)N_2} \tag{4}$$

and then

$$\Omega_{\text{inter,F–H}} = \phi_1^{-N_1}\phi_2^{-N_2} \tag{5}$$

The physical meaning of Eq. (4) is as follows. When a polymer chain is formed in the lattice, a first monomer is connected to a head one and the second one to the first one and then the final $(r-1)$th monomer is connected to the $(r-2)$th one. The head segment of the polymer chain can move around in the entire lattice space freely, while the movements of $(r-1)$ segments is restricted by the bond between the segments. The $P_{\text{inter,F–H}} = \phi_2^{(r-1)N_2}$ is a probability to fix the $N_2(\mathrm{r}-1)$ segments simultaneously to make N_2 polymer chains in solution.

If P is given by

$$P_{\text{inter,Rod}} = (rN_2/N)\{(rN_2-1)/(N-1)\} \cdots [rN_2 - \{(r-1)N_2 - 1\}]/[N - \{(r-1)N_2 - 1\}] \tag{6}$$

an equation derived using Eqs. (3) and (6) is given by

$$\Omega_{\text{inter,Rod}} = \Omega_0 P_{\text{inter,Rod}} = (N_1 + N_2)!/(N_1!N_2!) \tag{7}$$

This is a combinatory entropy of the solution of the rod polymer with the axis ratio r oriented parallel in the solvent and is also equal to that in an ideal mixture of N_1 molecules of species 1 and N_2 molecules of species 2. The physical meaning of $\{(rN_2-1)/(N-1)\}$ in $P_{\text{inter,Rod}}$ is as follows. When a rod polymer is formed, a first monomer is connected to a head one and the monomer is fixed permanently to the head. Therefore, in the calculation of the probability of fixing a second monomer the first segment is omitted from an ensemble in the calculation of probability. Then the probability for the second is given by $(rN_2-1)/(N-1)$ not rN_2/N. Both numbers of denominator and numerator in the probability of fixing, decrease one by one for each connection of segment to the chain. The probability $P_{\text{inter,Rod}}$ in Eq. (6) is smaller than $P_{\text{inter,F–H}}$ due to $(rN_2 - i)/(N-i) = \phi_2(1 - i\phi_1/rN_2) < \phi_2$ and therefore $S_{\text{inter,rod}} < S_{\text{inter,F–H}}$. In a previous work [19] we have derived an equation for an intermediate case between $P_{\text{F–H}}$ and P_{Rod}. In this work, we propose a more general and simple method for the calculation of combinatory entropy in a complex polymer solution.

Consider a polymer chain which consists of m repeated units. The unit consists of a flexible part with a segments and rod part with c segments and then $m(a+c) = r-1$. The probability P in Eq. (3) is expressed by the products of individual probability factor of p_a and $\mathrm{p_c}$ where p_a and $\mathrm{p_c}$ are probability for a flexible and rod parts, respectively. There are two approximate methods for an evaluation of p_a in the complex polymer chain. The first method is given by $p_a = \phi_2$ for all flexible parts of maN_2 in polymer chains. Therefore $P_a = p_a^{N_2ma} = \phi_2^{(N_2ma)}$ for all flexible parts. The other approximation is that p_a depends on the polymer chains. For example p_a in the first polymer is given by ϕ_2^{ma} and that of the second polymer is given by $p_a = \{(rN_2 - mc)/(N - mc)\}^a$.

A combinatory entropy for the inter-molecular part in the polymer solution calculated by $p_a = \phi_2$ for all flexible parts is given by

$$S_{\text{inter}}/R = S\text{inter, F–H}/R + (1 - mc\phi_2/r)\ln(1 - mc\phi_2/r) - \phi_2(1 - mc/r)\ln(1 - mc/r) \tag{8}$$

The S_{inter}/R for the complicated case for p_a mentioned above is given by

$$S_{\text{inter}}/R = S_{\text{inter,F–H}}/R + \{1 + a/c - (1 - r^{-1})\phi_2\} \times \ln\{1 - mc\phi_2/r\} - \phi_2\{a/c + r^{-1})\ln(1 - mc/r) \tag{9}$$

where $S_{\text{inter,F–H}}$ is that in the Flory–Huggins theory and is given by

$$S_{\text{inter,F–H}}/R = -(1-\phi_2)\ln(1-\phi_2) - (\phi_2/r)\ln\phi_2 \tag{10}$$

Both equations of Eqs. (8) and (9) are different. Eq. (9) is the same as that derived in the previous work [19]. A detailed calculation is given in Appendix.

