(20) Wiese, G. R.; Healy, T. W. *Trans. Faraday Soc.* **1970**, *66*, 490.
(21) Chan, D. Y. C.; White, L. R. *J. Colloid Interface Sci.* **1980**, *74*, 303.
(22) Barouch, E.; Matijevic, E. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1797.
(23) Barouch, E.; Matijevic, E.; Wright, T. H. *J. Chem. Soc., Faraday Trans. 1* **1985**, *81*, 1819.
(24) Reerink, H.; Overbeek, J. Th. G. *Discuss. Faraday Soc.* **1954**, *18*, 74.
(25) Goodwin, J. H.; Ottewill, R. H.; Pelton, R.; Vianello, R.; Yates, D. E. *Br. Polymer J.* **1978**, *10*, 173.
(26) Fitch, R. M.; Palmgren, T. H.; Aoyagi, T.; Zuikov, A. *Angew. Makromol. Chem.* **1984**, *123/4*, 261.
(27) Morton, M.; Kaizerman, S.; Altier, M. W. *J. Colloid Sci.* **1968**, *6*, 2859.
(28) Gilbert, R. G.; Napper, D. H. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1983**, *C23*, 127.
(29) Kolthoff, I. M.; Miller, I. K. *J. Am. Chem. Soc.* **1951**, *73*, 3055, 5188.
(30) Ballard, M. J.; Napper, D. H.; Gilbert, R. G.; Sangster, D. F. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1027.
(31) Ahmed, S. M.; El-Aasser, M. S.; Micale, F. J.; Poehlein, G. W.; Vanderhoff, J. W. In *Polymer* Colloids *II*; Fitch, R. M.; Ed.; Plenum: New York, 1980; p 265.
(32) Ottewill, R. H.; Walker, T. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 917.
(33) Penboss, I. A.; Gilbert, R. G.; Napper, D. H. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2247.
(34) Nomura, M.; Sasaki, S.; Harada, M.; Eguchi, W. *J. Appl. Polym. Sci.* **1978**, *22*, 1043.

Semiempirical Determination of Solution Structure in Polymer Solutions Based on the Clustering Theory

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Received March 26, 1987; Revised Manuscript Received May 29, 1987

ABSTRACT: The solution structure in polymer solutions polystyrene(PS)–toluene, PS–cyclohexane, natural rubber(NR)–benzene, poly(*n*-butyl acrylate)(PNBA)–toluene, and polyisobutylene(PIB)–*n*-pentane has been determined based on the clustering theory by Zimm and by Kirkwood and Buff, which is expressed by $G_{00}/\bar{v}_0 = -\phi_1\{\partial(a_0/\phi_0)/\partial a_0\}_{P,T} - 1$, where G_{00} is the clustering function of solvent, $\bar{v}_0$ is the partial molecular volume of solvent, a_0 is the activity of solvent, and ϕ_0 and ϕ_1 are the volume fraction of solvent and polymer, respectively. Values of $G_{00}/\bar{v}_0$ determined in this work are 0.54 for PS–toluene, 10.0 for PS–cyclohexane, 1.67 for NR–benzene, 0.13 for PNBA–toluene, and 5.0 for PIB–*n*-pentane. The volume or segment fraction activity coefficients of solvent for the polymer solutions are found to be expressed by using the clustering theory $a_0/\phi_0 = A_0(\phi_0 + \beta - 1)^{-\beta}$ for the infinite molecular weight of polymer, which is essentially equivalent with that of the Huggins–Miller–Guggenheim theory where A_0 and β are constants and β is defined by $1 + (G_{00}/\bar{v}_0)^{-1}$. It is also found that the equation of a_0/ϕ_0 obtained in this work explains the concentration dependence of the polymer–solvent interaction parameter.

Introduction

The Flory–Huggins theory is the most fundamental theory in investigating the thermodynamic properties of polymer solution where the polymer–solvent interaction parameter χ is assumed to be independent of concentration and inversely proportional to the absolute temperature of the solution.[1] Apart from the configurational entropy term of the chemical potential in the theory, the two main assumptions for the χ parameter have been modified through the experimental observation of the concentration dependence of the χ parameter and the lower critical solution temperature observed in most of the nonpolar polymer solutions.[1-6] New expressions of χ for temperature, pressure, and concentration in the corresponding states theory by Flory[7,8] and Patterson[9,10] predict the upper and lower critical solution temperatures and their pressure dependence[2-6,11-13] and concentration dependence on χ.[7,8,14] On the other hand, Koningsveld and Kleintjens[15] proposed a closed expression for χ with respect to polymer concentration, which is derived from the free-energy expression of the Flory–Huggins theory with a concentration-dependent function of the polymer–solvent interaction parameter.

