Macromolecules **1991,** *24,* 3368-3372

Equation of State Theory for Melting Point Depression in Miscible Polymer Blends

Won Ho Jo* and Ick Hwan Kwon

Department of Textile Engineering, Seoul National University, Seoul, 151-741, Korea

Received August 7, 1990; Revised Manuscript Received January 9, 1991

ABSTRACT: The equation for equilibrium melting point depression in a polymer mixture is derived based on the equation of state theory. For two miscible blend systems poly(methyl methacrylate)/poly(vinylidene fluoride) and poly(vinyl chloride)/poly(ethylene oxide), the newly derived equation is tested. The interaction parameter X_{12} between two polymers in a mixture can be estimated from this equation. When the estimated interaction parameter is converted to Flory-Huggins interaction paramter χ via the equation of state theory, the composition dependence of χ can be properly predicted. The equation for nonequilibrium melting point depression is also suggested; however, the interaction parameter in a polymer mixture cannot be precisely estimated without the correct consideration of a morphological effect on the nonequilibrium melting point depression.

Introduction

The thermodynamic properties of polymer solutions have been commonly interpreted with Flory-Prigogine's equation of state theory.[1-3] Flory-Prigogine's theory follows Prigogine's approaches,[4] which introduce the cell model to chain molecule liquids and factorize the degree of freedom of a molecule in a liquid into internal and external degrees of freedom. The basic assumptions of the theory[1] are the intermolecular energy, which depends only on the volume, and the hard-sphere repulsive potential for segments of the chain. The mean intermolecular energy is supposed to be of the van der Waals type, i.e., an energy inversely proportional to volume. This theory has been proven to be quite successful in explaining many thermodynamic properties such as the lower critical solution temperature behavior, volume change on mixing, heat of mixing, and composition dependence of the Flory-Huggins interaction parameter that Flory-Huggins theory failed to explain.[5,6]

The determination of interaction parameter X_{12} is a prerequisite to the prediction of the thermodynamic quantities of polymer mixtures from the equation of state theory. There are several ways to determine X_{12}. For instance, X_{12} can be determined by fitting the theoretical values of the thermodynamic quantity to its experimental data of the mixtures such as the heat of mixing,[7] liquid-liquid phase separation,[7,8] and chemical potential measured by the solvent vapor sorption technique[5] or membrane osmometry.[3]

The equations for the melting point depression in a polymer mixture have been derived on the concept of Flory-Huggins theory.[10-12] These equations are simple and widely used to determine the Flory-Huggins interaction parameter χ with the assumption of composition independence of χ. Nevertheless, χ is proven to be composition dependent,[5] and thus these simple equations may lead to an ambiguous estimation of the interaction parameter. Such an ambiguity can be overcome by use of the equation of state (EOS) theory. Recently Walsh et al.[9] and Rostami[19] have interpreted the melting point depression in a polymer mixture with the EOS theory. They derived the EOS equation for melting point depression based on the concept of the Kwei approach,[11] which seems to have some problems in basic assumptions. Furthermore, they committed mistakes in the derivation and the estimation of the interaction parameter. Rostami[19] has derived the equation for nonequilibrium melting point depression based on the irrelevant thermodynamic relation between the equilibrium and nonequilibrium melting temperatures. In Rostami's formalism, the difference between the nonequilibrium melting point, T_{mb}, and the equilibrium melting point, $T_{\mathrm{mb}}°$, of a polymer mixture arises from both morphological and thermodynamic interaction effects. However, according to the relation between T_{mb} and $T_{\mathrm{mb}}°$ proposed by Hoffman and Weeks,[13] the difference between T_{mb} and $T_{\mathrm{mb}}°$ is related only to the morphological effect. He has derived another melting point depression equation with the assumption that the equilibrium melting point, $T_{\mathrm{mb}}°$, in the blend is the same as the equilibrium melting point, $T_{\mathrm{m}}°$, in the pure crystalline polymer. Such an assumption is only permissible for the system in which there is no thermodynamic interaction between the constituents. Furthermore, he does not provide the method to determine the interaction parameter X_{12} with his equation.

