Application of Equation-of-State Theory to Random Copolymer Systems. 1. Copolymer Solutions in Solvent

Tomoo Shiomi,* Hirofumi Ishimatsu, Toshimasa Eguchi, and Kiyokazu Imai*

Department of Materials Science and Technology, Nagaoka University of Technology, Nagaoka, Niigata 940-21, Japan

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ABSTRACT: Flory's equation-of-state theory with modified combining rules was extended to random copolymer systems. In this extended theory, the characteristic parameters and the intermolecular parameters (the exchange enthalpy parameter and the parameter characterizing the deviation from additivity of the external degrees of freedom) for copolymers are obtained from those for the copolymer components by using the combining rules for the copolymer. The theory was applied to poly(ethylene-*co*-vinyl acetate) (EtVAc) and poly(vinyl acetate-*co*-vinyl chloride) (VAcVC) solutions in tetrahydrofuran (THF). For this purpose, the interaction parameter, χ, heats of mixing at infinite dilution, and excess volumes for these solutions were measured. The copolymer composition dependence of χ at infinite dilution for the EtVAc solutions showed a U-shaped curve. In application of the theory to these systems, the characteristic parameters for the copolymer components were evaluated from the *P*-*V*-*T* data for the homopolymers corresponding to the copolymer components, and the intersegmental parameters between the copolymer components were determined from the thermodynamic data for the homopolymer solutions and for the copolymer solution with a given copolymer composition. The theoretical calculations were performed over various copolymer compositions by using the parameters thus determined. In consequence, the theory gave satisfactory agreement with the experimental results for the dependence of the interaction parameter, χ, on the copolymer composition.

Introduction

Thermodynamic studies on polymer blends have been systematically carried out from experimental and theoretical aspects.[1-3] The equation-of-state theory[4,5] has successfully explained LCST (lower critical solution temperature) and UCST (upper critical solution temperature) phenomena for polymer blends[5-7] as well as polymer solutions.[8,9] Namely, this theory gives two types of temperature dependence of the interaction parameter, χ: a U-shaped curve and a monotonically increasing function. Also, the theory has given at least semiquantitative agreement with experiments of various thermodynamic quantities for the polymer blends. ten Brinke et al.,[10] Rostami and Walsh,[11] and Allen et al.[12] represented the phase diagrams for some real polymer blends on the basis of the equation-of-state theory. Furthermore, Zacharius et al.[13] suggested the existence of critical double points in the polystyrene/poly(*o*-chlorostyrene) blends by simulating spinodals using the theory.

For blends containing copolymers, more recently, the dependence of miscibility on the copolymer composition has been elucidated.[14-16] In some copolymer blends, miscibility changes to be immiscible → miscible → immiscible[14-17] or miscible → immiscible → miscible[18,19] with the copolymer composition. These miscibility behaviors have been explained by the fact that the sign of the Flory-Huggins intermolecular interaction parameter expressed in terms of the intersegmental interaction parameters can change to be positive → negative → positive or negative → positive → negative with the copolymer composition.[14-16] However, the traditional Flory-Huggins theory cannot explain the LCST phenomena; the description of the temperature dependence of χ is limited, while the equation-of-state theory can do that as mentioned above. ten Brinke et al.[15] represented qualitatively such a miscibility behavior in connection with the equation-of-state theory.

The Flory equation-of-state theory with the modified or generalized combining rules for the homopolymer systems given by Hamada and co-workers[20-22] reproduced well various thermodynamic properties for the homopolymer blends,[23-25] as well as polymer solutions,[20-22] by using the parameter c_{12}, which was first introduced by McMaster[6] and Lin,[26] characterizing the deviation from additivity for the external degrees of freedom even without using the completely adjustable parameter Q_{12}.[27] In the present and subsequent[28] papers, we extend the modified Flory equation-of-state theory[20-22] to random copolymer systems and apply it to real systems. Particularly, it is very interesting to examine how the temperature dependence of χ changes with the copolymer composition. In the present paper, the combining rules for the copolymer system are derived and applied to the copolymer solutions in the small molecular solvent, i.e., poly(ethylene-*co*-vinyl acetate) (EtVAc) and poly(vinyl acetate-*co*-vinyl chloride) (VAcVC) solutions in tetrahydrofuran (THF). Another purpose in this work is to determine various parameters required to calculate the temperature dependence of χ for the copolymer blends EtVAc/VAcVC, which will be presented in the subsequent paper.[28]

Theory

In the Flory-type equation-of-state theory, the corresponding state's principle and one-fluid model are assumed. The reduced pressure $\tilde{p}$, volume $\tilde{v}$, and temperature $\tilde{T}$ are defined by $\tilde{p} = p/p^*$, $\tilde{v} = v/v^*$, and $\tilde{T} = T/T^*$, respectively, denoting the respective characteristic parameters with the asterisk. Some combining rules or mixing rules for the characteristic parameters of mixtures are required. Hamada and co-workers[20-22] showed that thermodynamic quantities for various polymer solutions can be reproduced well by modifying the combining rules proposed by Flory[4] even though the completely adjustable parameter Q_{12}[27] is not used. In this section, we first brief their combining rules[20-22] for the binary mixture of N_1 r_1-mers and N_2 r_2-mers and then derive the combining rules for the mixture of two random copolymers.

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Following Hamada and co-workers,[20-22] the following combining rules are assumed for binary mixtures consisting of N_1 r_1-mers and N_2 r_2-mers. For the mass of the segment

$$m = \sigma_1 m_1 + \sigma_2 m_2 \quad (1)$$

For the characteristic volume or core volume v^* per segment

$$v^* = \sigma_1^2 v_1^* + \sigma_2^2 v_2^* + 2\sigma_1\sigma_2 v_{12}^* \quad (2)$$

where

$$v_{12}^* = [(v_1^{*1/3} + v_2^{*1/3})/2]^3 \quad (3)$$

For the characteristic pressure p^*

$$p^* = (\sigma_1\theta_1 p_1^* v_1^{*2} + \sigma_2\theta_2 p_2^{*2} + 2\sigma_1\theta_2 p_{12}^* v_{12}^{*2})/v^{*2} \quad (4)$$

in which p_{12}^* is the parameter related to the interaction energy between the components 1 and 2. Here, σ_i ($i = 1$ and 2) is the segment fraction given by

$$\sigma_1 = 1 - \sigma_2 = r_1N_1/(r_1N_1 + r_2N_2) \quad (5)$$

θ_i is the site fraction given by

$$\theta_1 = 1 - \theta_2 = s_1r_1N_1/(s_1r_1N_1 + s_2r_2N_2) \quad (6)$$

where s_i is the number of contact sites per segment. When the exchange enthalpy parameter, X_{12}, introduced by Flory et al. is defined by