The other assumption used in the Flory–Huggins theory is the random mixing approximation. One of the earliest attempts to include the effect of inhomogeneity on solution thermodynamics was that of Kirkwood and Buff.[16] Zimm[17,18] developed a simple relation between the activity coefficient and the solvent clustering function on the basis of the Kirkwood–Buff theory. Fixman[19] attempted to determine the free energy by using the concentration-dependent interacton potentials and radial distribution functions. Huggins[20] derived an equation for the additional entropy term to the combinatorial entropy resulting from the concentration dependence of the randomness of orientation. A correlation between the local composition and overall mean concentration has been proposed by Renuncio and Prausnitz[21] and Brandani.[22]

In this work, we have examined the random mixing approximation used in most polymer solution theories through determination of the clustering function $G_{00}/\bar{v}_0$ in the Kirkwood–Buff–Zimm theory. We have also discussed a semiempirical equation on the activity coefficient of solvent derived in this work on the basis of the Huggins–Miller–Guggenheim theory,[23-25] the Flory theory of corresponding states, and the Koningsveld and Kleintjens theory.[15]

Semiempirical Determination of Clustering Function Based on the Kirkwood–Buff–Zimm Theory

Zimm[17] has derived the clustering function based on the Kirkwood–Buff theory,[16] which is given by

$$G_{00}/\bar{v}_0 = kT\kappa/\bar{v}_0 - \phi_1\{\partial(a_0/\phi_0)/\partial a_0\}_{P,T} - 1 \qquad (1)$$

where κ is the isothermal compressibility of the system, $\bar{v}_0$ is the partial molecular volume, ϕ_i is the volume fraction of solvent (0) and polymer (1), a_0 is the activity of solvent, and k is the Boltzmann constant. In this calculation, we used two assumptions in determining $G_{00}/\bar{v}_0$ and the

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Table I
Clustering Constants β, K, and $G_{00}/\bar{v}_0$ and χ Parameters Determined in This Work

system[a]	temp, °C	β	$-K$	$G_{00}/\bar{v}_0$	$\ln A_0$	$\beta \ln \beta$	$\sum \chi_i$[b]
PS–toluene	60	2.85	1.54	0.54	2.99	2.98	0.23
PS–cyclohexane	34	1.10	11.0	10.0	0.105	0.105	1.64
NR–benzene	25	1.60	2.67	1.67	0.75	0.75	0.57
PNBA–toluene	23.5	9.00	1.13	0.13	19.8	19.8	0.06
PIB–*n*-pentane	25	1.20	6.00	5.00	0.215	0.218	1.15

[a] Segment fraction is used in determining these constants except for PS–cyclohexane where volume fraction is used. [b] Calculated by eq 31.

equation for the activity coefficient of solvent, a_0/ϕ_0. The first one is a neglection of the compressibility term in eq 1, which is very small. Therefore eq 1 is given by

$$G_{00}/\bar{v}_0 = -\phi_1 \{\partial(a_0/\phi_0)/\partial a_0\}_{P,T} - 1 \quad (2)$$

The second one is that $G_{00}/\bar{v}_0$ is constant over the entire concentration, which is expressed by

$$\phi_1 \{\partial(a_0/\phi_0)/\partial a_0\}_{P,T} = K \quad (3)$$

where K is a constant. The expression for $G_{00}/\bar{v}_0$ using eq 3 is given by

$$G_{00}/\bar{v}_0 = -(K + 1) \quad (4)$$

The following equation is derived by using eq 3:

$$(\partial a_0/\partial \phi_0)/a_0 = -(1 - \phi_0)/[\phi_0\{\phi_0(K + 1) - 1\}] \quad (5)$$