In this report, the equation for melting point depression of polymer blends is newly derived based on the equation of state theory and its applications are also discussed.

Theory

The reduced equation of state[1] derived from the partition function is given at zero pressure by

$$1/\hat{\nu}\hat{T} = \hat{\nu}^{1/3}/(\hat{\nu}^{1/3} - 1) \tag{1}$$

where $\hat{\nu}$ and $\hat{T}$ are the reduced volume and temperature, respectively. The hard-core volume per segment, ν^*, the characteristic pressure, P^*, and the characteristic temperature, T^*, can be calculated from the measurements of the thermal expansion coefficient, α, the specific volume, v, and the thermal pressure coefficient, γ. The relations are given by

$$\hat{\nu} = \nu/\nu^* = [1 + \alpha T/3(1 + \alpha T)]^3 \tag{2}$$

$$\hat{T} = T/T^* = (\hat{\nu}^{1/3} - 1)/\hat{\nu}^{4/3} \tag{3}$$

$$P^* = \gamma T\hat{\nu}^2 \tag{4}$$

The application of this theory to mixtures of N_1r_1-mers and N_2r_2-mers is based on the mean-field approximation. Each mer has to be chosen in such a way as to have equal hard-core volumes. An interaction parameter X_{12} is introduced, which arises from considering the difference

0024-9297/91/2224-3368$02.50/0

Table I
Characteristic Parameters for Pure Polymers

polymer	M_w	P^*, J/cm^3	T^*, K	v^*, cm^3/mol	S, Å^{-1}
PMMA[a]	36 600	628	8702	33.6	1.36
PVDF[b]	215 800	590	7516	33.6	0.96
PVC[c]	100 000	468	7788	35.2	0.73
PEO[d]	35 000	471	7627	35.2	0.80

[a] From ref 16. [b] From ref 8. [c] From ref 17. [d] From ref 9.

in interaction energy between like and unlike segmental pairs. The equation of state for a two-component mixture has a form identical with that for the pure component if the following mixing rules[2] are made

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 X_{12} \qquad (5)$$

$$\frac{1}{T^*} = \frac{(\phi_1 P_1^* + \phi_2 P_2^*/T_2^*)}{(\phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 X_{12})} \qquad (6)$$

$$\theta_2 = S\phi_2/(S\phi_2 + \phi_1) \qquad (7)$$

where ϕ_1 and ϕ_2 denote the segment fractions of components 1 and 2, respectively, and θ_2 is the surface fraction of component 2. S is defined as S_2/S_1, the ratio of surface area per unit core volume.

The chemical potential of component 2 in the mixture is given by eq 8 where V_2^* is molar core volume of the component 2 molecule. The chemical potential per mole of the crystallizable polymer unit in the liquid phase is obtained by dividing eq 8 by r_2, the number of units per molecule 2. The chemical potential of component 2 in the crystalline phase can be written as

$$(\mu_2 - \mu_2{}^\circ)/RT = \ln \phi_2 + (1 - r_2/r_1)\phi_1 + P_2^* V_2^*/RT\{3\hat{T}_2 \ln [(\hat{\nu}_2{}^{1/3} - 1)/(\hat{\nu}^{1/3} - 1)] + (1/\hat{\nu}_2 - 1/\hat{\nu})\} + V_2^* X_{12} \theta_1{}^2 S/(\hat{\nu}RT) \qquad (8)$$

$$\begin{aligned}\mu_{2u} - \mu_{2u}{}^\circ &= -(\Delta H_{2u} - T_{mb}{}^\circ \Delta S_{2u}) \\ &= -\Delta H_{2u}(1 - T_{mb}{}^\circ/T_m{}^\circ) \qquad (9)\end{aligned}$$

where ΔH_{2u} and ΔS_{2u} are the enthalpy and entropy of fusion per mole of repeating unit, $T_m{}^\circ$ and $T_{mb}{}^\circ$ are the equilibrium melting temperatures in pure and mixed state, respectively, and $\Delta H_{2u}/\Delta S_{2u}$ is equal to $T_m{}^\circ$.