1.2. Intra-molecular contribution in combinatory entropy in complex polymer solution

In the Flory–Huggins theory an intra-molecular contribution in the combinatory entropy of polymer solution is given by

$$\Omega_{\text{intra,F–H}} = [\{(z-1)/e\}^{(r-1)}r]^{N_2} \tag{11}$$

In the case of the solution of polymer with rod and flexible parts, the $\Omega_{\text{intra,r–f}}$ is given by

$$\Omega_{\text{intra,r–f}} = [\{(z-1)/e\}^{(ma+m)}(ma+m)]^{N_2} \tag{12}$$

where each rod parts has one flexible part and the total

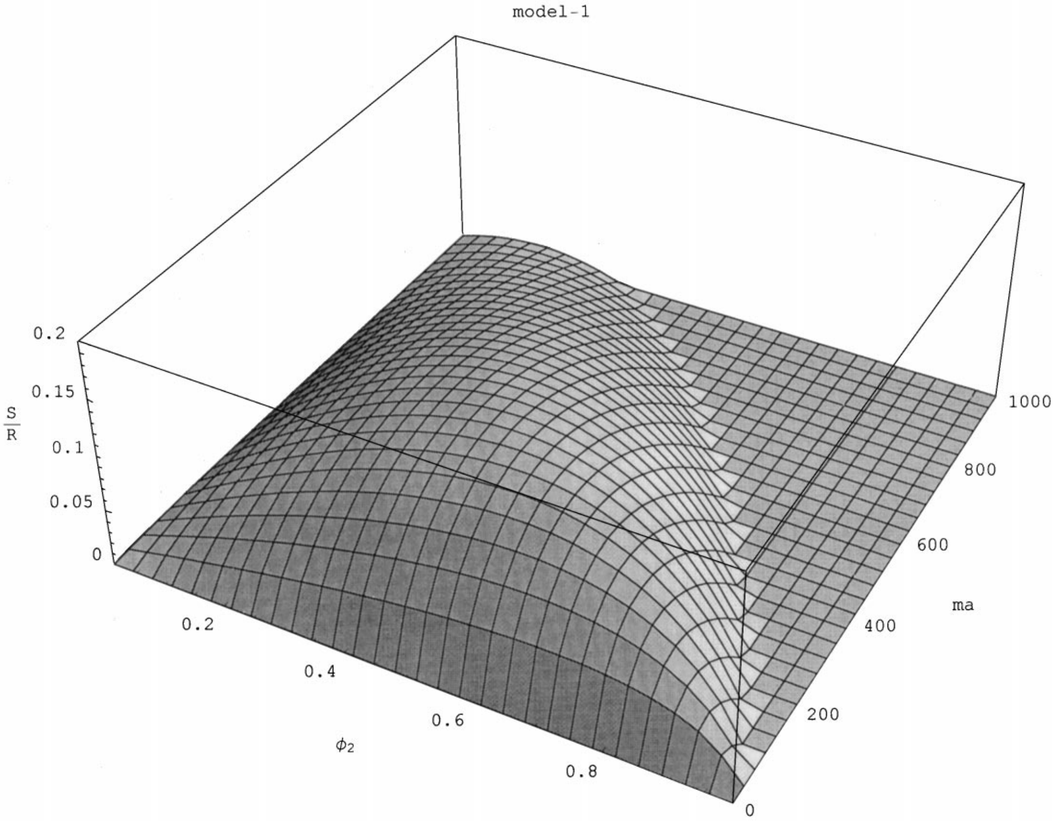

Fig. 1. $S/R - \phi_2 - ma$ three-dimension plot for polymer solution (model-1) in Eq. (17) with $r = 1000$, $m = 10$ and $z = 2.2$.

number of flexible parts in a chain is $ma + m$. The z in Eq. (12) is an average coordination number.