By integrating eq 5 with respect to ϕ_0, we obtained

$$\ln (a_0/\phi_0) = -\{K/(K + 1)\} \ln |\phi_0(K + 1) - 1| + \ln C(P,T) \quad (6)$$

or

$$a_0/\phi_0 = C(P,T)|\phi_0(K + 1) - 1|^{-K/(K+1)} \quad (7)$$

$$a_0/\phi_0 = A_0(P,T)|\phi_0 - 1 + \beta|^{-\beta} \quad (8)$$

where A_0 and β are defined by

$$\beta = K/(K + 1) \quad (9)$$

and

$$A_0(P,T) = C(P,T)|1/(1 - \beta)|^{-\beta} \quad (10)$$

The relation between $G_{00}/\bar{v}_0$ and β is given by using eq 4 and 9 as

$$G_{00}/\bar{v}_0 = 1/(\beta - 1) \quad (11)$$

Experimental Determination of the Clustering Constant β or K Based on the Semiempirical Equation 8

Determination of β or K in eq 8 has been carried out using the experimental data for the activity coefficient for various polymer solutions such as polystyrene(PS)–toluene,[26] PS–cyclohexane,[27] natural rubber(NR)–benzene,[14] poly(*n*-butyl acrylate)(PNBA)–toluene,[28] and polyisobutylene(PIB)–*n*-pentane.[29] These data are analyzed by using the segment fraction for these polymer solutions except for polystyrene–cyclohexane where the volume fraction is used. The segment fraction defined in the corresponding states theory is expressed by[7,8]

$$\psi_i = w_i v^*_{i,sp}/(w_0 v^*_{0,sp} + w_1 v^*_{1,sp}) \quad (12)$$

where w_i is the weight fraction of solvent (0) and polymer (1) and $v^*_{i,sp}$ is the specific characteristic volume reduction parameter of component i. We use ϕ as a concentration for further discussions. Values of β in eq 8 are determined by

$$\ln (a_0/\phi_0) = \ln A_0 - \beta \ln |\phi_0 + \beta - 1| \quad (13)$$

The plots of $\ln (a_0/\phi_0)$ vs $\ln |\phi_0 + \beta - 1|$ are shown in Figures 1–3 where a linearity is observed over the wide concentration range within experimental error. Values of β, K, and $G_{00}/\bar{v}_0$ determined in this work are listed in Table I where it is shown that $G_{00}/\bar{v}_0$ values for these polymer solutions are positive, suggesting that the mean number of solvent molecules in excess of the mean concentration in the neighborhood of a given solvent molecule characterized by $\phi_0 G_{00}/\bar{v}_0$[30] is positive and increases with in-

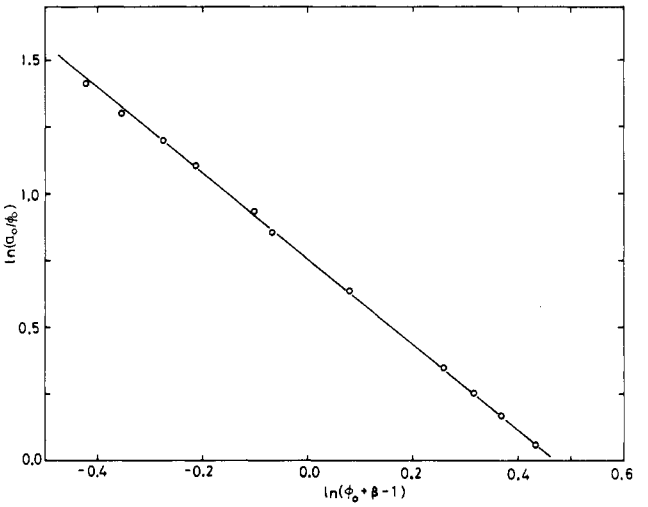

Figure 1. $\ln (a_0/\phi_0)$ vs $\ln (\phi_0 + \beta - 1)$ plot for natural rubber–benzene at 25 °C with $\beta = 1.60$. Data are taken from ref 14.