On the condition that the chemical potentials of component 2 in the crystalline and liquid phase should be identical at $T_{mb}{}^\circ$, we obtain eq 10 from eqs 8 and 9.

$$-\Delta H_{2u}(T_m{}^\circ - T_{mb}{}^\circ)/(RT_m{}^\circ T_{mb}{}^\circ) = \ln \phi_2/r_2 + (1/r_2 - 1/r_1)\phi_1 + P_2^* \nu_2^*/RT\{3\hat{T}_2 \ln [(\hat{\nu}_2{}^{1/3} - 1)/(\hat{\nu}^{1/3} - 1)] + (1/\hat{\nu}_2 - 1/\hat{\nu})\} + \nu_2^* X_{12} \theta_1^2 S/(\hat{\nu}RT) \qquad (10)$$

Results and Discussion

EOS Equation for Melting Point Depression. For two miscible blend systems poly(methyl methacrylate) (PMMA)/poly(vinylidene fluoride) (PVDF) and poly(vinyl chloride) (PVC)/poly(ethylene oxide) (PEO), the EOS equation for melting point depression is tested. The characteristic parameters of a pure component should be predetermined to interpret the melting point depression in a polymer mixture. The characteristic parameters taken from the literature[8,9,16,17] are listed in Table I. The ratio of surface area S_2/S_1 accessible for interactions with neighboring molecules is not regarded as an adjustable parameter but as a constant.

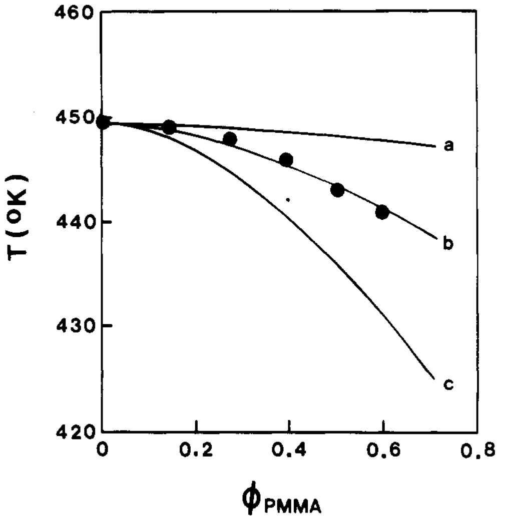

Figure 1. Equilibrium melting point depression of PMMA/PVDF blends as a function of PMMA volume fraction. The filled circles represent experimental values. The curves are calculated from eq 10: (a) X_{12} = -5 J/cm^3, (b) X_{12} = -17 J/cm^3, (c) X_{12} = -35 J/cm^3.

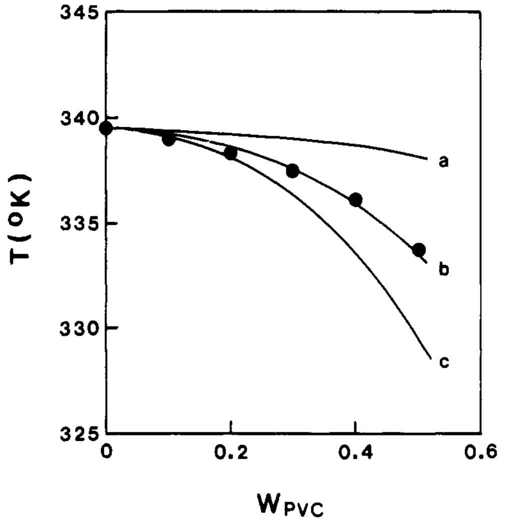

Figure 2. Equilibrium melting point depression of PVC/PEO blends as a function of PVC weight fraction. The filled circles represent experimental values. The curves are calculated from eq 10: (a) X_{12} = -5 J/cm^3, (b) X_{12} = -24 J/cm^3, (c) X_{12} = -40 J/cm^3.