$$X_{12} = s_1\Delta\eta/2v_1^{*2} \quad (7)$$

where $\Delta\eta = \eta_{11} + \eta_{22} - 2\eta_{12}$ characterizes the exchange energy on mixing, then eq 7 can be expressed as

$$X_{12} = p_1^* + (v_2^*/v_1^*)(s_1/s_2)p_2^* - 2(v_{12}^*/v_1^*)p_{12}^* \quad (8)$$

in which p_{12}^* is related to X_{12}. For the external degrees of freedom c

$$c = \sigma_1c_1 + \sigma_2c_2 - \sigma_1\theta_2c_{12} \quad (9)$$

where c_{12} is the parameter[6,20-22,26] characterizing the deviation from additivity for the external degrees of freedom. The parameter c is related to the characteristic temperature, T^*, by the following definition:

$$T^* = p^*v^*/cR \quad (10)$$

Namely, the characteristic temperature, T^*, for the mixture is given by

$$1/T^* = (\sigma_1p_1^*v_1^*/T_1^* + \sigma_2p_2^*v_2^*/T_2^* - \sigma_1\theta_2Rc_{12})/(p^*v^*) \quad (11)$$

From the partition function proposed by Flory et al.[4] and the above combining rules, we can derive the heat of mixing, excess volume on mixing, and the interaction parameter, χ, or the residual chemical potential defined by[4]

$$\chi = (\mu_1 - \mu_1^\circ)^R/(RT\phi_2^2) = (\mu_1 - \mu_1^\circ)/(RT\phi_2^2) - [\ln(1 - \phi_2) + (1 - r_1v_1^*/r_2v_2^*)\phi_2]/\phi_2^2 \quad (12)$$

where ϕ_i is the core volume fraction of the component i given by

$$\phi_i = r_iN_iv_i^*/(r_1N_1v_1^* + r_2N_2v_2^*) \quad (13)$$

The expressions of the residual chemical potential, the heat of mixing ΔH^M, the heat of mixing $\Delta H^M(\infty)$ per gram of component 2 at infinite dilution, and the excess volume ratio V^E/V° (where V° is the sum of the volumes of the pure components) are as follows:

$$\begin{aligned}(\mu_1 - \mu_1^\circ)^R = {} & r_1RT\{3\theta_2^2c_{12}\ln[(2\pi mkT)^{1/2}/h(gv^*)^{1/3}(\tilde{v}^{1/3} - 1)] + 3c_1\ln(m_1/m)^{1/2} + (3/2)c(m - m_1)/m\} + \\ & p_1^*r_1v_1^*\tilde{T}_1\{\ln(v_1^*/v^*) + 3\ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)]\} + \\ & 2p^*r_1v^*\tilde{T}(v^* - \sigma_1v_1^* - \sigma_2v_{12}^*)/v^* + p_1^*r_1v_1^*/\tilde{v}_1 + \\ & (p^*r_1v^*/\tilde{v})[(\theta_1/\sigma_1) - 2(v^* - \sigma_1v_1^* - \sigma_2v_{12}^*)/v^* - \\ & 2(\theta_1p_1^*v_1^{*2} + \theta_2p_{12}^*v_{12}^{*2})/(p^*v^{*2})] \quad (14)\end{aligned}$$

where g is the geometric factor, which has been taken as $(4\pi/3)2^{1/2}$.[20-22]

$$\Delta H^M = (r_1N_1 + r_2N_2)[-(3/2)\sigma_1\theta_2r_1c_{12}RT + \sigma_1p_1^*v_1^*/\tilde{v}_1 + \sigma_2p_2^*v_2^*/\tilde{v}_2 - p^*v^*/\tilde{v}] \quad (15)$$

$$\begin{aligned}\Delta H^M(\infty)\ (\text{per gram of component 2}) = {} & (p_1^*v_{sp,2}^*/\tilde{v}_1)(v_1^*/v_2^*)(1 + \alpha_1T)[(s_2/s_1) + \\ & 2(v_{12}^*/v_1^*) - 2] + p_2^*v_{sp,2}^*[\alpha_1T(T_1^*/T_2^*)/\tilde{v}_1 + 1/\tilde{v}_2] - \\ & 2(p_{12}^*v_{sp,2}^*/v_1)(v_1^*/v_2^*)(v_{12}^*/v_1^*)^2(s_2/s_1)(1 + \alpha_1T) - \\ & RTc_{12}(v_{sp,2}^*/v_2^*)(s_2/s_1)[(3/2) + \alpha_1T/(\tilde{v}_1\tilde{T}_1)] \quad (16)\end{aligned}$$

where $v_{sp,2}^*$ is the characteristic volume per gram of the component 2 and α_1 is the thermal expansion coefficient of the component 1.

$$V^E/V^\circ = \tilde{v}v^*/(\sigma_1\tilde{v}_1^*v_1 + \sigma_2\tilde{v}_2^*v_2) - 1 \quad (17)$$

These expressions of the thermodynamic functions are somewhat different from those derived by McMaster[6] and Lin.[26] In the Appendix, such differences will be described and some calculated results will be compared among the present, McMaster's modified,[6] and Flory's original[4,27] formulations.

Next, we derive the combining rules for the mixture comprising two random copolymers, $(A_xB_{1-x})_{r_1}$ (1) and $(C_yD_{1-y})_{r_2}$ (2). (In this paper, the subscripts k and l indicate the segments and the subscripts i and j the molecules.)

According to Flory's expression,[4] we can write the total energy, E_o, for the mixture as

$$-E_o = \sum_{k,l}A_{kl}\eta_{kl}/v \quad (18)$$

where the summation is over the k–l pairs written below, η_{kl}/v is the energy per k–l contact, and A_{kl} is the number of the k–l contacts given by

$$\begin{aligned}2A_{AA} + A_{AB} + A_{AC} + A_{AD} &= N_1r_1xs_A \\ 2A_{BB} + A_{AB} + A_{BC} + A_{BD} &= N_1r_1(1 - x)s_B \\ 2A_{CC} + A_{AC} + A_{BC} + A_{CD} &= N_2r_2ys_C \\ 2A_{DD} + A_{AD} + A_{BD} + A_{CD} &= N_2r_2(1 - y)s_D \quad (19)\end{aligned}$$

where s_k (k = A–D) is the number of contact sites per segment or the surface area per segment. For a random mixture