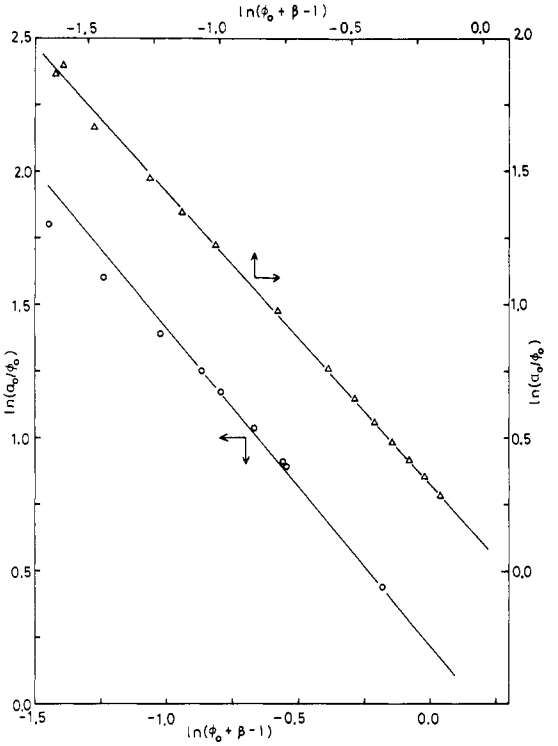

Figure 2. $\ln (a_0/\phi_0)$ vs $\ln (\phi_0 + \beta - 1)$ plot for polyisobutylene–*n*-pentane (○, ref 29) at 25 °C with $\beta = 1.20$ and polystyrene–cyclohexane (△, ref 27) at 34 °C with $\beta = 1.10$.

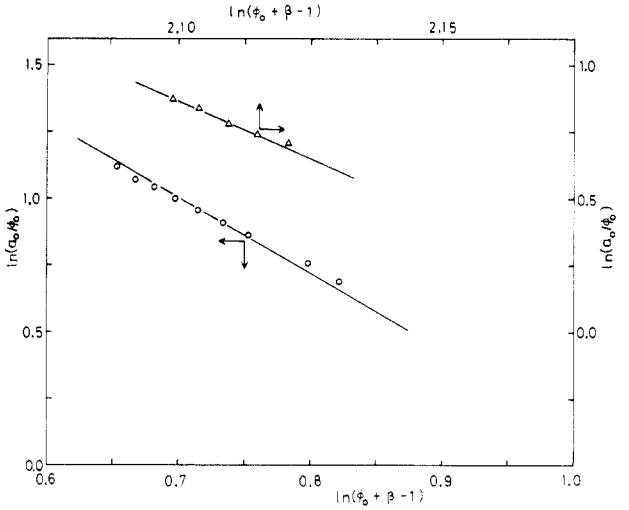

Figure 3. ln (a_0/ϕ_0) vs ln $(\phi_0 + \beta - 1)$ plot for polystyrene–toluene (○, ref 26) at 60 °C with $\beta = 2.85$ and poly(*n*-butyl acrylate)–toluene (△, ref 28) at 23.5 °C with $\beta = 9.00$.

creasing the solvent concentration. The clustering tendency of solvent molecule in solution indicates a state of inhomogeneous concentration or nonrandom mixing for polymer solutions. Values of $G_{00}/\bar{v}_0$ for poor solvent systems such as PS–cyclohexane and PIB–*n*-pentane are much larger than one, while those for PS–toluene and PNBA–toluene are almost zero, which indicates a state of homogeneous-like solution structure.

Discussions

It is interesting to compare the expression of a_0/ϕ_0 derived in this work based on the clustering theory and that of the Huggins–Miller–Guggenheim theory based on the lattice theory, which is expreessed for a system with negligible polymer–solvent interaction by

$$a_0/\phi_0 = 1/\{1 - 2(1 - r^{-1})(1 - \phi_0)/z\}^{z/2} \qquad (14)$$

where r is the ratio of molar volume of polymer to that of solvent, ϕ_0 is the volume fraction of solvent, and z is the coordination number in the lattice. It is convenient to rewrite eq 14 as

$$a_0/\phi_0 = \{z/2(1 - r^{-1})\}^{z/2}/\{z/2(1 - r^{-1}) - 1 + \phi_0\}^{z/2} \qquad (15)$$