From eq 10, the equilibrium melting temperatures of polymer mixtures can be determined for any given X_{12} value and blend composition according to the following procedure. $\hat{T}$ is defined as $T_{mb}{}^\circ/T^*$ in which the characteristic temperature of mixture T^* can be determined from eq 6. When $T_{mb}{}^\circ$ is arbitrarily chosen lower than the known $T_m{}^\circ$ in sequence, $\hat{\nu}$ can be determined from eq 3 at each arbitrary $T_{mb}{}^\circ$. Each of $T_{mb}{}^\circ$, $\hat{T}$, and $\hat{\nu}$ being substituted into eq 10, both sides of eq 10 can be calculated. The temperature at which the difference between the squared values of the left-hand side and the right-hand side of eq 10 shows a minimum is taken as the true equilibrium melting temperature ($T_{mb}{}^\circ$) at any given composition and X_{12} value.

The theoretical curves of $T_{mb}{}^\circ$ for the two miscible blend systems PMMA/PVDF and PVC/PEO are shown in Figures 1 and 2 at various X_{12} values. As might be expected, the lower X_{12} value, which denotes the stronger intermolecular interaction between the constituents of the mixture, leads to the more depression of $T_{mb}{}^\circ$. The X_{12} value of the blend system is determined when the

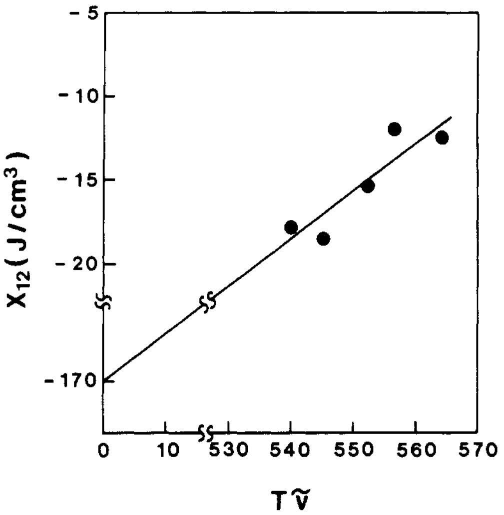

Figure 3. Plot of the interaction parameter X_{12} calculated from the experimental data versus $T\hat{\nu}$ in PMMA/PVDF blends.

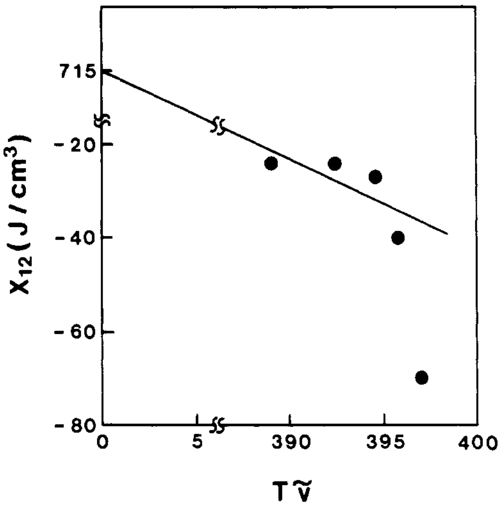

Figure 4. Plot of the interaction parameter X_{12} calculated from the experimental data versus $T\hat{\nu}$ in PVC/PEO blends.

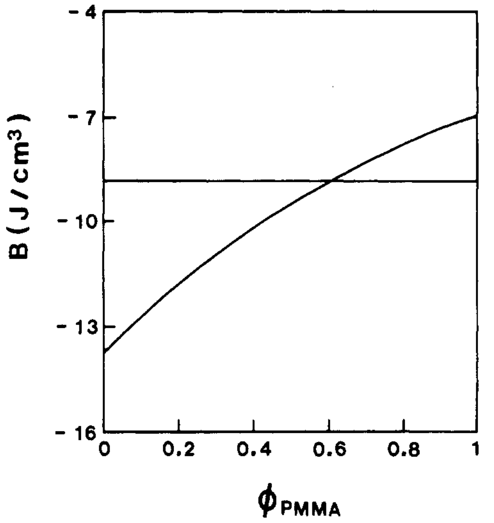

Figure 5. Theoretically calculated interaction energy density B as a function of PMMA volume fraction in PMMA/PVDF blends (X_{12} = -17 J/cm^3). The straight line represents the composition-independent B (-8.83 J/cm^3) determined from the Nishi-Wang equation.

theoretical $T_{\text{mb}}°$ shows a best fit to the experimental $T_{\text{mb}}°$ and its values are found to be -17 J/cm^3 for PMMA/PVDF and -24 J/cm^3 for PVC/PEO blends. Considering that the reported values of X_{12} for miscible polymer blends fall into the range of 0 to -50 J/cm^3,[8,9,16,18] these values for PMMA/PVDF and PVC/PEO blends seem to be quite reasonable.