1.3. Combinatory entropy in star polymer solution

The combinatory entropy of star polymer solution is derived based on the lattice theory by using a mean field approximation. Consider a star polymer with r segments which consists of a core of the star and n branches and each branch has x segments and therefore $(r-1) = nx$. We make the star polymer from n linear polymer chains with $x+1$ segments per chain hypothetically. The total number of segments in the n linear polymers are $n(x+1) = r + n - 1$, which is larger than the original total segment r by $n-1$. As is mentioned earlier, the probability P in a linear polymer with r segments is $\phi_2^{(r-1)}$. The probability P for n linear polymer chains with $x+1$ segments per chain is $\phi_2^{nx} = \phi_2^{(r-1)}$ where $nx = r-1$ is used. Now we make a star polymer with a core made up of a segment by combining the n free ends of the linear polymers. Therefore, $(n-1)$ segments must disappear. The P for star polymer with r segments is $\phi_2^{r-1-(n-1)} = \phi_2^{(r-n)}$. The intra-molecular contribution for the star polymer is given by $\{(x+1)(z-1)^x/e^x\}^n$ where no intra-molecular interaction between branches is assumed.

The configurations for solution of N_2 star polymers with r segments and N_1 solvent molecules is $\Omega_0 P_{\rm star}^{N_2}$ and given by

$$\Omega_{\rm star} = \Omega_0[\phi_2^{(r-n)}\{(x+1)(z-1)^x/e^x\}^n]^{N_2} \tag{13}$$

In the case of $n = 1$ and $x = r-1$, Eq. (13) is reduced to that of Flory–Huggins theory.

1.4. Total combinatory entropy S in complex polymer solutions

The combinatory entropy in the original Flory–Huggins theory [1] is given by

$$S_{F\text{–}H}/R = -(1-\phi_2)\ln(1-\phi_2) - (\phi_2/r)\ln\phi_2 + (\phi_2/r)\ln[\{(z-1)/e\}^{(r-1)}r] \tag{14}$$

The combinatory entropy in the rod polymer solution derived by Flory [7] is

$$S_{\rm rod,F}/R = S_{\rm inter,F\text{–}H}/R + \{1-(1-y/r)\phi_2\} \times \ln\{1-(1-y/r)\phi_2\} + (\phi_2/r)[\ln(ry^2) - y + 1] \tag{15}$$

An equation derived from Eq. (15) using the maximum condition with respect to y is given by

$$S_{\rm rod,F}/R = S_{\rm inter,F\text{–}H}/R - 2(1-\phi_2)/y + (\phi_2/r)[\ln(ry^2) - y - 1] \tag{16}$$

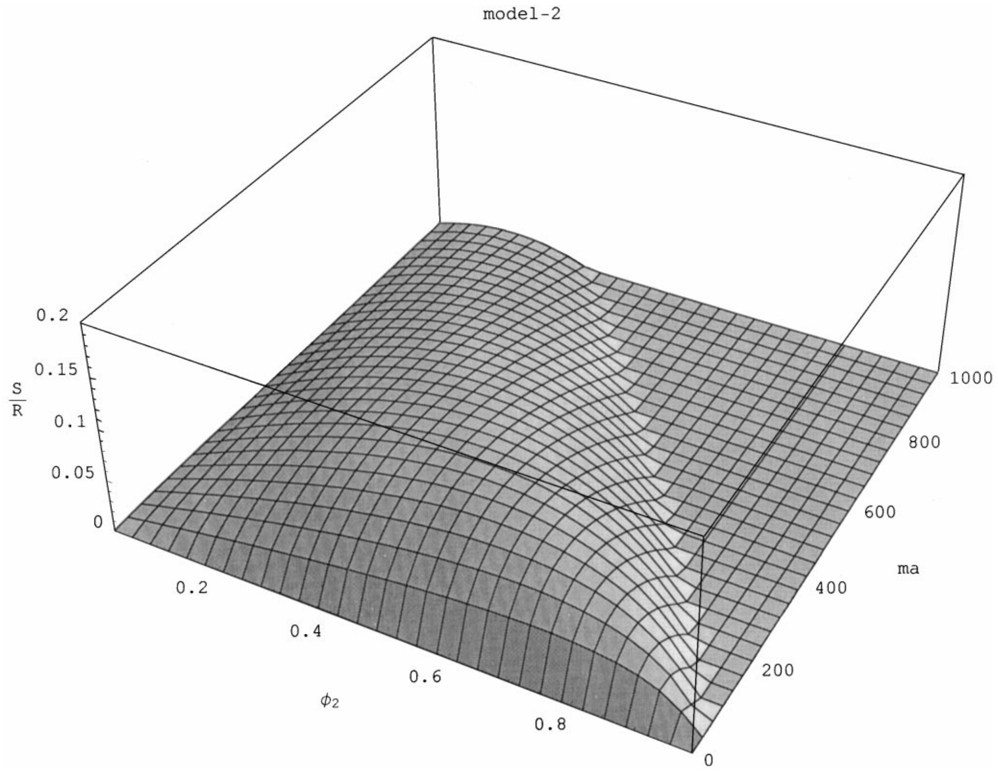

Fig. 2. $S/R - \phi_2 - ma$ three-dimension plot for polymer solution (model-2) in Eq. (18) with $r = 1000$, $m = 10$ and $z = 2.2$.

where y is defined by $y = r \sin\theta$ and θ is an angle of inclination of a particle to the domain axis.

