Macromol. Symp. **2003**, *203*, 225-228

Rationalizing the Meaning of Coefficients in Flory-Huggins Approach to Polymer-Solvent Interactions

Emilio Lucchelli, Luciano Caccianotti*

Centro Ricerche Novara "Istituto Guido Donegani", Polimeri Europa,Via Giacomo Fauser 4, 28100 Novara, Italy
E-mail: emilio.lucchelli@polimerieuropa.com

Summary: The Flory-Huggins interaction parameter for a polymer solution can be represented as the product of two functions, which separately take into account the effects of the polymer volume fraction and temperature. The latter factor contains three constants, usually viewed as best-fit coefficients. They are expressed in terms of two thermodynamic quantities, namely, the excess partial molar heat capacity of the solution and a reference temperature, thus allowing to guess their physical meaning. The formulae so obtained were tested with satisfactory results for two solutions of polystyrene in acetone and for two polymer blends (PC/PMMA and PS/PVME.) Furthermore, an attempt was made to calculate the above-mentioned reference temperature from data referring to the phases in solution.

Keywords: blends; calculations; Flory-Huggins interaction parameter; solution properties; thermodynamics

Introduction

The χ interaction parameter of the Flory-Huggins lattice theory can be described[1] by assigning a functional form that takes into account its dependence on both temperature and composition:

$$\chi(T, \varphi_2) = (1 + b_1\varphi_2 + b_2\varphi_2^2)\cdot(d_0 + d_1/T + d_2\ln T) \qquad (1)$$

where T is the absolute temperature and φ_2 the volume fraction of one component of the binary solution or blend.

The coefficients b_1, b_2, d_0, d_1, d_2 appearing in (1) are usually considered as adjustable constants, and they are chosen in such a way to get the best fit of the experimental data.

An attempt is presented here to express such coefficients in terms of physical quantities which are known or measurable. This is a first step towards the goal of clarifying their physical meaning and hence lending the χ parameter a less empirical role.

DOI: 10.1002/masy.200351323

Theoretical Background

The function $D(T) = d_0 + d_1/T + d_2\ln T$ is expressed[1] as the sum of an enthalpy term κ and an entropy term ψ:

$$D(T) = \kappa + \psi \tag{2}$$

Both the following relationships[2] hold for the entropy contribution ψ:

$$\psi = d(TD)/dT = D + TdD/dT \tag{3}$$

$$d\psi/dT = \xi/T \tag{4}$$

where ξ is the excess partial molar heat capacity, averaged over a proper temperature range. Deriving ψ directly from (3) and taking (4) into account gives

$$\xi = 2TdD/dT + T^2d^2D/dT^2 \tag{5}$$

and this further yields

$$\psi - \xi = D - TdD/dT - T^2d^2D/dT^2 \tag{6}$$

Since D(T) has the functional form reported in (1), its first- and second-order derivatives are

$$dD/dT = - d_1/T^2 + d_2/T \tag{7a}$$

$$d^2D/dT^2 = 2d_1/T^3 - d_2/T^2 \tag{7b}$$

Substituting (7a) and (7b) into (6) gives

$$\psi - \xi = d_0 + d_2\ln T \tag{8}$$

By integration of (4) we get

$$\psi = \xi\ln T + \text{const} \tag{9}$$

This allows to write

$$d_0 = \xi\ln T + \text{const} - \xi - d_2\ln T \tag{10}$$

Since d_0 is an adjustable constant, the sum of the terms containing the varying quantity T on the right-hand side of (10) must be identically equal to zero. Thus

$$\xi\ln T - d_2\ln T = 0 \tag{11}$$

from which it can immediately be concluded

$$d_2 = \xi \tag{12}$$

The temperature T* at which the first-order derivative of D(T) vanishes is given[1] by

$$T^* = d_1/d_2 \tag{13}$$

which in turn yields

$$d_1 = \xi T^* \tag{14}$$

Taking into account both (10) and (11) leads to the conclusion that

$$d_0 = \mathrm{const} - \xi \qquad (15)$$

The term labeled as const in (15) is an arbitrary integration constant. It was guessed to have the following expression:

$$\mathrm{const} = -\xi \ln T^* \qquad (16)$$

so that d_0 becomes

$$d_0 = -\xi \cdot (1 + \ln T^*) \qquad (17)$$

Some remarks should be made about the calculation of the three coefficients d_0, d_1 and d_2:

(1) the determination of ξ is inherently difficult (no direct calorimetric measurements are available for this purpose);

(2) the physical meaning of T^* is not fully clear.