$$\begin{aligned}A_{AB} &= N_1r_1xs_A\theta_B = N_1r_1(1 - x)s_B\theta_A \\ A_{AC} &= N_1r_1xs_A\theta_C = N_2r_2ys_C\theta_A \\ A_{AD} &= N_1r_1xs_A\theta_D = N_2r_2(1 - y)s_D\theta_A \\ A_{BC} &= N_1r_1(1 - x)s_B\theta_C = N_2r_2ys_C\theta_B \\ A_{BD} &= N_1r_1(1 - x)s_B\theta_D = N_2r_2(1 - y)s_D\theta_B \\ A_{CD} &= N_2r_2ys_C\theta_D = N_2r_2(1 - y)s_D\theta_C \quad (20)\end{aligned}$$

where θ_k is the site fraction of the segment k given by

$$\begin{aligned}\theta_A &= N_1 r_1 x s_A/\bar{r}Ns\\ \theta_B &= N_1 r_1 (1-x) s_B/\bar{r}Ns\\ \theta_C &= N_2 r_2 y s_C/\bar{r}Ns\\ \theta_D &= N_2 r_2 (1-y) s_D/\bar{r}Ns \qquad (21)\end{aligned}$$

in which

$$\bar{r}Ns = N_1 r_1 x s_A + N_1 r_1 (1-x) s_B + N_2 r_2 y s_C + N_2 r_2 (1-y) s_D \qquad (22)$$

Defining the characteristic pressure by

$$\begin{aligned}p_A^* &= s_A \eta_{AA}/2v_A^{*2}, \quad p_B^* = s_B \eta_{BB}/2v_B^{*2}\\ p_C^* &= s_C \eta_{CC}/2v_C^{*2}, \quad p_D^* = s_D \eta_{DD}/2v_D^{*2} \qquad (23)\end{aligned}$$

and

$$\begin{aligned}p_{AB}^* &= s_A \eta_{AB}/2v_{AB}^{*2}, \quad p_{AC}^* = s_A \eta_{AC}/2v_{AC}^{*2}\\ p_{AD}^* &= s_A \eta_{AD}/2v_{AD}^{*2}, \quad p_{BC}^* = s_B \eta_{BC}/2v_{BC}^{*2}\\ p_{BD}^* &= s_B \eta_{BD}/2v_{BD}^{*2}, \quad p_{CD}^* = s_C \eta_{CD}/2v_{CD}^{*2} \qquad (24)\end{aligned}$$

where

$$v_{kl}^* = [(v_k^{*1/3} + v_l^{*1/3})/2]^3 \qquad (25)$$

then we can rewrite eq 18 as

$$\begin{aligned}-E_o(v/\bar{r}N) = {}& \sigma_1\theta_1[x\theta_{1A}p_A^*v_A^{*2} + (1-x)\theta_{1B}p_B^*v_B^{*2} +\\ & 2x\theta_{1B}p_{AB}^*v_{AB}^{*2}] + \sigma_2\theta_2[y\theta_{2C}p_C^*v_C^{*2} +\\ & (1-y)\theta_{2D}p_D^*v_D^{*2} + 2y\theta_{2D}p_{CD}^*v_{CD}^{*2}] +\\ & 2\sigma_1\theta_2[x\theta_{2C}p_{AC}^*v_{AC}^{*2} + (1-x)\theta_{2C}p_{BC}^*v_{BC}^{*2} +\\ & x\theta_{2D}p_{AD}^*v_{AD}^{*2} + (1-x)\theta_{2D}p_{BD}^*v_{BD}^{*2}] \qquad (26)\end{aligned}$$

where

$$\theta_1 = 1 - \theta_2 = [r_1 N_1 x s_A + r_1 N_1 (1-x) s_B]/\bar{r}Ns \qquad (27)$$

and

$$\begin{aligned}\theta_{1A} &= 1 - \theta_{1B} = \theta_A/\theta_1 = x s_A/[x s_A + (1-x) s_B]\\ \theta_{2C} &= 1 - \theta_{2D} = \theta_C/\theta_2 = y s_C/[y s_C + (1-y) s_D] \qquad (28)\end{aligned}$$

Defining the exchange enthalpy parameters X_{kl} between the components k and l in the same way as eq 7 as

$$X_{kl} = s_k \Delta\eta_{kl}/2v_k^{*2} \qquad (29)$$

where

$$\Delta\eta_{kl} = \eta_{kk} + \eta_{ll} - 2\eta_{kl} \qquad (30)$$

then we have

$$X_{kl} = p_k^* + (v_l^*/v_k^*)(s_k/s_l)p_l^* - 2(v_{kl}^*/v_k^*)p_{kl}^* \qquad (31)$$

in which p_{kl}^* can be related to X_{kl}. As is obvious from eq 28, θ_{1A}, etc., are dependent on only copolymer composition but not the number of molecules.

Since we can write the energy for the mixture consisting of the polymers 1 and 2 as[20-22]

$$-E_o(v/\bar{r}N) = \sigma_1\theta_1 p_1^* v_1^{*2} + \sigma_2\theta_2 p_2^* v_2^{*2} + 2\sigma_1\theta_2 p_{12}^* v_{12}^{*2} \qquad (32)$$

the comparison between eqs 26 and 32 may give the parameters for copolymers by using those for the components of the copolymer as

$$p_1^* = [x\theta_{1A}p_A^*v_A^{*2} + (1-x)\theta_{1B}p_B^*v_B^{*2} + 2x\theta_{1B}p_{AB}^*v_{AB}^{*2}]/v_1^{*2} \qquad (33)$$

$$p_2^* = [y\theta_{2C}p_C^*v_C^{*2} + (1-y)\theta_{2D}p_D^*v_D^{*2} + 2y\theta_{2D}p_{CD}^*v_{CD}^{*2}]/v_2^{*2} \qquad (34)$$

$$p_{12}^* = [x\theta_{2C}p_{AC}^*v_{AC}^{*2} + (1-x)\theta_{2C}p_{BC}^*v_{BC}^{*2} + x\theta_{2D}p_{AD}^*v_{AD}^{*2} + (1-x)\theta_{2D}p_{BD}^*v_{BD}^{*2}]/v_{12}^{*2} \qquad (35)$$

where v^*_1 and v^*_2 are assumed to be

$$v_1^* = x^2 v_A^* + 2x(1-x)v_{AB}^* + (1-x)^2 v_B^* \qquad (36)$$

and

$$v_2^* = y^2 v_C^* + 2y(1-y)v_{CD}^* + (1-y)^2 v_D^* \qquad (37)$$

respectively. The exchange enthalpy parameter X_{12} between the copolymers 1 and 2 can be related to p_{12}^* by the same equation as in eq 8.

