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Phase Behavior of Blends of Vinyl Chloride–Vinyl Acetate Copolymers with Polymethacrylates

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ABSTRACT: The phase behavior of binary blends of vinyl chloride–vinyl acetate copolymers with two polymethacrylates, poly(methyl methacrylate) (PMMA) and poly(*n*-butyl methacrylate) (PnBMA), has been examined as a function of the vinyl acetate (VAc) content in the copolymer. From the variation of cloud points with the copolymer composition, segmental contact energy parameters X_{ij}'s for various monomeric unit pairs have been estimated by using a copolymer model based on Patterson's equation of state theory. It has been found that the segmental interaction of vinyl acetate with methyl methacrylate and vinyl chloride is attractive in each case, indicating that poly(vinyl acetate) is miscible with PMMA and poly(vinyl chloride) (PVC). The incorporation of the VAc unit into PVC did not raise the cloud points of PMMA/PVC and PnBMA/PVC blends. The effect of the VAc unit on the phase behavior of both blends was analyzed according to the copolymer model based on Patterson's theory.

Introduction

Comonomers incorporated into one or both components of a miscible polymer blend can cause a significant change in the phase behavior of the blend system. Especially, the temperature at which the blends phase separate on heating, i.e., lower critical solution temperature (LCST), changes dramatically with the content and type of comonomer. Since polymer–polymer miscibility has been viewed as a balance between an unfavorable free volume term and a favorable interaction term,[1] a more detailed understanding for the effect of comonomer on the two terms mentioned above may give a priori guidance on how to select comonomers that will give the desirable effect of raising the LCST of a blend system.

In a previous paper,[2] we have discussed the effect of comonomer on the LCST behavior of copolymer belnds according to a new model based on Prigogine–Flory–Patterson's equation of state theory. The present model explains that the intramolecular interaction within copolymers due to the incorporation of comonomer contributes to the free volume term of copolymer blends as well as to the interaction term. Unlike its contribution to the interaction term, the intramolecular repulsion is not always favorable to the free volume term. This results from the fact that the free volume term is controlled by the two factors: the intramolecular interaction and the relative magnitude of the characteristic parameters of the comonomer. The various theoretical possibilities for the contribution of the comonomer to the free volume term are schematically discussed in ref 3.

The objective of this study is to justify the copolymer blend model based on Prigogine–Flory–Patterson's theory by testing the model for several blend systems. In order to accomplish this objective, the following blend systems were selected: poly(methyl methacrylate) (PMMA) and vinyl chloride–vinyl acetate (VC–VAc) copolymers; poly(*n*-butyl methacrylate) (PnBMA) and VC–VAc copolymers.

Theoretical Background

At atmospheric pressure, Flory's equation of state[4] for chain molecules can be expressed in a reduced form as

$$\tilde{T} = \frac{\tilde{v}^{1/3} - 1}{\tilde{v}^{4/3}} \tag{1}$$

where $\tilde{v} = v/v^*$ is the reduced volume and $\tilde{T} = T/T^*$ is the reduced absolute temperature. The starred reducing quantities reflect the molecular characteristics of the chain molecule. All $\tilde{v}^{1/3}$ values are found between the extremes of 1 and $^4/_3$ due to the limit of the thermal expansion of chain molecules.

The application of this theory to mixtures of $N_A r_A$-mers and $N_B r_B$-mers assumes the mean-field approximation. Each mer has to be chosen in such a way as to have equal hard-core volume. An additional contact energy parameter X_{AB}, which arises from the difference in the interaction energy between like and unlike segment pairs, is introduced. The equation of state for the two-component mixtures has a form identical with that for a pure component if the following mixing rules are made:

$$P^* = \Phi_A P_A^* + \Phi_B P_B^* - \Phi_A \Theta_B X_{AB} \tag{2}$$

$$T^* = \frac{P^* v^*}{ck} = \frac{P^*}{\Phi_A(P_A^*/T_A^*) + \Phi_B(P_B^*/T_B^*)} \tag{3}$$

$$\Theta_B = 1 - \Theta_A = \frac{r_B N_B s_B}{r_A N_A s_A + r_B N_B s_B} = \frac{(s_B/s_A)\Phi_B}{\Phi_A + (s_B/s_A)\Phi_B} \tag{4}$$

where Φ_i, with i = A, B, denotes the segment fraction of component i, Θ_i is the site fraction of component i, s_i is the number of contact sites per segment, and P_i^* is the characteristic pressure of component i.