or

$$a_0/\phi_0 = C_0^{C_0}/(C_0 - 1 + \phi_0)^{C_0} \qquad r \gg 1 \qquad (16)$$

where C_0 is given by

$$C_0 = z/2 \qquad (17)$$

It is obvious that eq 16 is essentially equivalent with eq 8 derived from the clustering function, which confirms the validity of the assumption of eq 3. The constant C_0 in eq 16 is equal to $z/2$ and also to β in eq 8, although the physical meaning is quite different because β is related to $G_{00}/\bar{v}_0$ in eq 11. It is found from eq 11 that if β is very large, $G_{00}/\bar{v}_0$ approaches zero, indicating no cluster tendency or random mixing and $z \gg 1$. In the Flory–Huggins theory, it is assumed that the coordination number z is infinite and there is maximum flexibility of the polymer chain and also random mixing. One can say from these facts that the Flory–Huggins theory corresponds to the case of $G_{00}/\bar{v}_0 = 0$ or $\beta \to \infty$, while the Huggins–Miller–Guggenheim theory for the case of $G_{00}/\bar{v}_0 \neq 0$ or β is finite. It is also interesting to point out that the clustering function $\phi_0 G_{00}/\bar{v}_0$ approaches zero in the limit of $\phi_0 = 0$, corresponding to a pure state of polymer. On the other hand, the polymer solution in the neighborhood of zero solvent concentration is in a state of homogeneous concentration or randomly or uniformly mixing irrespective of the systems. The result comes from the assumption that $G_{00}/\bar{v}_0$ is constant. (See eq 3.)

Extensive work on the polymer solution thermodynamics has been done by many authors theoretically and experimentally.[31-36] One of the central problems in the polymer solution thermodynamics is the concentration dependence of the χ parameter since its first treatment by Flory.[1] Flory derived χ as a function of temperature, pressure, and concentration based on the corresponding states theory where the partition function for the mixture is expressed by

$$Z_{mix} = Z_{comb}\Omega \exp(-E_0/kT) \qquad (18)$$

and the Gibbs free energy of mixing is given by

$$\Delta G_{mix} = \Delta G_{comb} + G^R \qquad (19)$$

where Z_{comb} is a combinatorial factor, Ω is related to the total free volume available to the system, and E_0 is the mean intermolecular energy of the system. The quantity ΔG_{comb} is equal to $-T\Delta S_{comb}$, while G^R is the residual free energy arising from the equation of state part of the partition function, $\Omega \exp(-E_0/kT)$. The chemical potential is given by

$$(\mu_0 - \mu_0^0)/RT = \ln a_0 = \ln (1 - \phi_1) + (1 - r^{-1})\phi_1 + \{(\mu_0 - \mu_0^0)^R/RT\phi_1^2\}\phi_1^2 \qquad (20)$$

The χ parameter is defined by the reduced residual chemical potential,

$$\chi \equiv (\mu_0 - \mu_0^0)^R/RT\phi_1^2 \qquad (21)$$

Expansion of χ in powers of ϕ_1 leads to

$$\chi = \chi_1 + \chi_2\phi_1 + \chi_3\phi_1^2 + \ldots \qquad (22)$$

On the other hand, Koningsveld and Kleintjens[15] proposed the closed expression for χ by taking into account the difference between the site or interacting surface fraction and the volume fraction based on the free enthalpy of mixing, G_{fe},

$$G_{fe}/NRT = \phi_0 \ln \phi_0 + \sum_i \phi_i m_i^{-1} \ln \phi_i + \Psi(\phi_1) \qquad (23)$$

where m_i is the chain length of polymer species i and

$$\Psi(\phi_1) = g\phi_0\phi_1 \qquad (24)$$

where

$$g = \alpha + (z - 2)(\Delta w_{0p}/RT)(1 - 2\,\phi_1/z)^{-1} \qquad (25)$$

The quantity Δw_{0p} expresses the difference between the interaction free enthalpy of unlike neighbors and the arithmetic mean of the values for identical neighbors and α is an empirical entropy correction of the form $\alpha\phi_0\phi_1$. The interaction parameter χ corresponding to eq 21 is given by

$$\chi = g - \phi_0\,(\partial g/\partial\phi_1) = \alpha + \beta_0(1 - \gamma)/(1 - \gamma\phi_1)^2 \qquad (26)$$

where γ corresponds to $2/z$ and β_0 to $(z - 2)(\Delta w_{0p}/RT)$.

It is interesting to compare the equation for χ by Flory and Koningsveld and Kleintjens with that derived in this work, which is expressed by using eq 8, 20, and 21 as

$$\chi = \{\ln A_0(\beta - \phi_1)^{-\beta} - (1 - r^{-1})\phi_1\}/\phi_1^2 \qquad (27a)$$

or

$$\chi = \{\ln A_0(\beta - \phi_1)^{-\beta} - \phi_1\}/\phi_1^2 \qquad r \gg 1 \qquad (27b)$$

If we use a condition that a_0/ϕ_0 approaches one in the limit of $\phi_0 \to 1.0$, the result $A_0 = \beta^\beta$ is obtained from eq 8. The