We put the external degrees of freedom for the copolymers 1 and 2 as

$$c_1 = x c_A + (1-x)c_B - x\theta_{1B}c_{AB} \qquad (38)$$

$$c_2 = y c_C + (1-y)c_D - y\theta_{2D}c_{CD} \qquad (39)$$

respectively, by analogy to that for the mixture. The characteristic temperature for the copolymers 1 and 2 can be obtained according to eq 10 as follows:

$$T_1^* = p_1^* v_1^*/c_1 R \qquad (40)$$

$$T_2^* = p_2^* v_2^*/c_2 R \qquad (41)$$

Furthermore, the parameter c_{12} for the mixture is assumed to be

$$c_{12} = x\theta_{2C}c_{AC} + x\theta_{2D}c_{AD} + (1-x)\theta_{2C}c_{BC} + (1-x)\theta_{2D}c_{BD} \qquad (42)$$

As derived above, the characteristic parameters p_i^*, v_i^*, and T_i^* (i = 1 and 2) for the copolymers and the intermolecular parameter p_{12}^* or X_{12} and c_{12} can be expressed in terms of those for the components of copolymers. Also, the characteristic parameters for the mixture can be obtained from these parameters by use of eqs 1–11. In evaluating the thermodynamic quantities, therefore, the same expressions,[20-22] i.e., eqs 12 and 14–17, for the thermodynamic functions as derived for the binary mixture of solvent/homopolymer or homopolymer/homopolymer can be used.

Experimental Section

Materials. Poly(vinyl acetate) (PVAc) was prepared by radical polymerization in 50 wt % methanol solution for 100 min at 50 °C using AIBN as an initiator. The resulting polymer was crudely fractionated from the methanol solution by using petroleum ether as a precipitant. A large second fraction was used for measurements. Poly(vinyl chloride) (PVC), which was TK-800 supplied by Shin-Etsu Chemical Co., Ltd., was reprecipitated by putting the THF solution in a large excess amount of methanol and dried under vacuum. Poly(ethylene-*co*-vinyl acetate)s (EtVAc) with the following vinyl acetate contents were used: 87.1, 83.2, 70, and 50 wt %. The former two samples were supplied by Kuraray Co. and the latter two by Bayer, Japan. These EtVAc polymers were purified by reprecipitating from the toluene solution with a large excess of petroleum ether. Two poly(vinyl acetate-*co*-vinyl chloride)s (VAcVC) with VC contents of 90 and 81 wt %, purchased from Scientific Polymer Products, Inc., were obtained by reprecipitating from the THF solution with a large excess of petrleum ether. Weight-average molecular weights and copolymer

Table I
Molecular Weights and Copolymer Composition of Polymers Used for Measurements

sample[a]	M_w[b]	VAc content,[c] wt %
PVAc	1.5×10^5	
PVC	1.5×10^5	
EtVAc87.1	2.0×10^5	87.1
EtVAc83.2	1.6×10^5	83.2
EtVAc70	2.2×10^5	70
EtVAc50	2.4×10^5	50
VAcVC81	3.7×10^4	19[d]
VAcVC90	9.1×10^4	10

[a] The numeral values indicate the copolymer compositions expressed in weight percent. [b] Measured by GPC, relative to polystyrene standards. [c] Nominal. [d] Including 2 wt % maleic acid.

compositions for all the polymers used for measurements are listed in Table I.

Measurements. Specific volumes v_{sp} for THF were measured with a pycnometer at 25 °C. Thermal expansion coefficients, α, at 25 °C were determined from the slope of the temperature–v_{sp} curve obtained at 20–30 °C by using a pycnometer. Thermal pressure coefficients, γ, for THF at 25 °C were obtained by interpolation of γ measured at 20–30 °C according to the method of Orwoll and Flory.[29]

The interaction parameter, χ, was obtained from osmotic pressures by using the equation

$$-\pi V_s/RT = \ln (1 - \phi_1) + (1 - m_s v_{sp,s}^*/m_1 v_{sp,1}^*)\phi_1 + \chi\phi_1^2$$

where V_s is the molar volume of the solvent, m_s and m_1 are the masses of the solvent and polymer, respectively, $v_{sp,s}^*$ and $v_{sp,1}^*$ are the characteristic of core volumes per gram of the solvent and polymer, respectively, and ϕ_1 is the core volume fraction of the polymer. The osmotic pressure was measured in the bath thermostated at 25 ± 0.03 °C by using a high-pressure osmometer similar to that used by Eichinger and Flory.[27] Heats of mixing at infinite dilution $\Delta H^M(\infty)$ were measured with a Tian–Calvet microcalorimeter. Excess volume ratios V^E/V° were determined from the respective specific volumes by using

$$V^E/V^\circ = v_{sp}/(w_s v_{sp,s} + w_1 v_{sp,1}) - 1$$

where w_s and w_1 are the weight fractions of the solvent and polymer, respectively.

Results

In order to calculate the thermodynamic quantities for the mixture, it is required to determine the equation-of-state parameters for the component molecules and the parameters s_j/s_i, X_{ij}, and c_{ij} between the different molecules i and j. For the copolymer systems, we can evaluate these parameters from those for the components of the copolymers using the combining rules for the copolymer system represented in the theoretical section. The systems in this work are the mixtures of the solvent and copolymer. Therefore, hereafter the copolymer 1 (A_xB_{1-x}) and the copolymer 2 (C_yD_{1-y}) expressed in the theoretical section should be read as the solvent, s (with $x = 1$ in (A_xB_{1-x}), and the copolymer 1 (C_yD_{1-y}), respectively.

In the calculation, the characteristic parameters p^*, v^*, and T^* for the copolymer components were assumed to be equal to those for the corresponding homopolymers. The parameters X_{kl} and c_{kl} between the copolymer components were determined as follows: $X_{Et/VAc}$ and $c_{Et/VAc}$ were evaluated from the equation-of-state data for the EtVAc copolymer, and X_{kl} and c_{kl} for other combinations of the copolymer components were determined from the thermodynamic data for the homopolymer solutions, except $X_{THF/Et}$ and $c_{THF/Et}$, which were obtained from the thermodynamic data for the copolymer solution with a given copolymer composition. The evaluation method of these parameters will be described later in detail.