The combinatory entropy for rod-like polymer solutions in this work designated by model-1 is given by

$$\begin{aligned} S_{\text{rod,model-1}}/R = {} & S_{\text{inter,F–H}}/R + (1 - mc\phi_2/r)\ln(1 - mc\phi_2/r) \\ & - (1 - mc/r)\phi_2 \ln(1 - mc/r) \\ & + (\phi_2/r)\ln[\{(z-1)/e\}^{(ma+m)}(ma+m)] \end{aligned} \tag{17}$$

while that in the rod-like polymer solution in the previous work [19] designated by model-2 is

$$\begin{aligned} S_{\text{rod,model-2}}/R = {} & S_{\text{inter,F–H}}/R + \{1 + a/c - (1 - r^{-1})\phi_2\} \\ & \times \ln\{1 - mc\phi_2/r\} - \phi_2\{a/c + r^{-1}) \ln(1 - mc/r) \\ & + (\phi_2/r)\ln[\{(z-1)/e\}^{(ma+m)}(ma+m)] \end{aligned} \tag{18}$$

The combinatory entropy for star polymer solution is given by

$$\begin{aligned} S_{\text{star}}/R = {} & S_{\text{inter,F–H}}/R - \phi_2\{(n-1)/r\}\ln\phi_2 \\ & + (\phi_2/r)\ln[\{(n + r - 1)/n\}n(z-1)^{(r-1)}/e^{(r-1)}] \end{aligned} \tag{19}$$

where $nx = r - 1$.

2. Results

Calculations of S/R for various polymer solutions have been carried out and are shown in three dimensions in Figs. 1–3. The variables in Figs. 1 and 2 are polymer concentration ϕ_2 and the total number of flexible segments ma per chain, while those in Fig. 3 are ϕ_2 and y. The y in the Flory theory is related to flexibility of polymer because $y = 1$ corresponds to a rigid rod-polymer and $y = r$ to the flexible polymer. Therefore, both parameters y and ma give the same measure of the flexibility in the polymer chain.

The flat region or $S/R = 0$ in Figs. 1–3 corresponds to regions showing negative values of S/R because the plot range in all figures is set to be larger than zero. The negative regions are nonsense thermodynamically. The critical line between the positive and negative region corresponds to a complete order state of $\Omega = 1$ and $S/R = 0$. It is demonstrated that a similar behavior of S/R in the Flory-rod model in Fig. 3 is obtained in our model-1 and -2 with a small coordination number $z = 2.2$. The similar behavior of S/R showing a limited negative region is found in this work for z satisfying $(z - 1)/e < 1$.

Values of S/R in the Flory rod model in Fig. 3 decreases suddenly in the vicinity of $y = 1$ with decreasing y, while S/R in Figs. 1 and 2 decreases slowly with decreasing of ma in the vicinity of $ma = 0$. It is found in the Flory rod model that there is a small region showing negative S/R in the vicinity of $\phi_2 = 0$ and $y = 1$, which means that the complete order region appears in the dilute solution of rod