Following Flory's arguments,[3] the entropic correction factor Q_{12} should be added to the potential energy. The product of the binary parameter Q_{12} by R is considered to represent the entropy due to interaction between unlike segments. Thus X_{12} in eq 10 can be replaced by $X_{12}' - T\hat{\nu}Q_{12}$, where X_{12}' and Q_{12} are not dependent on the blend composition, but X_{12} $(=X_{12}' - T\hat{\nu}Q_{12})$ depends on the blend composition owing to the composition dependence of $\hat{\nu}$.

When the experimentally determined equilibrium melting temperatures of mixtures are substituted to $T_{\text{mb}}°$ in eq 10, the values of X_{12} may be calculated as a function of blend composition as shown.

$$X_{12} = \frac{\hat{\nu}RT}{\nu_2^*\theta_1{}^2S}\left[\frac{\Delta H_{2\text{u}}(T_{\text{m}}° - T_{\text{mb}}°)}{RT_{\text{m}}°T_{\text{mb}}°} + \frac{\ln\phi_2}{r_2} + \left(\frac{1}{r_2} - \frac{1}{r_2}\right)\phi_1 + \frac{3P_2^*\nu_2^*\hat{T}_2}{RT}\ln\left(\frac{\hat{\nu}_2^{1/3} - 1}{\hat{\nu}^{1/3} - 1}\right)\right] = X_{12}' - T\hat{\nu}Q_{12} \quad (11)$$

At first glance Q_{12} and X_{12}' seem to be estimated from the slope and intercept of the plot of X_{12} against $T\hat{\nu}$, respectively. However, for both PMMA/PVDF and PVC/PEO blend systems the smooth straight lines are not obtained as shown in Figures 3 and 4; thus, the slope Q_{12} determined from the least-squares method gives a large error. Furthermore, since $T\hat{\nu} = 0$, to which X_{12} should be extrapolated in order to estimate the intercept X_{12}', is so far away from the experimental variation range of $T\hat{\nu}$, the unreasonably large positive or negative value of X_{12}' is obtained. It is also noteworthy that the variation range of the X_{12} value decreases with the increase of the amorphous polymer volume fraction when the error range in the experimentally determined $T_{\text{mb}}°$ is assumed to be constant in the whole blend composition. Therefore, at the high volume fraction of a crystalline polymer, the small error of $T_{\text{mb}}°$ has a large effect on the value of X_{12}. Consequently, the composition dependence of X_{12} does not seem to be properly interpreted. For PMMA/PVDF and PVC/PEO blends, the values of X_{12}' are -170 and 715 J/cm^3, respectively. Therefore, it is very erroneous to simultaneously determine X_{12}' and Q_{12} from melting point depression data, and only one parameter, the composition independent X_{12}, should be determined from eq 10.

The estimation of the interaction parameter determined from the EOS equation for melting point depression should be compared with that determined from the equation based on Flory-Huggins theory. The Flory-Huggins interaction parameter χ is identified as the residual chemical potential[5] and defined by eq 12.

$$\chi = \frac{(\mu_2 - \mu_2°)^R}{r_2(1 - \phi_2)^2RT} = \frac{BV_{1\text{u}}}{RT} = \frac{P_2^*\nu_2^*}{RT\phi_1{}^2}\left[3\hat{T}_2\ln\left(\frac{\hat{\nu}_2{}^{1/3} - 1}{\hat{\nu}^{1/3} - 1}\right) + \left(\frac{1}{\hat{\nu}_2} - \frac{1}{\hat{\nu}}\right)\right] + \frac{\nu_2^*X_{12}\theta_1{}^2S}{\phi_1{}^2\hat{\nu}RT} \quad (12)$$

By use of the above expression, the interaction energy density B can be calculated as a function of blend composition as shown in Figures 5 and 6. B values determined by the equation[10] based on Flory-Huggins theory are shown as the straight lines, indicating that B does not depend upon composition, and placed in the theoretically predicted range.