Table II
Characteristic Parameters at 25 °C

sample	v_{sp}^*, g/cm^3	v^*, cm^3/segment·mol	T^*, K	p^*, J/cm^3
(a) Homopolymers or Components				
THF	0.8753	62.12	4685	624
PVAc[a] (VAc)	0.7131	62.07	6628	592
PEt[a] (Et)	1.0454	94.14	7566	446
PVC[a] (VC)	0.6222	72.56	7943	607
(b) Copolymers[b]				
EtVAc87.1	0.7532	65.85	6842	565
EtVAc83.2	0.7655	67.01	6902	558
EtVAc70	0.8076	71.01	7093	534
EtVAc50	0.8730	77.29	7325	507
VAcVC81	0.6390	70.00	7631	624
VAcVC90	0.6311	71.17	7774	606

[a] Determined from P–V–T data.[30–32] See text. [b] Calculated from the characteristic parameters for the homopolymers[30–32] and from the intersegmental parameters shown in Table IIIa by using the combining rules for the random copolymer. See text.

(1) Equation-of-State Parameters of Homopolymers. The characteristic parameters for the homopolymers PEt, PVAc, and PVC and the solvent THF were evaluated according to Flory's method.[4] Namely, we can determine the equation-of-state parameters from the specific volume, v_{sp}, thermal expansion coefficient, α, and thermal pressure coefficient, γ, using the reduced equation of state at $p = 0$

$$\tilde{T} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \tag{43}$$

and the following equations derived from eq 43:

$$\tilde{v}^{1/3} - 1 = (\alpha T/3)/(1 + \alpha T) \tag{44}$$

$$p^* = \gamma T \tilde{v}^2 \tag{45}$$

These parameters for THF were determined from $v_{sp} = 1.1327$ cm^3/g, $\alpha = 1.236 \times 10^{-3}$ K^{-1}, and $\gamma = 1.249$ J/cm^3 measured at 25 °C in this study. The characteristic parameters for the homopolymers PVAc, PEt, and PVC at 25 °C were evaluated by extrapolating the values obtained from the P–V–T data measured at the temperatures above the glass transition or melting temperatures by Olabisi and Simha[30] and Hellwege et al.[31] For PEt, the data of the low-density PEt were used,[30,31] and γ was estimated according to the method of Manzini and Crescenzi.[32] These equation-of-state parameters are listed in part a of Table II. In this table, v^* which is the characteristic volume per segment was determined according to the method described elsewhere.[20,21]

(2) EtVAc Solutions in THF. (a) Equation-of-State Parameters of EtVAc. The characteristic parameters for the copolymer EtVAc can be evaluated from eqs 31, 34, 37, 39, and 41 by using those for the components, Et and VAc, of the copolymer and by using s_l/s_k, X_{kl}, and c_{kl} between the components k and l. In this study, the values of p^*, T^*, and v^* for the copolymer components were assumed to be equal to those for the corresponding homopolymers. For the EtVAc copolymers, X_{kl} and c_{kl} were determined to fit as well as possible all three experimental values of v_{sp}, α, and γ obtained from the P–V–T data measured for a series of EtVAc by Zoller et al.[33] The surface ratio, s_l/s_k, used here was determined from Bondi's table[34] in which the van der Waals radii, volumes, and surfaces for various groups are listed. The values of X_{kl}, c_{kl}, and s_l/s_k for EtVAc are shown in Table IIIa, and the characteristic parameters for the EtVAc

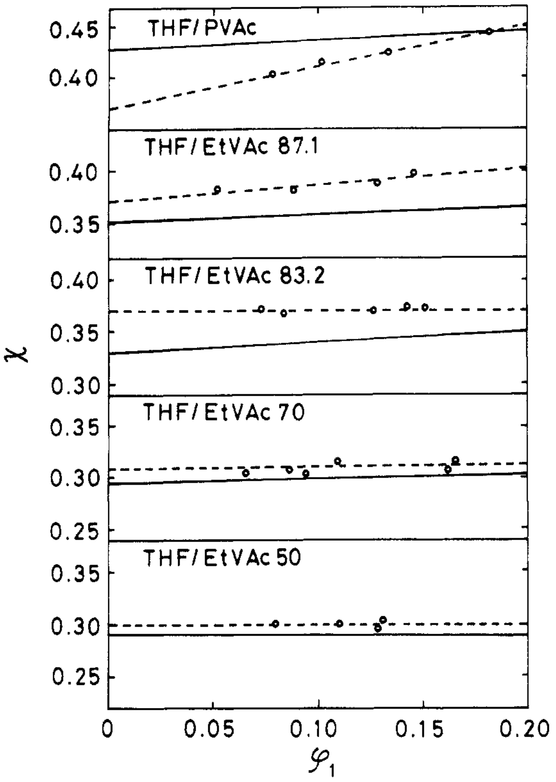

Figure 1. Dependence of the interaction parameter, χ, on the core volume fraction, ϕ_1, of the polymer for the PVAc homopolymer and the EtVAc copolymer solutions in THF at 25 °C. The solid lines are the calculated ones.

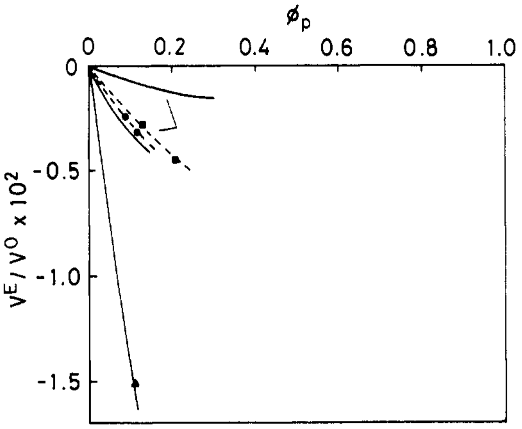

Figure 2. Excess volume ratio, V^E/V°, at 25 °C: (■) THF/EtVAc70; (●) THF/PVC; (▲) THF/EtVAc70/PVC. (This ternary system will be described in the subsequent paper.[28]) The solid lines are the calculated ones.

copolymers determined by the method described above are listed in part b of Table II.

(b) Thermodynamic Properties of Solutions. The dependence of χ on the polymer concentration measured for the PVAc and EtVAc solutions in THF are shown in Figure 1, and the excess volume ratios, V^E/V°, and the heats of mixing at infinite dilution, $\Delta H^M(\infty)$ are shown in Figure 2 and in Table IV, respectively.

Table III
Intersegmental and Intermolecular Parameters

system (i/j)	s_j/s_i	X_{ij}, J/cm^3	c_{ij}
(a) Component or Homopolymer Systems (k/l)			
Et/VAc	0.680	63.0	0.117
VAc/VC	1.099	12.9	0.00005
THF/VAc (PVAc)	1.011	11.5	0.0062
THF/Et	1.487	47.5	0.0057
THF/VC (PVC)	1.111	14.5	0.0090
(b) Copolymer Systems[a] (s/1)			
THF/EtVAc50	1.245	16.6	0.0059
THF/EtVAc70	1.150	9.0	0.0054
THF/EtVAc83.2	1.088	7.3	0.0061
THF/EtVAc87.1	1.071	7.51	0.0061
THF/VAcVC81	1.087	11.7	0.0084
THF/VAcVC90	1.098	12.8	0.0087

[a] Determined from the parameters shown in part a by using the combining rules. See text.

