Mixing Free Energy of Polymer Blend*

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Received March 30, 1994.

Keywords: segmental concentration, molecular concentration, chainhead concentration, polymer blend, mixing free energy.

A classical problem in polymer physics is the mixing free energy of polymer binary blends. Flory and Huggins[1] have proposed a famous formula

$$\frac{F}{kT} = \frac{\Phi_1}{N_1}\log\ \Phi_1 + \frac{\Phi_2}{N_2}\log\Phi_2 + x\,\Phi_1\Phi_2, \tag{1}$$

where Φ_1 and Φ_2 are the volume fractions of two components; N_1 and N_2 are their chain lengths; x is the Flory-Huggins constant; k is the Boltzmann constant, and T is the temperature of the blend. This formula has wide application, but also is subject to many criticisms due to its mean field approximation. Some new theories have been proposed, for example, the random phase approximation (RPA) method[2—9]. On the one hand some criticism problems remain to be solved in new theories; on the other hand, it is difficult and complex for its application to describe the physical picture and mathematical calculation. To describe the experiment results of polymer phenomena, an improved theory is needed. We regard the Flory-Huggins formula as easy to understand and apply in the polymer physics because of its distinct physical pictures and simple mathematical form. From this point we expect to deduce the mixing free energy formula on the basis of the new physical concepts which is able not only to keep the advantage of the mean field theory, but also to extend the mean field theory from small molecules to macromolecules.

It is well known that the concentration is an important parameter to describe the character of small molecule solutions. For the solution of macromolecules, however, except temperature and the chain length, we consider that only one concentration quantity for each component volume fraction is not enough. According to the connected property of macromolecules we propose here two concentration variables: segmental and

* National Basic Research Project *Macromolecular Condensed State*, and supported by the Polymer Physics Laboratory of Academia Sinica.

molecular concentrations. We know that the total entropy is an important thermodynamic quantity of the polymer solution. But it contributes from two parts: positional entropy and conformational entropy. The former one is corresponding to the possible position distribution of the macromolecules and reflects the fact that the macromolecules as a whole (but not as a crowd of dispersed, individual segments) have the same rule as a small molecule. The latter one is corresponding to all the possible configurations which are dependent on the flexibility of the chain. It reflects the thermodynamical tendency of forming macromolecular coil. This is a characteristic phenomenon distinguished from the small molecule solution. In a word, the two kinds of entropies in the polymer solution come from different physical bases and they have different physical laws. If the total entropy is not divided into two parts, it is obvious that the sum of the positional and conformational entropies may not have any clear physical meaning.

In the case of condense polymer solution and polymer blends, the macromolecular configurations will interfere with each other. It must be noticed that the positional and conformational entropies are dependent on the different polymer concentrations. In order to resolve such a problem we propose the concept of two kinds of concentrations: segmental and molecular concentrations, instead of the traditional unique concentration volume fraction.

First we should give the definitions of the segmental and molecular concentrations. The segmental concentration can be defined as the number of the segment of one component in the unit volume. For convenience, we would take the segmental volume as the unit so that the segmental concentration is equivalent to the conventional volume fractions Φ_1 and Φ_2. But the definition of molecular concentration is a complex concept, because a macromolecule consists of many segments and every segment has its own position; a long macromolecular chain occupies many positions in the space. It is necessary to define the position of macromolecules. For example, we can define the gravity centre as the molecular position for easy understanding. However, in Monte Carlo simulation it is the most convenient to take the first segment of molecular chain, which can be called the chainhead, as the molecular position. In this case the molecular position can be defined as the number of the chainhead in the unit volume, denoted as C_1 and C_2. Because the chainhead is a segment itself, when the segmental concentration is taken as a continuous spatial function, the chainhead concentration (as well as the concentration of macromolecule gravity center) can be regarded as a continuous spacial function. If at a position the chainhead concentration (or of the gravity centre) is C_1, we can say that there are C_1 macromolecules at this position. So this quantity can be regarded as that number concentration of macromolecules and can be called molecular concentration for short.

The concepts of the segmental and the molecular concentrations are very

important. It should be emphasized that each thermodynamical quantity of the polymer systems is dependent on only one of the two concentrations, not the other. This case is the same as in some equations concerning the concentration. It is important to distinguish those two concepts. For example, in the scattering experiments each segment is a scattering centre; therefore the scattering function of the polymer systems should be the mean square fluctuation of the segmental concentration, but not the molecular concentration. On the other hand, in polymer blends, the mixing entropy is the entropy of the mixture of macromolecules of two components, but not the entropy of the mixture of two groups of dispersive and individual segments. Therefore the mixing entropy should be a function of the molecular concentration. If the thermodynamic relations of the polymer blend are based on these concepts, it will have an advantage of clear physical pictures and a concise mathematical form.

Now we will discuss the position entropy of a component before the mixing. We assume that in volume V_1 there are n_1 macromolecules and the position of each macromolecule is represented by its chainhead. Because the macromolecular chain is very long, the chainhead number in the unit volume is very small, like rare gas. For simplicity we describe its entropy by use of the formula of ideal gas. Considering the conformational entropy, we have

$$S_1 = kn_1 \log\left(\frac{V_1}{n_1}\right) + n_1 S_{1c}, \tag{2}$$

where S_{1c} is the conformational entropy per chain of the first component. We can write the same formula for the second component.