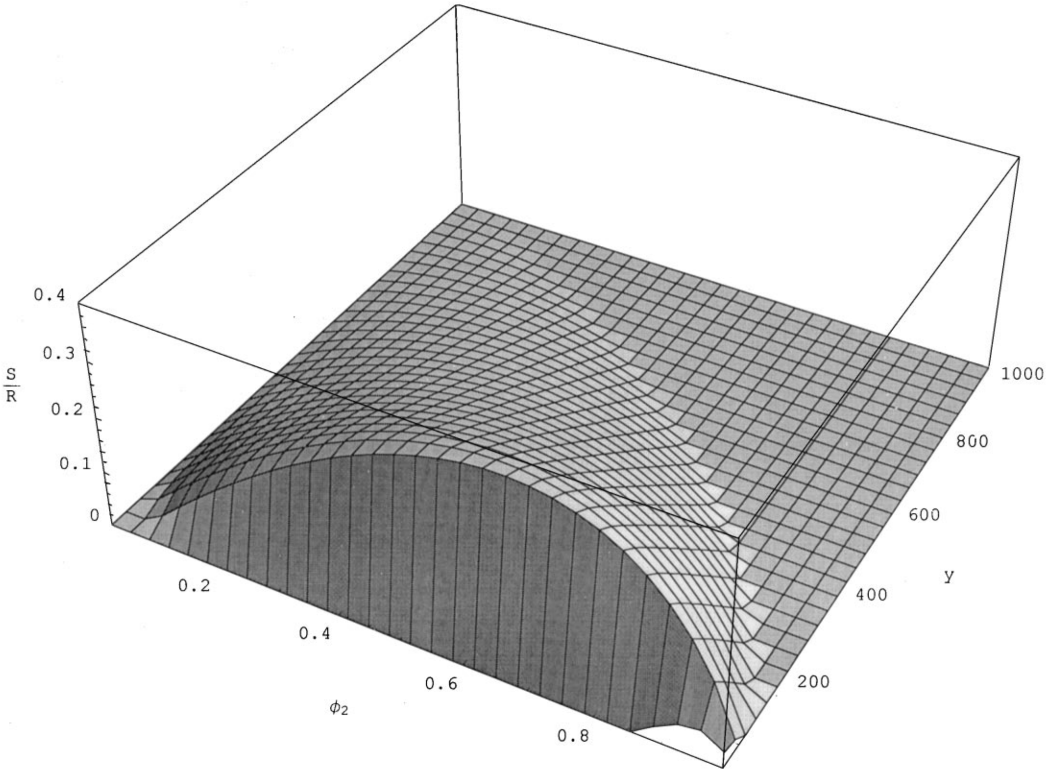

Fig. 3. $S/R - \phi_2 - y$ three-dimension plot for rod-like polymer solution (Flory-rod model) in Eq. (16) with $r = 1000$.

polymer in solvent. The behavior was not observed in our models in Figs. 1 and 2. It is suggested from Figs. 1–3 that the behavior of maximum of S/R with respect to chain flexibility parameters such as ma and y is one of the important features characterizing the rod-like polymer solution.

The combinatory entropy of star polymer solution S_{star} calculated by Eq. (19) with $z = 3.0$ is shown in Fig. 4. The S_{star} differs from $S_{\mathrm{F-H}}$ by $-\phi_2\{(n-1)/r\} \ln \phi_2$ and $S_{\mathrm{star,inter}} > S_{\mathrm{F-H,inter}}$. The S_{comb}/R in the flexible polymer solution for various z is shown in Fig. 5. The z parameter reflects the flexibility of the polymer chain in the Flory–Huggins theory where S_{comb}/R increases with increasing z.

3. Discussions

It is interesting to compare the combinatory entropy in the rod-like polymer solution in this work with that in the Flory theory. If a relation $y = r - mc$ is used, Eq. (15) in the Flory-rod theory becomes the same function as Eq. (17) derived in this work except for the last positive term $-\phi_2(1 - mc/r) \ln(1 - mc/r)$. It is also found through the calculation that the values of S/R in Eq. (15) of the Flory-rod model are negative over the range of entire concentration of ϕ_2 and $y > 1$, although the values of S/R in Eq. (16) derived using the maximum condition are positive over the limited range of y and ϕ_2 as is shown in Fig. 3. The term $-2(1 - \phi_2)/y$ plays an important role in the Flory-rod model.

A main reason for a decrease of S/R with increasing y over large values of y in the Flory-rod model is mainly attributed to the negative term $-(y+1)\phi_2/r$, which comes from the intra-molecular contribution of S in Eq. (16). In our model the intra-molecular contribution of $(\phi_2/r)(ma + m) \ln\{(z-1)/e\}$ with $(z-1)/e < 1$ is negative and increases with ma, which is the same behavior as the Flory-rod model. On the other hand the increase of S/R with increase of y in the vicinity of $y = 1$ is responsible to the negative term of $-2(1 - \phi_2)/y$ from the inter-molecular contribution in the Flory model. In our model the increase of S/R with increase of ma over the small ma is responsible to a positive term of $-\phi_2(1 - mc/r) \ln(1 - mc/r) = -\phi_2\{(1 + ma)/r\} \ln\{(1 + ma)/r\}$ from the inter-molecular contribution of S in Eq. (17). The positive term increases with ma. The essential difference between our model and Flory model is that S_{inter}/R is the negative -2 in the vicinity of $y = 1$ and $\phi_2 = 0$ but that is zero in the vicinity of $\phi_2 = 0$ in this work.