Table IV
Heats of Mixing at Infinite Dilution

	$\Delta H^M(\infty)$, J/g	
system	exptl	calcd[a]
THF/PVAc	4.52[b]	4.83
THF/EtVAc70	-1.33[b]	-1.05
THF/PVC	-3.41[c]	-3.29

[a] Calculated at 25 °C. [b] Measured at 31.5 °C. [c] Obtained at 30 °C by Maron et al. (Maron, S. H.; Filisko, F. E. *J. Macromol. Sci., Phys.* 1972, *B6*, 413).

Table V
$\Delta H^M(\infty)$ Calculated by Using Equations A-2 (Flory) and A-4 (McMaster)[a]

	$\Delta H^M(\infty)$, J/g		
		calcd[c]	
system (i/j)	exptl[b]	Flory	McMaster
THF/PVAc	4.52	4.52	4.52
THF/PVC	-3.41	-3.41	-3.41

[a] Our calculated results are shown in Table IV. [b] The sources are shown in Table IV. [c] Calculated at 25 °C.

Table VI
Intermolecular and Intersegmental Parameters Used in Calculations

		X_{ij}, J/cm^3		
system (i/j)	s_j/s_i	Flory	McMaster	c_{ij}: McMaster
THF/VAc (PVAc)	1.011	9.69	10.69	0.004 47
THF/VC (PVC)	0.951	2.08	2.40	0.001 56
VAc/VC	0.940		1.10	0.000 18
THF/VAcVC81[a]	0.965$_4$		4.07	0.002 29
THF/VAcVC90[a]	0.958$_7$		3.28	0.001 96

[a] Determined from the values for the homopolymer systems using the combining rules for the copolymer systems.

In order to calculate these thermodynamic quantities for the EtVAc copolymer solutions, we need the values of the intermolecular parameters X_{s1}, c_{s1}, and s_1/s_s for the THF/EtVAc in addition to the equation-of-state parameters determined above. These intermolecular parameters can be obtained from the intersegmental parameters for THF/Et, THF/VAc, and Et/VAc according to the combining rules for the system $(A_xB_{1-x})/(C_yD_{1-y})$ with $x = 1$, where A = THF, C = Et, and D = VAc. s_1/s_s can be evaluated from

$$s_1/s_s = [ys_C + (1-y)s_D]/[xs_A + (1-x)s_B] \quad (46)$$

X_{kl} and c_{kl} for Et/VAc have already been obtained in the course of evaluation of the characteristic parameters for EtVAc. For THF/VAc, we determine X_{kl} and c_{kl} by using the experimental data for the PVAc homopolymer solution, under the assumption that the intersegmental parameters for THF/VAc are equal to the intermolecular parameters for THF/PVAc. To determine those for THF/Et, on the other hand, we cannot use the experimental result for the PEt homopolymer solutions in THF. Therefore, we determined $X_{\mathrm{THF/Et}}$ and $c_{\mathrm{THF/Et}}$ from the experimental data for the THF/EtVAc70 system. When the values of the parameters X_{ij} and c_{ij} for THF/EtVAc70 shown in

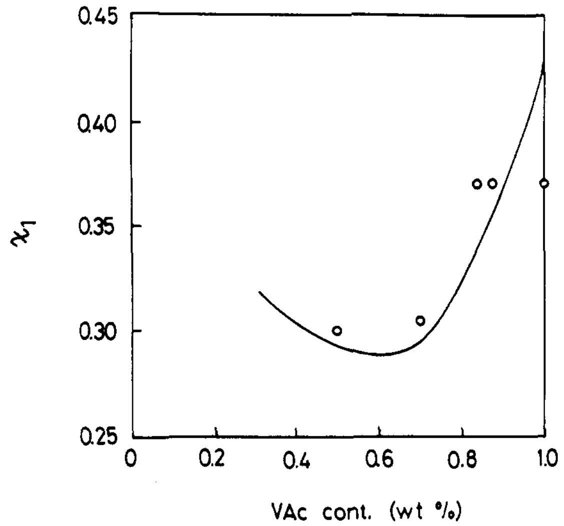

Figure 3. Dependence of χ_1 on the copolymer composition for the EtVAc solutions at 25 °C. The solid line has been calculated according to eq 47 with eqs 12 and 14.

Table IIIb are used, the calculated χ, V^E/V°, and $\Delta H^M(\infty)$ agree fairly well with the experimental ones as shown in Figures 1 and 2 and Table IV, respectively. By the use of these values together with X_{kl} and c_{kl} for THF/VAc and Et/VAc, the values of $X_{\mathrm{THF/Et}}$ and $c_{\mathrm{THF/Et}}$ were evaluated according to eqs 8, 35, and 31 and eq 42, respectively. These intersegmental parameters are listed in Table IIIa, and the intermolecular parameters for a series of the THF/EtVAc systems are shown in Table IIIb.

Now we can calculate the thermodynamic quantities for the THF/EtVAc systems with various copolymer composition. The dependence of χ on the polymer concentration for the THF/EtVAc systems calculated by using the above parameters is shown by the solid lines in Figure 1. The deviation in the slope for the PVAc homopolymer solution may come from s_1/s_s determined from Bondi's table. In Figure 3 are shown the copolymer composition dependences of χ_1 defined by

$$\chi_1 = \lim_{\phi_2 \to 0} \chi \tag{47}$$

(3) VAcVC Solutions in THF. The concentration dependence of χ measured for the THF/VAcVC solutions at 25 °C are shown by the open circles in Figure 4. In order to calculate these χ parameters, we need the intersegmental parameters X_{kl}, c_{kl}, and s_l/s_k for the combinations of THF/VC and VAc/VC, in addition to the characteristic parameters for VAc, VC, and THF and the intersegmental parameters for THF/VAc determined already. In this system, THF, VAc, and VC are corresponding to A, C, and D, respectively, in the system A/(C_yD_{1-y}).