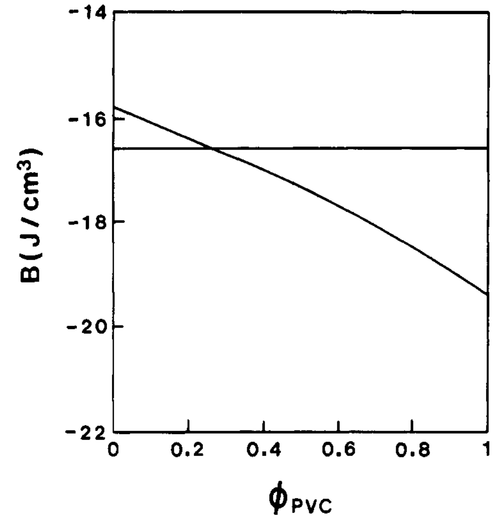

Figure 6. Theoretically calculated interaction energy density B as a function of PVC volume fraction in PVC/PEO blends ($X_{12} = -24$ J/cm^3). The straight line represents the composition-independent B (-16.6 J/cm^3) determined from the Nishi-Wang equation.

The concentration dependence of the calculated B values is sensitive to the value chosen for S_1/S_2. Although the equation of state contribution to B is insensitive to S_1/S_2, the values of $(\theta_1/\phi_1)^2 X_{12}$ in eq 12 depend markedly on S_1/S_2. When S_1/S_2 is larger than unity, the values of B increase with the volume fraction of component 1 as in the case of PMMA/PVDF blends. Since S_1/S_2 is less than unity in PVC/PEO blends, the value of B decreases as the volume fraction of PVC increases. Therefore, the introduction of S_1/S_2 as an arbitrary parameter should be avoided, and thus the accuracy in estimate of S_1/S_2 from the molecular geometry is essential.

Interpretation of the Kwei Equation. The nonequilibrium melting point depression may be interpreted with EOS theory. Kwei[11] reported the following equation to interpret the variation of nonequilibrium melting points on the concept of Flory-Huggins theory

$$\Delta H_{2u}(T_m - T_{mb})/\phi_1 R T_m - T_{mb}/r_1 - \phi_1 T_{mb}/2r_2 = C/R - T\chi\phi_1 \quad (13)$$

where T_m and T_{mb} are nonequilibrium melting temperatures in pure and mixed state, respectively, and C is a morphological correction constant. Kwei assumed that the morphological effect on the free energy or crystal size was linearly proportional to the volume fraction of amorphous polymer in a polymer mixture. $C\phi_1$ denotes the morphological variation with composition as

$$C\phi_1 = 2\sigma_e/L_B - 2\sigma_e/L \quad (14)$$

where σ_e is the fold surface free energy, L is the crystalline thickness of the pure crystallizable polymer, and L_B is the crystalline thickness of the crystalline component in the blend. When eq 13 is reformulated by the equation of state theory, it would then become

$$\Delta H_{2u}(T_m - T_{mb})/(\phi_1 R T_m) + T_{mb}/r_2(\ln(\phi_2)/\phi_1 + 1 - r_2/r_1) + P_2^* v_2^*/\phi_1 R(3\hat{T}_2 \ln[(\hat{v}_2^{1/3} - 1)/(\hat{v}^{1/3} - 1)] + (1/\hat{v}_2 - 1/\hat{v}) = C/R - v_2^* X_{12}\theta_1^2 S/(\phi_1 R\hat{v}) \quad (15)$$

Table II
Variation of Melting Temperature and Morphology with the Volume Fraction of PMMA in PMMA/PVDF Blends

ϕ_1(PMMA)	T_m,[a] K	$T_m°$,[a] K	$2\sigma_e/L$, J/mol	$2\sigma_e/L_B - 2\sigma_e/L$	$C\phi_1$, J/mol
0	444.3	449.5	83.6		
0.142	444.0	449.0	80.5	-3.1	-4.5
0.272	442.8	447.9	82.3	-1.3	-8.7
0.391	440.7	445.8	82.7	-0.9	-12.5
0.499	438.1	442.8	76.7	-6.9	-15.9
0.599	436.3	440.8	73.8	-9.8	-19.1

[a] From ref 14.