In our model the ratio of $(z-1)$ and e is critically important. A maximum point in S/R vs. ma curve appears only in the case of $(z-1)/e < 1$. The quantity $(z-1)/e$ is related to a ratio of gain of entropy due to chain flexibility $(z-1)$ to loss of one dimensional communal entropy due to chain connection per segment. If the $(z-1)/e$ is less than one, the negative intra-molecular contribution to S/R can overcome the positive inter-molecular one over the range of large ma, which leads to an ordered state in spite of increasing of chain length of flexible part.

Recently an effect of polymer architectures on the phase

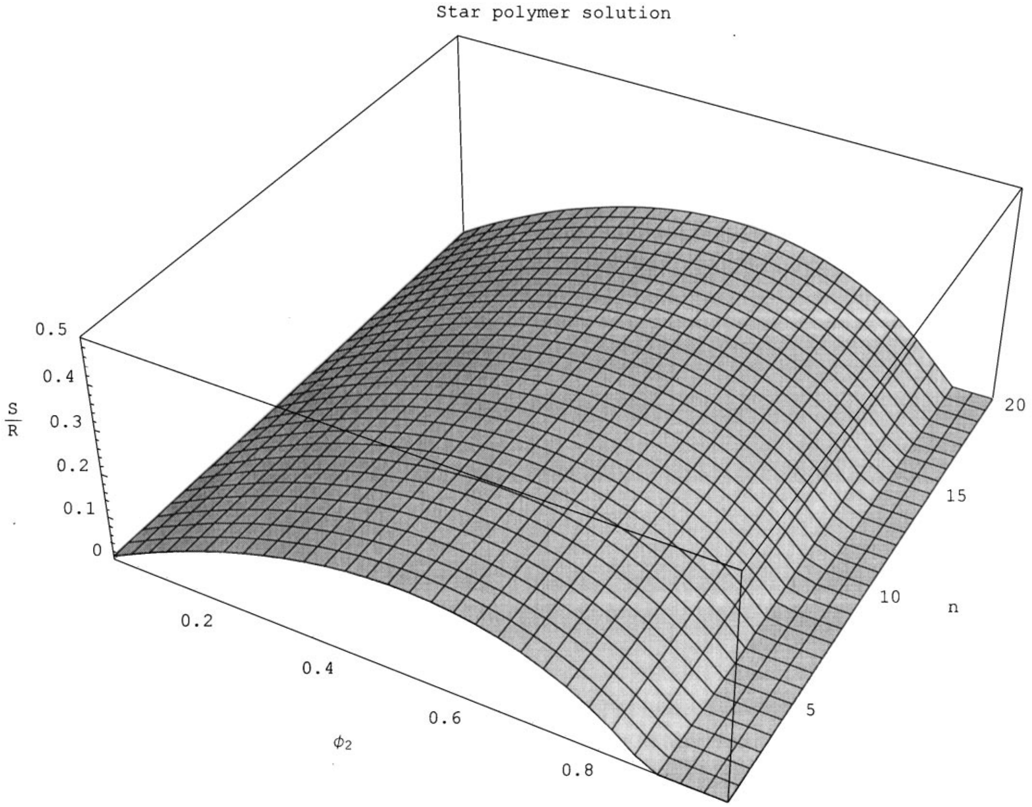

Fig. 4. $S/R - \phi_2 - n$ three-dimension plot for star polymer solution in Eq. (19) with $r = 1000$ and $z = 3.0$.