Using the corresponding state theory and the van der Waals model, Biros et al.[5] have derived an expression for the Flory–Huggins interaction parameter χ_{AB}

$$\frac{\chi_{AB}(T)}{C_A} = \frac{\tilde{v}_A^{\,1/3}}{\tilde{v}_A^{\,1/3} - 1}\left[\frac{X_{AB}}{P_A^*}\right] + \frac{\tilde{v}_A^{\,1/3}}{2(4/3 - \tilde{v}_A^{\,1/3})}\left[1 - \frac{T_A^*}{T_B^*}\right]^2 \tag{5}$$

where C_A satisfies the relation $C_A = P_A^* V_A^*/RT_A^*$ and

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reflects the flexibility of the reference molecule. Since the reduced volume is related to the reduced temperature by the equation of state (eq 1), eq 5 is a function of temperature. The first term on the right-hand side of eq 5 is the interaction term, and the second is the free volume term. If the interaction term is negative and outweighs the free volume term at a given temperature, it indicates that the blend is miscible. As the temperature (or the reduced volume) increases, the magnitude of the interaction term decreases while that of the free volume term increases in an appropriate manner. At the temperature where the free volume term cancels the interaction term, the blend phase separates. This defines a LCST. For finite molecular weights of polymers, the critical value of χ_{AB} is given by

$$\frac{\chi_{AB,crit}}{C_A} = \frac{RT_A^*}{2P_A^*}\left[\frac{1}{V_A^{*1/2}} + \frac{1}{V_B^{*1/2}}\right]^2 \qquad (6)$$

In order to apply Patterson's theory expressed by eq 5 to copolymer blends, the effective contact energy parameter X_{AB} and the characteristic temperature of the copolymers should be formulated in terms of segmental contact energy parameter X_{ij}, copolymer composition, and the characteristic parameters of each component. According to Flory's treatment for mixtures, we have formulated these parameters in the previous paper.[2] In the development, it was assumed that the external degrees of freedom of copolymers follow the simple additive rule of copolymer components. For blends of homopolymer A of monomer 1 and copolymer B of monomers 2 and 3, X_{AB}, P_B^*, and T_B^* can be expressed as

$$X_{AB} = \theta_B^{(2)}X_{12} + \theta_B^{(3)}X_{13} - (s_A/s_B)\phi_B^{(2)}\theta_B^{(3)}X_{23} \qquad (7)$$

$$P_B^* = \phi_B^{(2)}P_2^* + \phi_B^{(3)}P_3^* - \phi_B^{(2)}\theta_B^{(3)}X_{23} \qquad (8)$$

$$T_B^* = \frac{\phi_B^{(2)}P_2^* + \phi_B^{(3)}P_3^* - \phi_B^{(2)}\theta_B^{(3)}X_{23}}{\phi_B^{(2)}P_2^*/T_2^* + \phi_B^{(3)}P_3^*/T_3^*} \qquad (9)$$

where symbols with the parenthesized superscript i, i = 2 and 3, represent the copolymer composition of the component i in the copolymer. Equations 8 and 9 have a form identical with those for mixtures of components 2 and 3. On the assumption that the number of contact sites per segment is the same for all segments, eqs 7–9 reduce to eqs 10–12.