The parameters $X_{\mathrm{THF/VC}}$ and $c_{\mathrm{THF/VC}}$ can be determined from the PVC homopolymer solutions. Using the values shown in part a of Table III together with the characteristic parameters for THF and PVC, we obtain good agreements for χ, V^E/V°, and $\Delta H^M(\infty)$ in the PVC solutions as shown in Figures 4 and 2 and Table IV, respectively. The remaining parameters, $X_{\mathrm{VAc/VC}}$ and $c_{\mathrm{VAc/VC}}$, cannot be evaluated independently in the present stage. Therefore, the interaction parameters, χ, for a series of VAcVC solutions were calculated by use of suitable values of $X_{\mathrm{VAc/VC}}$ and $c_{\mathrm{VAc/VC}}$, which are shown in part a of Table III. The concentration dependence of χ calculated thus for the VAcVC solutions is shown by the solid lines in Figure 4. The deviation in the slope may come from the surface ratio for the THF/VAc system as described above.

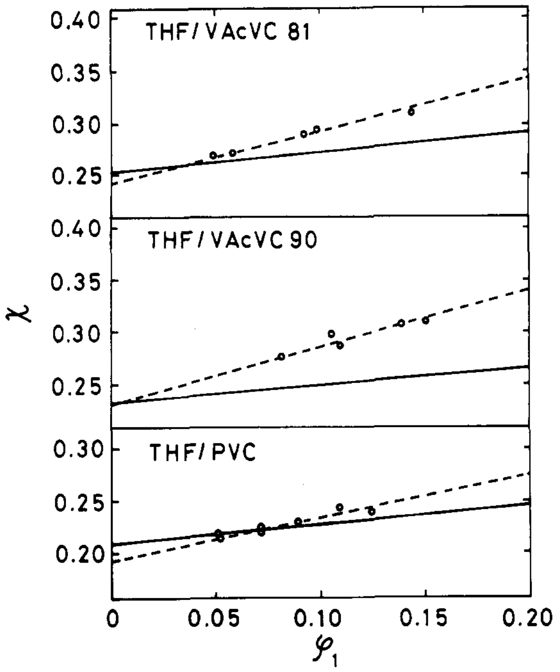

Figure 4. Dependence of the interaction parameter, χ, on the core volume fraction, ϕ_1, of the polymer for the PVC homopolymer and the VAcVC copolymer solutions in THF at 25 °C. The solid lines are the calculated ones.

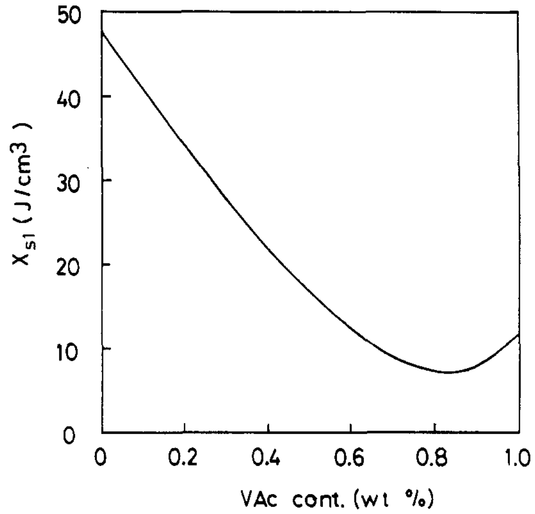

Figure 5. Dependence of the exchange enthalpy parameter, X_{s1}, on the copolymer composition of VAc for the THF/EtVAc system.

Discussion

The dependence of χ_1 on the copolymer composition for THF/EtVAc, as shown in Figure 3, is a U-shaped curve, which corresponds to the copolymer composition dependence of the exchange enthalpy parameter, X_{s1}, shown in Figure 5. This means that affinity of the copolymers EtVAc for THF is stronger than that of both homopolymers of PEt and PVAc due to the repulsive effects between the components Et and VAc of EtVAc.[17] The theory reproduces this fact well though the theoretical χ is somewhat shifted from the experimental one in the VAc-rich region.

Although there are some deviations in the calculated results, the combining rules derived here for the copolymer systems appear to successfully represent, as a whole, the dependences of the thermodynamic properties on the copolymer composition by using the characteristic parameters for the corresponding homopolymers and the intersegmental parameters X_{kl} and c_{kl}. In the subsequent

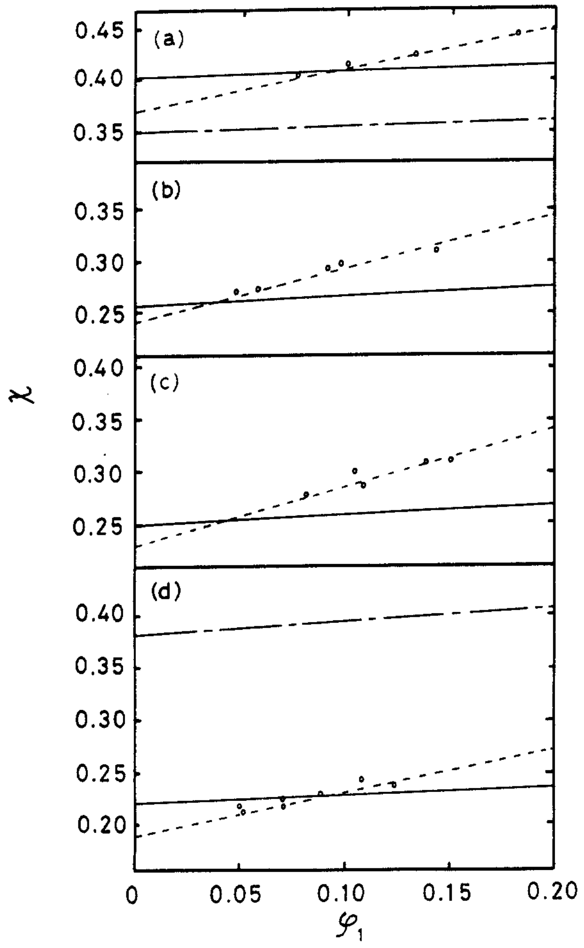

Figure 6. Concentration dependence of χ for the THF/VAcVC systems at 25 °C: (a) THF/PVAc; (b) THF/VAcVC81; (c) THF/VAcVC90; (d) THF/PVC. The dot-dashed and solid curves have been calculated by using eqs A-1 (Flory) and A-3 (McMaster), respectively.

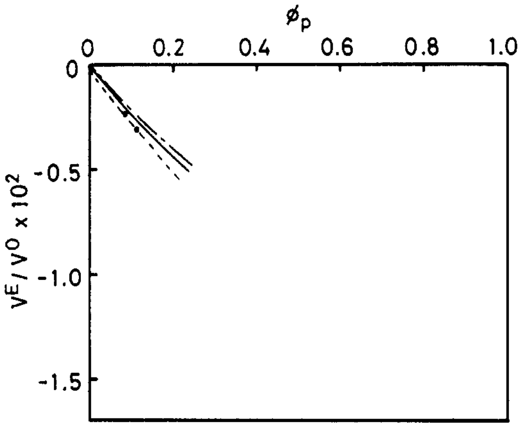

Figure 7. Excess volume ratio for the THF/PVC system. The dot-dashed and solid curves have been calculated by using Flory's and McMaster's formulations, respectively.

paper,[28] the values of the parameters determined here will be used in the calculations of the interaction parameter, χ, for the copolymer blends.