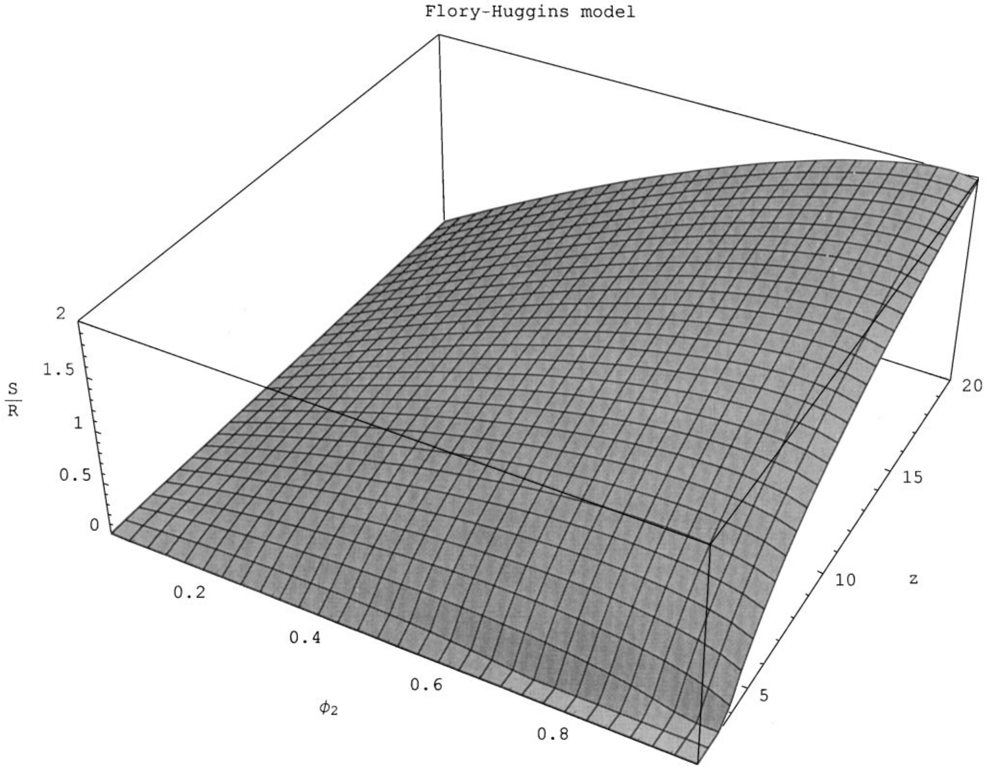

Fig. 5. $S/R - \phi_2 - z$ three-dimension plot for the Flory–Huggins model in Eq. (14) with $r = 1000$.

diagram of polymer solution has been investigated extensively [21–25]. Nose et al [21,22] have found the critical concentration of the star polystyrene–cyclohexane system is different from that of linear polystyrene of the same molecular weight. According to the Flory–Huggins theory the critical concentration $\phi_{2,\mathrm{c}}$ is given by

$$\phi_{2,\mathrm{c,flexible}} = 1/(1 + r^{1/2}) \tag{20}$$

The $\phi_{2,\mathrm{c}}$ for star polymer solution calculated by Eq. (19) is given by

$$\phi_{2,\mathrm{c,star}} = 1/[1 + (r/n)^{1/2}] \tag{21}$$

Eq. (21) means that an apparent number of segments in star polymer is r/n which is the number of segments for one branch. The value of $\phi_{2,\mathrm{c}}$ for star polymer with 6 arms calculated by Eq. (21) is 0.0719 for $r = 1000$, while that in the Flory–Huggins model by Eq. (20) is $\phi_{2,\mathrm{c}} = 0.0306$. The experimental data show that $\phi_{2,\mathrm{c}}$ in the linear polystyrene(PS)–cyclohexane system for molecular weight of $M_\mathrm{w} \sim 10^6$ is about 0.03, while that in star PS with 6.3 arms with the same molecular weight is about 0.04. Our model predicts a tendency of large $\phi_{2,\mathrm{c}}$ in the star polymer solution compared to that in linear polymer solution successfully. Nose et al [22] reported that the $\phi_{2,\mathrm{c}}$ in solutions of randomly branched PS and comb-shaped PS in methyl cyclohexane are larger than that linear PS with $M_\mathrm{w} = 10^6$ by about 0.02. These results suggest that the combinatory entropy in complex polymer solutions depend on the polymer architecture.

The polymer chain consisting of rod and flexible parts in this work gives a general model of complex linear polymers such as copolymer, rod polymer with some flexible parts and semi-flexible polymer. The phase diagram in the solution of linear polymer has been investigated by the Monte Carlo method. Panagiotopoulos et al [26] have calculated the critical concentration of solution of flexible and semi-flexible polymer and found the critical concentration for $r = 100$ in both solutions is nearly the same. Hu et al [27] have found that the critical concentration of polymer solution with $r = 200$ is about $\phi_{2,\mathrm{c}} = 0.16$, which is much larger than 0.066 calculated by the Flory–Huggins theory.