Table II
Experimental Values of χ_1 and χ_2 in the Poly(dimethylsiloxane) Solutions[37] and χ_i Calculated by Using Equation 30

system	temp, °C	$\chi_{1,obsd}$	$\chi_{2,obsd}$	$\chi_{1,calcd}$	$\chi_{2,calcd}$	β
PDMS–chlorobenzene	20	0.475	0.324	0.485	0.314	1.03
PDMS–chlorobenzene	60	0.455	0.319	0.472	0.297	1.06
PDMS–toluene	20	0.455	0.297	0.463	0.286	1.08
PDMS–cyclohexane	20	0.409	0.169	0.382	0.194	1.31

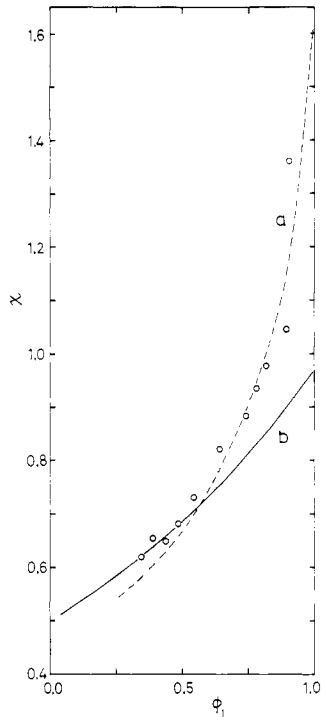

Figure 4. Polymer–solvent interaction parameter χ vs ϕ_1 volume fraction of solvent in the polystyrene–cyclohexane system; (O) experimental data (ref 27); (a) $\chi - \phi_1$ calculated by eq 28 with $\beta = 1.10$; (b) $\chi - \phi_1$ calculated by eq 26 with $\alpha = -0.1597$, $\gamma = 0.2365$, and $\beta_0 = \beta_{00} + \beta_{01}/T$, where $\beta_{00} = 0.4987$, $\beta_{01} = 111.74$, and $T = 307$ K (34 °C). (See ref 15.)

expression of χ is given more simply by using the above result as

$$\chi = -\{\beta \ln (1 - \phi_1/\beta) + \phi_1\}/\phi_1^2 \quad r \gg 1 \qquad (28)$$

where χ is expressed by a single parameter, β. Typical values of χ calculated by eq 28 for PS–cyclohexane are shown in Figure 4, in which values of χ calculated by using eq 26 are also included. It is also interesting to find a relation between β and χ parameters over the moderately concentrated range $0.1 < \phi_1 < 0.3$, where ϕ_1 is much smaller than one. We also assume that the lattice theory is valid over the concentration range, except an extremely diluted concentration range. The function of χ is given by using the Taylor expansion of eq 28

$$\chi = (2\beta)^{-1} + (3\beta^2)^{-1}\phi_1 + (4\beta^3)^{-1}\phi_1^2 + \ldots \qquad (29)$$

From correspondence between eq 22 and 29, it is obtained that

$$\chi_i = \{(i + 1)\beta^i\}^{-1} \quad (i = 1, 2, 3, \text{etc.}) \qquad (30)$$

It is found experimentally that values of $\chi_1 = 0.50$ and $\chi_2 = 0.31$ for polyisobutylene–benzene at 24.5 °C (the θ point)[31] and $\chi_1 = 0.50$ and $\chi_2 = 0.33$ for PS–cyclohexane at 34 °C (the θ point),[27] which agree with the prediction by eq 30 with $\beta \approx 1.0$. It is shown in Table II that a reasonable agreement between eq 30 and experimental values of χ_1 and χ_2 is obtained in the poly(dimethylsiloxane) solutions.[37]

It is also pointed out that the condition $\ln A_0 = \beta \ln \beta$ is satisfied in the polymer solutions in this work within experimental error. (See Table I.) The value of $\sum\chi_i$ is evaluated from the value of χ in the limit of $\phi_1 = 1.0$ by using eq 28 and

$$\sum\chi_i = -\{\beta \ln (1 - \beta^{-1}) + 1\} \qquad (31)$$

which are listed in Table I. It is noteworthy that if β approaches to one from a value larger than one, $G_{00}/\bar{v}_0$ becomes infinite. (See eq 11.)