After mixing, the total volume of the system is $V_1 + V_2$. The ideal gas model is again used, and then the total entropy is

$$\begin{aligned} S_{\text{total}} = {} & kn_1 \log\left(\frac{V_1 + V_2}{n_1}\right) + n_1 S_{1c} \\ & + kn_2 \log\left(\frac{V_1 + V_2}{n_2}\right) + n_2 S_{2c}. \end{aligned} \tag{3}$$

Before mixing, the volumes of the two components are $V_1 = n_1 N_1$ and $V_2 = n_2 N_2$, respectively. If the conformational entropy does not change during the mixing, the mixing entropy of the unit volume is easily obtained:

$$\begin{aligned} S_M &= \frac{(S_{\text{total}} - S_1 - S_2)}{(V_1 + V_2)} \\ &= -k\,(C_1 \log(C_1 N_1) + C_2 \log(C_2 N_2)), \end{aligned} \tag{4}$$

where C_1 and C_2 are the molecular concentrations of two components respectively, defined as the number of the molecules in the unit (segmental) volume

$$C_1=\frac{n_1}{V_1+V_2}\ ,\quad C_2=\frac{n_2}{V_1+V_2}\ . \tag{5}$$

Since the relationship between the average values of the segmental and the molecular concentration is $\Phi_1=N_1\cdot C_1$, $\Phi_2=N_2\cdot C_2$, Eq. (4) is in agreement with the Flory-Huggins formula. Considering the influence of the mixing on the chain configuration, the following term should be added too.

$$\Delta S=C_1\Delta S_{1c}+C_2\Delta S_{2c}\ , \tag{6}$$

where ΔS_{1c} and ΔS_{2c} are the increment of the conformational entropy of the two components respectively when they are mixed.

The mixing heat should be proportional to the number of contact points between the two components. We regard the idea as acceptable that the local contact number is proportional to the multiplication of the local segmental concentrations of the two components $\Phi_1\Phi_2$. For polymer blends, however, considering that the density of the segments is not uniform in space, generally they always appear as many individual coils in the space. Accordingly a term of the mixing heat should be the mean value of the total heat amount for the unit volume. From this point we have

$$\frac{H}{kT}=x\overline{\Phi_1\Phi_2}. \tag{7}$$

Obviously the quantity $\overline{\Phi_1\Phi_2}$ is not equal to $\overline{\Phi_1}\cdot\overline{\Phi_2}$; on the other hand,

$$\Phi_1+\Phi_2=1;$$

so we have

$$\frac{H}{kT}=x(\overline{\Phi_1}\cdot\overline{\Phi_2}-\overline{\Delta\Phi_1^2}), \tag{8}$$

where the last term is the mean square fluctuation of the segmental concentration of the first component. It can be calculated from the function of the chain configuration. From all the contribution terms the mixing free energy can be written as

$$F_{mix}=kT\{C_1\log(C_1N_1)+C_2\log(C_2N_2)+x\overline{\Phi_1\Phi_2}\}-T\Delta S. \tag{9}$$

It is well known that the Flory-Huggins formula has been subject to a lot of criticisms for many years. One is the limited lattice model adopted[2,3]; the other is the "homogeneous mixing" approximation in their mean field theory[6—8]. In this work the lattice model is not applied to calculating the mixing free energy of the polymer blend. The limitation of the mean field theory does not stem from the homogeneous mixing approximation, but the confusion between the concepts of the segment and macromolecule concentrations, which leads to the difficulties of theoretical interpretation for many problems. For example, in the Flory-Huggins formula (1)

the parameter x of the last term is a constant, but it is shown by simulation calculation that x relates to the chain configuation and concentration of the solution[6—8]. It is easy to understand that the mixing term in solution is affected by three factors: the interaction constant, the number density of macromolecules and the average contact number of the segments of a macromolecule with the solvent molecules. If the mixing heat is simply written as the multiplication of the average concentration and contact x just like in Eq. (1), the effect of a chain length and the configuration of a macromolecule will be included in the parameter x. This is the reason why the Flory-Huggins parameter x cannot keep constant. If we introduce two concepts to describe the concentration of the polymer blend, some confusion concepts will become clear and simple.

References

1 Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ., Ithaca, New York, 1958.
2 Schweizer, K. S. & Curro, J. G., *J. Chem. Phys.*, 1989, **91**: 5059.
3 Pesci, A. I. & Freed, K. F., *J. Chem. Phys.*, 1989, **90**: 2003.
4 Sariban, A. & Binder, K., *Macromolecules*, 1988, **21**: 711.
5 Dudowitz, J., Freed, K. F. & Madder, W. G., *J. Chem. Phys.*, 1990, **23**: 4803.
6 Lu Jian-Ming & Yang Yu-Liang, *Science in China* (in Chinese, Series A), 1992, (3): 1002.
7 Cifra, P., Karasz, F. E. & Macknight, W. J., *J. Polym. Sci.*, Part B, 1988, **26**: 2379.