The $\phi_{2,\mathrm{c}}$ has been calculated for solution of polymer with rods and flexible parts by the same procedure as in the Flory–Huggins theory. In model-1 in this work the $\phi_{2,\mathrm{c}}$ is determined by an equation

$$\phi_{2,\mathrm{c}}/(1 - \phi_{2,\mathrm{c}})^2 - 1/(1 - \phi_{2,\mathrm{c}}) + 1 - r^{-1} - \beta^3\phi_{2,\mathrm{c}}^2/(1 - \beta\phi_{2,\mathrm{c}})^2 = 0 \tag{22}$$

and in model-2 by

$$\phi_{2,\mathrm{c}}/(1 - \phi_{2,\mathrm{c}})^2 - 1/(1 - \phi_{2,\mathrm{c}}) + 1 - r^{-1} - (\beta^2\phi_{2,\mathrm{c}}^2)(1 - r^{-1})/(1 - \beta\phi_{2,\mathrm{c}})^2 = 0 \tag{23}$$

where $\beta = mc/r$. The values of $\phi_{2,\mathrm{c}}$ in model-1 and -2 for $r = 200$ and $mc/r = 0.8$ are 0.090 and 0.101, respectively, while those for $r = 200$ and $mc/r = 0.5$ are 0.070 for model-1 and 0.074 for model-2. In both the models the $\phi_{2,\mathrm{c}}$ increases with increase of mc/r.

4. Conclusion

The combinatory entropy of solution of rod-like particles first derived by Flory has been reproduced by our method of calculation of combinatory entropy for polymer solution. An origin of specific behavior of rod-like polymer solution has been analyzed in detail. It is suggested that the combinatory entropy in rod-like polymer solution is characterized by a maximum point with respect to the flexible parameters such as y and ma at constant polymer concentrations.

The combinatory entropy for star polymer solution has been derived in this work. We have done a critical test for the star polymer model through the experimental data of critical concentration in star and linear polymer solutions. Our model has predicted the experimental result that the critical concentration in the star polymer solution is larger than that in the solution of the linear polymer of the same molecular weight. It has also been predicted in this work that the critical concentration in the solution of polymer with rod and flexible parts increases with increasing segments for the rod part in a polymer chain.

Appendix A

A.1. Derivation of Eq. (8) for model-1

In this model the probability factor for all flexible parts is ϕ_2 and that for the rod part depends on an inserting order of polymers to lattice. The total probability P is given by

$$P_{\mathrm{total},1} = [(rN_2/N)\{(rN_2 - mc)/(N - mc)\} \cdots \{rN_2 - (N_2 - 1)mc\}/\{N - (N_2 - 1)mc\}]^{mc}(rN_2/N)^{maN_2} \tag{A1}$$

$$= [\{(rN_2/mc)!(N/mc - N_2)!\}/\{(rN_2/mc - N_2)!(N/mc)!\}]^{mc} \times (rN_2/N)^{maN_2} \tag{A2}$$

Eq. (8) is obtained by $\Omega = P_{\mathrm{total},1}\Omega_0$ and $S/R = \ln \Omega/N$ where $\Omega_0 = N!/\{N_1!(rN_2)!\}$. In the calculation the Stirling approximation is used.

A.2. Deviation of Eq. (9) for model-2

The detailed deviation of Eq. (9) is shown in Ref. [19] but it is derived more simply as follows. In this model, both the probability factors for rod parts and flexible parts depend on an inserting order of polymers to lattice. The probability factor for the first polymer is $(rN_2/N)^{ma+mc}$ for rod and flexible parts and that of the second one is

$[(rN_2 - mc)/(N - mc)]^{ma+mc}$ and xth polymer $[(rN_2 - (x-1)mc)/\{N - (x-1)mc\}]^{ma+mc}$. The total P for the polymer solution is

$$P_{\text{total},2} = [(rN_2/N)\{(rN_2 - mc)/(N - mc)\} \cdots \{rN_2 - (N_2 - 1)mc\}/\{N - (N_2 - 1)mc\}]^{(ma+m)} \tag{A3}$$

$$= [\{rN_2/mc\}!(N/mc - N_2)!]/\{(rN_2/mc - N_2)!(N/mc)!\}]^{(r-1)} \tag{A4}$$

where $ma + mc = r - 1$ is used. Eq. (9) is obtained from $\Omega = P_{\text{total},2}\Omega_0$ and $S/R = \ln \Omega/N$.

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