Table III
Variation of Melting Temperature and Morphology with the Weight Fraction of PVC in PVC/PEO Blends

w_1(PVC)	T_m,[a] K	$T_m°$,[a] K	$2\sigma_e/L$, J/mol	$2\sigma_e/L_B - 2\sigma_e/L$	$C\phi_1$, J/mol
0	333.0	339.5	152.4		
0.1	337.7	339.0	30.5	-121.9	-88.4
0.2	337.3	338.3	23.5	-128.9	-176.8
0.3	335.9	337.5	37.7	-114.7	-265.3
0.4	333.9	336.1	52.1	-100.3	-353.7
0.5	330.9	333.7	66.8	-85.6	-442.1

[a] From ref 15.

Before the melting point depression is interpreted in terms of eq 15, Kwei's assumption should be examined. According to the Hoffman-Weeks relationship,[13] the melting point depression ($\Delta T_m = T_m - T_{mb}$) is composed of two terms, one due to the thermodynamic depression ($\Delta T_m° = T_m° - T_{mb}°$) and another due to the difference in crystal thickness:

$$T_m = T_m°(1 - 2\sigma_e/\Delta H_{2u}L) \quad (16)$$

$$T_{mb} = T_{mb}°(1 - 2\sigma_e/\Delta H_{2u}L_B) \quad (17)$$

$$\Delta T_m = \Delta T_m° + 2\sigma_e/\Delta H_{2u}(T_{mb}°/L_B - T_m°/L) \quad (18)$$

The nonequilibrium melting temperature of an isothermally crystallized sample and equilibrium melting temperatures for PMMA/PVDF[14] and PVC/PEO[15] are shown in Tables II and III. When nonequilibrium melting points and equilibrium melting points are substituted into eqs 16 and 17, $2\sigma_e/L$ and $2\sigma_e/L_B - 2\sigma_e/L$ can be determined with the values of ΔH_{2u}(PVDF) = 7229 J/mol and ΔH_{2u}(PEO) = 7958 J/mol. When the left-hand side of eq 13 is plotted against ϕ_1, a slope of a straight line gives $-T\chi$ and an intercept is C/R. Thus the parameters C and χ are determined. The parameters C and χ of PMMA/PVDF blends are -31.9 J/mol and -0.11 at 443 K, and for PVC/PEO blends C and χ are -884.2 J/mol and -0.73 at 333 K. If Kwei's assumption (eq 14) is correct, the values of last two columns in Tables II and III should be equal. However, an extreme discrepancy is observed for PVC/PEO blends. Therefore, the assumption seems to lose adequacy. Such an unreasonable assumption may exert a bad effect upon determining the χ parameter. As a result, $\chi(T_m°)$ determined from equilibrium melting temperatures and $\chi(T_m)$ from nonequilibrium melting temperatures are -0.27 and -0.73 for PVC/PEO blends, respectively.

Walsh and co-workers[9] derived an equation for melting point depression according to Kwei's approach. The $C\phi_1$ term, which cannot properly reflect the morphological variation is also present in eq 15; thus X_{12} or X_{12}' cannot be precisely determined. When eq 15 is used to determine X_{12} in spite of such a shortcoming, the value of C obtained from the original Kwei equation should be used for C in eq 15. Following the method discussed in a previous section, the composition-independent X_{12} values are determined to show a best fit of the theoretical curve calculated from eq 15 to the experimental nonequilibrium melting points. The estimated X_{12} values are −19 J/cm^3 for PMMA/PVDF blends and −79 J/cm^3 for PVC/PEO blends. For PVC/PEO blends the X_{12} value (−79 J/cm^3) determined from nonequilibrium melting points is much different from the X_{12} value (−24 J/cm^3) determined from equilibrium melting points. This seems to result from the error in measuring the morphological variation.