It is very interesting to refer to the theoretical works of the solution structure. Fixman[19] pointed out that the properties of a random distribution of segments at high concentration are explained by the fact that the nonrandom distribution of segments belonging to a single polymer molecule is precisely compensated by a deficiency of segments belonging to other molecules and the deficiency approaches a constant value as the concentration is increased. Huggins[20] also pointed out that the magnitude of the departure of the combinatorial entropy of solution from that calculated on the assumption of perfect randomness should be a function of the equilibrium constant K, which governs the relative total contact areas for the different types. According to the present analysis of experimental data for the activity coefficient in polymer solutions, it is suggested that the structure of polymer solution is characterized by a solution of inhomogeneous concentration in most of the systems and the cluster of solvent in the solution becomes smaller with increasing polymer concentration and disappears at the limit of zero solvent concentration where the concentration is uniform and the system is in a state of random mixing. It is also found that the concentration dependence of the polymer–solvent interaction parameter is attributed to the clustering tendency of solvent β, and a large concentration dependence of χ occurs at a small value of β. Essentially an equivalence between the equation of the Huggins–Miller–Guggenheim theory on the activity coefficient of solvent and that derived from the clustering theory by the Kirkwood–Buff–Zimm theory is also obtained in this work.

Registry No. PS, 9003-53-6; PNBA, 9003-49-0; PIB, 9003-27-4; toluene, 108-88-3; cyclohexane, 110-82-7; benzene, 71-43-2; pentane, 109-66-0.

References and Notes

(1) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University: Ithaca, NY, 1953.
(2) Flory, P. J.; Shih, H. *Macromolecules* **1972**, *5*, 761.
(3) Saeki, S.; Holste, J. C.; Bonner, D. C. *J. Polym. Sci., Polym. Phys.* **1981**, *19*, 307.
(4) Freeman, P. I.; Rowlinson, J. S. *Polymer* **1960**, *1*, 20.
(5) Cowie, J. M. G.; Maconnachie, A.; Ranson, R. J. *Macromolecules* **1971**, *4*, 57.
(6) Saeki, S.; Kuwahara, N.; Konno, S.; Kaneko, M. *Macromolecules* **1973**, *6*, 246.
(7) Flory, P. J.; Orwoll, R. A.; Vrij, A. *J. Am. Chem. Soc.* **1964**, *86*, 3507.
(8) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833.
(9) Patterson, D.; Delmas, G. *Trans. Faraday Soc.* **1969**, *61*, 708.
(10) Patterson, D. *J. Polym. Sci.*, Part C **1968**, *16*, 3379.
(11) Zeman, L.; Patterson, D. *J. Phys. Chem.* **1972**, *76*, 1214.
(12) Saeki, S.; Kuwahara, N.; Kaneko, M. *Macromolecules* **1976**, *9*, 101.
(13) Saeki, S.; Kuwahara, N.; Hamano, K.; Kenmochi, Y.; T. *Yamaguchi*, T. *Macromolecules* **1986**, *19*, 2353.
(14) Eichinger, B. E.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *64*, 2035.

(15) Koningsveld, R.; Kleintjens, L. A. *Macromolecules* **1971**, *4*, 637.
(16) Kirkwood, J. G.; Buff, F. P. *J. Chem. Phys.* **1951**, *19*, 774.
(17) Zimm, B. H. *J. Chem. Phys.* **1953**, *21*, 934.
(18) Zimm, B. H.; Lundberg, J. L. *J. Phys. Chem.* **1956**, *60*, 425.
(19) Fixman, M. *J. Chem. Phys.* **1960**, *35*, 889.
(20) Huggins, M. L. *J. Phys. Chem.* **1971**, *75*, 1255.
(21) Renuncio, J. A. R.; Prausnitz, J. M. *Macromolecules* **1969**, *9*, 898.
(22) Brandani, V. *Macromolecules* **1979**, *5*, 883.
(23) Huggins, M. L. *Ann. N. Y. Acad. Sci.* **1942**, *43*, 9.
(24) Miller, A. R. *Proc. Cambridge, Philos. Soc.* **1943**, *39*, 54.
(25) Guggenheim, E. A. *Proc. R. Soc. London, Ser. A.* **1944**, *183*, 203.
(26) Unpublished results, 1987.
(27) Krigbaum, W. R.; Geymer, D. O. *J. Am. Chem. Soc.* **1959**, *81*, 1859.
(28) Saeki, S.; Holste, J. C.; Bonner, D. C. *J. Polym. Sci., Polym. Phys.* **1983**, *21*, 2049.
(29) Eichinger, B. E.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *64*, 2066.
(30) Lundberg, J. L. *J. Macromol. Sci. Phys.* **1969**, *B3*(4), 693.
(31) Flory, P. J.; Daoust, H. *J. Polym. Sci.* **1957**, *25*, 429.
(32) Sanchez, I. C.; Lacombe, R. H. *Macromolecules* **1978**, *11*, 1145.
(33) Hamada, F.; Shiomi, T.; Fugiwara, K.; Nakajima, A. *Macromolecules* **1980**, *13*, 729.
(34) Sanchez, I. C.; Lohse, D. J. *Macromolecules* **1981**, *14*, 131.
(35) Masegosa, R. M.; Prolongo, M. G.; Horta, A. *Macromolecules* **1986**, *19*, 1478.
(36) Nakajima, N.; Huang, C. D. *J. Macromol. Sci. Phys.* **1986**, *B25*(4), 395.
(37) Kuwahara, N.; Okazawa, T.; Kaneko, M. *J. Polym. Sci., Part C* **1968**, *23*, 543.