An explicit expression was elaborated for the parameter T^*, following the approach of Shiomi et al.:[3]

$$T^* = 2v^*\chi_{12}/(3Rv_1c_{12}) \qquad (18)$$

where R is the universal gas constant, v^* is the volume of the repeat unit of the polymer having a high molecular weight, v_1 is the ratio between the cell volume and v^* (a cell is one of the elementary spaces into which the polymeric system can be ideally subdivided.) On the other hand, χ_{12} and c_{12} are fitting parameters allowing an empirical description of the interaction between polymer and solvent (or two polymers in a binary blend.) Their values, as well as the ratio v_1, were reported[4] only for the PS/PVME blend: therefore it was possible to use (18) only in this case.

Materials

Two solutions of PS in acetone (labeled I and II) and two polymer blends (PC/PMMA and PS/PVME) were taken as testing examples to assess the reliability of the above-derived expression for d_0. As already pointed out in the presentation of the theoretical background, T^* was calculated according to (18) for the latter blend. In the three other cases it results from (13), through the empirical values[1] of d_1 and d_2. The properties of both PS/acetone solutions are reported elsewhere[5] as well as those of PC/PMMA[6] and PS/PVME.[4] The values of ξ were taken from the references.

Results and Discussion

Table 1 summarizes the values of T* and d_0 calculated in the way described in the present paper, and provides a comparison of d_0, as obtained by us, with d_0 determined[1] as the best-fit value to the experimental data.

Table 1. Values of T*, d_0, d_1, d_2.

Solution or blend	Calculated values (this paper)		Best-fit values as reported in ref. [1]		
	T*(K)	d_0	d_0	d_1	d_2
PS/acetone I	314.09	- 7.4246	- 6.8829	345.5	1.1
PS/acetone II	342.00	- 7.5183	- 6.9933	376.2	1.1
PC/PMMA	482.53	7.1790	7.1864 b)	- 482.53 b)	- 1.0 b)
PS/PVME	3081 a)	0.02345	0.02215	- 8.0	0.0

a) Calculated from (18).

b) Given by Qian, Mumby and Eichinger in a demonstration issue of "Phase-Diagram" software (Biosym.).

The agreement between the calculated values of d_0 and the best-fit values[1] is satisfactory for the two PS/acetone solutions and very good for the two blends. Since d_0 is derived from (10) and (11), which yield d_1 and d_2 as well, such an agreement is evidence of the self-consistency of the analytical expressions found for these three coefficients.

Conclusions

Analytical expressions were found for the three coefficients d_0, d_1 and d_2 that appear in the definition of the Flory-Huggins interaction parameter. In principle, they depend only on the excess partial molar heat capacity ξ of the solution (or blend) and a reference temperature T*. Such a result was tested by comparison with values of d_0, fitted to experimental data relevant to two solutions and two blends: the agreement between predicted and best-fit values proved to be good. An independent determination of d_1 and d_2 would require direct measurements or calculations of both ξ and T*.

[1] Caibao Qian, Stephen J. Mumby, B. E. Eichinger, *Macromolecules* **1991**, *24*, 1655.
[2] B. E. Eichinger, *J. Chem. Phys.* **1970**, *53*, 561.
[3] T. Shiomi, F. Hamada, T. Nasako, K. Yoneda, K. Imai, A. Nakajima, *Macromolecules* **1990**, *23*, 229.
[4] D. J. Walsh, G. T. Dee, J. L. Halary, J. M. Ubiche, M. Millequant, J. Lesec, L. Monnerie, *Macromolecules* **1989**, *22*, 3395.
[5] K. S. Siow, G. Delmas, D. Patterson, *Macromolecules* **1972**, *5*, 29.
[6] T. Kyu, D. Lim, *J. Polym. Sci., Part C* **1989**, *27*, 421.