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Appendix

The expressions for the residual chemical potential and the heat of mixing at infinite dilution in Flory's original equation-of-state theory[4,27] and McMaster's modification[6,26] are as follows:

Flory's original theory

$$(\mu_1 - \mu_1^\circ)^R = p_1^* r_1 v^* \{3\tilde{T}_1 \ln [(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + (\tilde{v}_1^{-1} - \tilde{v}^{-1})\} + (r_1 v^* X_{12}/\tilde{v})\theta_2^2 - TQ_{12} r_1 v^* \theta_2^2 \quad \text{(A-1)}$$

$$\Delta H^M(\infty) \text{ (per gram of component 2)} = (v_{sp,2}^*/\tilde{v}_1)\{(1 + \alpha_1 T)X_{12}(s_2/s_1) + p_2^*[(\tilde{v}_1/\tilde{v}_2) - 1 - (1 - T_1^*/T_2^*)\alpha_1 T]\} \quad \text{(A-2)}$$

McMaster's modification

$$(\mu_1 - \mu_1^\circ)^R = 3r_1 RT\phi_2^2(c_1 - c_2 + 2\phi_1 c_{12}) \ln (m_1/m_2)^{1/2} + 3r_1 RT\phi_2^2 c_{12} \ln [(2\pi m_2 kT)^{1/2}/h(gv^*)^{1/3}(\tilde{v}^{1/3} - 1)] + 3p_1^* r_1 v^* \tilde{T}_1 \ln [(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + p_1^* r_1 v^* (\tilde{v}_1^{-1} - \tilde{v}^{-1}) + r_1 v^* \theta_2^2 (X_{12}/\tilde{v} - T\tilde{v}_1 Q_{12}) \quad \text{(A-3)}$$

$$\Delta H^M(\infty) \text{ (per gram of component 2)} = (v_{sp,2}^*/\tilde{v}_1)\{(1 + \alpha_1 T)X_{12}(s_2/s_1) + p_2^*[(\tilde{v}_1/\tilde{v}_2) - 1 - (1 - T_1^*/T_2^*)\alpha_1 T]\} - RTc_{12}[(9/2) + 4\alpha_1 T]v_{sp,2}^*/v^* \quad \text{(A-4)}$$

Equations A-3 and A-4 are somewhat different from the corresponding expressions given by Hamada et al.[20-22] (eqs 14 and 16 in the text, respectively). In the former expression of the residual chemical potential the contribution of the segment mass to the chemical potential vanishes for $c_1 = c_2$ and $c_{12} = 0$, while in the latter it vanishes for $c_1 = c_2$, $c_{12} = 0$, and $m_1 = m_2$. This comes from the difference in the assumption for the segment mass in the mixture; in the former the mass in the mixture is expressed in eq 1 of the text, and in the latter m_1 and m_2 are preserved in the mixture. Another difference is in the assumption for the core volume, v^*, of the segment in the mixture; in the present paper the core volume, v^*, in the mixture has been given by eq 2 in the text while v^* is assumed to be of equal size among components 1 and 2 and their mixture in McMaster's and Flory's combining rules. Finally, the external degrees of freedom, c, in the mixture is assumed to be

$$c = \phi_1 c_1 + \phi_2 c_2 - \phi_1 \phi_2 c_{12} \quad \text{(A-5)}$$

in McMaster's version, which is compared with eq 9. In the present paper, furthermore, the entropy parameter Q_{12} has been neglected by the reason described in the introduction section.

Figures 6 and 7 show the results of χ and V^E/V°, respectively, calculated according to McMaster's and Flory's expressions with neglect of Q_{12} for the THF/VAcVC systems. The results of $\Delta H^M(\infty)$ are shown in Table V. The values of the characteristic parameters v_{sp}^*, T^*, and p^* in the pure components were the same as those shown in Table II. In the calculations according to McMaster's expression, the size of the core volume, v^*, per segment for the pure components and the mixture was put to be equal to that per molecule for THF, while it is unnecessary in the calculation according to Flory's because $r_1 v^* = M_1 v_{sp,1}^*$ where M_1 is the molecular weight of component 1. The values of s_l/s_k, X_{kl}, and c_{kl} used in the calculations are shown in Table VI. The surface ratios s_l/s_k of the segment are different from those in Table III because of the difference in the assumption for the segment size. In application of McMaster's approach to copolymer systems, the same combining rules as ours for the copolymer were assumed except the segment core volumes, which are of equal size between components 1 and 2 in his approach.

As compared with the results shown in Figure 6 and Figures 1 and 4 in the text, the calculated χ's are not so different from those obtained from the expressions by McMaster and Hamada et al. On the other hand, the value of χ calculated from Flory's formulation with $Q_{12} = 0$ deviates from the experimental one for the THF/PVC system. In Flory's original theory, as reported previously,[35,36] the contribution of the Q_{12} term to the chemical potential is very large for the poly(dimethylsiloxane) solutions. If the entropy parameter Q_{12} is used, the calculated χ may fit to the experimental one without affecting any other calculated thermodynamic quantities, because the Q_{12} term is added only to the chemical potential as a correction term. The calculations for the copolymer systems using Flory's original theory were not performed because a relation between the intermolecular and intersegmental Q_{ij} parameters is required. All the values of $\Delta H^{\mathrm{M}}(\infty)$ calculated from the three formulations are in very good agreement with the experimental ones. The values of V^{E}/V° calculated for the THF/PVC system are also almost the same among the three formulations as shown in Figures 7 and 2, while it was reported previously[20] that the assumption eq 2 in the segment core volume gave the better results of the excess volume for the poly(dimethylsiloxane) systems.

As mentioned above, the results calculated from the McMaster and Hamada et al. modified versions of Flory's equation-of-state theory may be not so different from each other as long as the massses of the components 1 and 2 are not largely different from each other. Both versions without the Q_{12} term give satisfactory agreement with experiments. However, further investigations about the contribution of the Q_{12} and c_{12} parameters to the chemical potential are desirable.

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Registry No. EtVAc (copolymer), 24937-78-8; VAcVC (copolymer), 9003-22-9; THF, 109-99-9.