Ordered Packing Arrangements of Spherical Micelles of Diblock Copolymers in Two and Three Dimensions

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ABSTRACT: Structural data are presented on the ordered arrangements of spherical micelles of diblock copolymers in two dimensions [transmission electron microscopy (TEM) of solution cast films containing a single layer of domains] and in three dimensions [TEM of microtomed sections and small-angle X-ray scattering (SAXS) from bulk samples]. The lattice type of the micelle cores in the two-dimensional thin film is hexagonal, and in the three-dimensional bulk state it is body centered cubic. A simple packing model that addresses the problem of uniform covering of the matrix space by the corona chains for a given lattice suggests that considerable interpenetration of neighboring micelle segmental density profiles occurs. The mode of packing is dictated by the optimal covering lattice that minimizes the unfavorable deformation of the matrix chains as they uniformly fill the matrix space.

Introduction

There have been numerous studies of the morphology and thermodynamics of block copolymers in the last two decades. The scale of microphase separation is typically hundreds of angstroms so that SAXS and TEM have proven to be useful techniques for structural investigations. Such studies established that under nearly equilibrium conditions, the microphase separation results in the formation of regular arrays of spheres, cylinders or lamellae, depending on the volume fractions of the components.[1] Recently an additional morphology, that of the ordered bicontinuous double diamond structure, was discovered.[2]

Theoretical statistical mechanical treatments of block copolymers have been primarily concerned with the location of the microphase transition and with elucidation of the ranges of the various sample morphologies (e.g., spheres, cylinders, lamellae) as a function of molecular weight and composition. In the compositional range for spherical microdomains (micelles), the treatments of Meier[3] and Helfand and Wasserman[4] both assume a priori FCC packing of spheres and proceed to calculate micelle core size and intermicelle distance as a function of block molecular weight and composition. Leibler's[5] approach utilizes fluctuation theory to determine the symmetry of the microphase separated state at the onset of the transition from the high-temperature homogeneous state. He evaluated several possible lattice types for spherical domains (SC, BCC, FCC, and rhombohedral) and found that the BCC arrangement offered the lowest free energy. Ohta and Kawasaki's recent calculations show that a BCC arrangement is only slightly more favored than FCC[6].

The best experimental evidence[7,8] for the lattice type of block copolymer samples exhibiting a spherical microdomain morphology strongly suggests a BCC arrangement does indeed occur, although there are a number of published reports of SC, FCC, and even orthorhombic arrangements.[9-13] The data are of two kinds: (i) TEM of OsO_4-stained sections wherein different symmetry projections are identified and assigned to various (*hkl*) projections and the relative interdomain spacings compared to the various lattice arrangements and (ii) SAXS of bulk samples where based on micelle core size from the position of the form factor peak and on the intermicelle separation from the position of the lower angle interference peaks, the volume fraction of domains is compared to the known volume fraction of the domain forming minority component. A critical issue on proper assignment of the lattice type is attainment of pseudoequilibrium conditions—evidenced by development of long-range order in the sample. In all cases the studies[9-13] suggesting non-BCC structures suffer from the lack of well-developed long-range order, and, for this reason, their assignment of a particular lattice type is highly suspect.

In the course of our investigations on diblock copolymers, we have encountered the ordering of spherical domains in bulk and in ultrathin films. As will be shown, the lattice structure of spherical microdomains in the bulk

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0024-9297/87/2220-2934$01.50/0