By comparison of the equation derived by Walsh et al. with eq 15, the discrepancy can be observed in several terms, which originate from the chemical potential of component 2 in the amorphous region. It seems that the sign of $\mu_2 - \mu_2^\circ$ is incorrectly treated in their derivation. In Walsh's expression, X_{12} was replaced by $X_{12}' - T\hat{v}Q_{12}$; therefore, C/R, X_{12}', and Q_{12} should be determined. To avoid the complexity in determining the above parameters, they first arbitrarily choose X_{12}' in a moderate range and then the remaining parameters C/R and Q_{12} are determined by the least-squares method. C and Q_{12} would seem to be determined from the plot of $(C/R + v_2^*\theta_1^2ST/(\phi_1R)Q_{12})$ against $v_2^*\theta_1^2ST/(\phi_1R)$, but this plot is subject to the great variation by the small experimental error of determining T_{mb}. For PVC/PEO blends, the value (−884.2 J/mol) of C determined from the original Kwei equation is not equal to the value (−606.5 J/mol) determined from this plot. Moreover, the slope of the plot gives an unreasonably large positive Q_{12} value (0.8247). Thus, the use of the least-squares fitting method for the estimation of C and Q_{12} brings about the erroneous results. In their results, the value of C/R, which was known to be positive,[18] changed into negative due to the unreasonable regression.

Conclusions

The EOS equation for melting point depression is newly derived. From this equation the interaction parameter X_{12} can be determined. For PMMA/PVDF and PVC/PEO blends, X_{12} is estimated to be −17 and −24 J/cm^3, respectively. The composition dependence of the Flory–Huggins interaction parameter (χ) is properly predicted with the predetermined X_{12} value. It was realized that the simultaneous determination of X_{12}' and Q_{12} from experimental data would give erroneous results. It was found that the equation following Kwei's approach has some problems in determining X_{12} because of incorrect consideration of morphological effect on the nonequilibrium melting point depression.

References and Notes

(1) Flory, P. J.; Orwoll, R. A.; Vrij, A. *J. Am. Chem. Soc.* **1964**, *86*, 3507.
(2) Flory, P. J. *J. Am. Chem. Soc.* **1965**, *87*, 1833.
(3) Eichinger, B. E.; Flory, P. J. *Trans. Faraday Soc.* **1968**, *64*, 2035.
(4) Prigogine, I. *The Molecular Theory of Solutions*; North-Holland Publishing Co.: Amsterdam, The Netherlands, 1957.
(5) Flory, P. J.; Hocker, H. *Trans. Faraday Soc.* **1971**, *67*, 2258.
(6) McMaster, L. P. *Macromolecules* **1973**, *6*, 760.
(7) Walsh, D. J.; Higgins, J. S.; Rostami, S.; Weeraperuma, K. *Macromolecules* **1983**, *16*, 391.
(8) ten Brinke, G.; Eshuis, A.; Roerdink, E.; Challa, G. *Macromolecules* **1981**, *14*, 867.
(9) Walsh, D. J.; Rostami, S.; Singh, V. B. *Makromol. Chem.* **1985**, *186*, 145.
(10) Nishi, T.; Wang, T. T. *Macromolecules* **1975**, *8*, 909.
(11) Kwei, T. K.; Frisch, H. L. *Macromolecules* **1978**, *11*, 1267.
(12) Rim, P. B.; Runt, J. P. *Macromolecules* **1984**, *17*, 1520.
(13) Hoffman, J. D.; Weeks, J. J. *J. Res. Natl. Bur. Stand., Sect. A* **1962**, *66*, 13.
(14) Morra, B. S.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 2243.
(15) Katine, I. A.; Anasagasti, M. S.; Peleteiro, M. C.; Valenciano, R. *Eur. Polym. J.* **1987**, *23*, 2907.
(16) Riedl, B.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 1769.
(17) Sham, C. K.; Walsh, D. J. *Polymer* **1987**, *28*, 804.
(18) Walsh, D. J.; Singh, V. B. *Makromol. Chem.* **1984**, *185*, 1979.
(19) Rostami, S. *Polymer* **1990**, *31*, 899.