$$X_{AB} = \phi_B^{(2)}X_{12} + \phi_B^{(3)}X_{13} - \phi_B^{(2)}\phi_B^{(3)}X_{23} \qquad (10)$$

$$P_B^* = \phi_B^{(2)}P_2^* + \phi_B^{(3)}P_3^* - \phi_B^{(2)}\phi_B^{(3)}X_{23} \qquad (11)$$

$$T_B^* = \frac{\phi_B^{(2)}P_2^* + \phi_B^{(3)}P_3^* - \phi_B^{(2)}\phi_B^{(3)}X_{23}}{\phi_B^{(2)}P_2^*/T_2^* + \phi_B^{(3)}P_3^*/T_3^*} \qquad (12)$$

Experimental Section

Materials. The characteristics of polymers used in this study are described in Table I. PMMA and PnBMA were purchased from Scientific Polymer Products, Inc. The other polymers were obtained from an industrial source (Hanyang Chemical Co., Korea). All polymers were used as received without further purification.

Preparation of Blends. Blends containing PMMA were prepared by dissolving component polymers in 2-butanone (MEK) at 65 °C. The solutions were cast on an aluminum dish, and most of the solvent was allowed to evaporate slowly under ambient conditions. The resulting films were then further dried in a vacuum oven for at least 3 days. For blends containing PnBMA, films were cast from tetrahydrofuran (THF) solutions. The composition of all blends investigated was 50/50 by weight.

Table I
Properties of Polymers Used in This Study

polymer[a]	designation	copolym composn, vol % of VAc	DP[b]	T_g, °C
poly(methyl methacrylate)	PMMA		33000[c]	117
poly(*n*-butyl methacrylate)	PnBMA			40
poly(vinyl chloride)	PVC		800	78
poly(VC-*co*-VAc)	VC–VAc5	5.9	700	74
poly(VC-*co*-VAc)	VC–VAc10	11.7	700	72
poly(VC-*co*-VAc)	VC–VAc13	15.1	500	71

[a] VC = vinyl chloride. VAc = vinyl acetate. [b] Number-average degree of polymerization. [c] Nominal molecular weight.

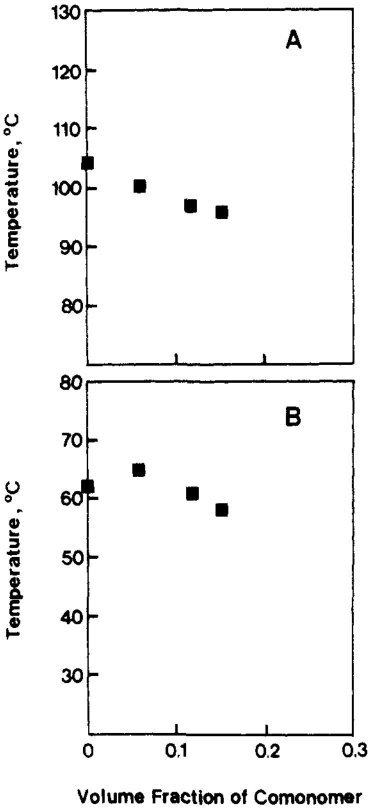

Figure 1. Glass transition temperatures for 50/50 (w/w) blends of VC–VAc copolymer with (A) PMMA and (B) PnBMA.

Thermal Analysis. A Du Pont 1090 thermal analyzer equipped with a differential scanning calorimeter (DSC) was used for the determination of glass transition temperatures. Each sample was heated from room temperature to 130 °C at a rate of 20 °C/min and maintained for 1 min. It was then rapidly cooled to 0 °C and reheated to 130 °C at a heating rate of 20 °C/min. The glass transition temperature of each sample was taken as the midpoint of the heat capacity change in the second scan.

Cloud-Point Measurement. The sample film was placed between two slide glasses and heated with a hot plate at a heating rate of 3 °C/min. The temperature at which, by visual inspection, the transparent film became opaque was designated as the cloud point.

Results and Discussion

Miscibility. In Figure 1, the glass transition temperatures for the blends from DSC measurements are shown as a function of the vinyl acetate (VAc) content in the VC–VAc copolymer. All blends exhibit single glass transition temperatures intermediate between those of the component polymers. When the difference in the

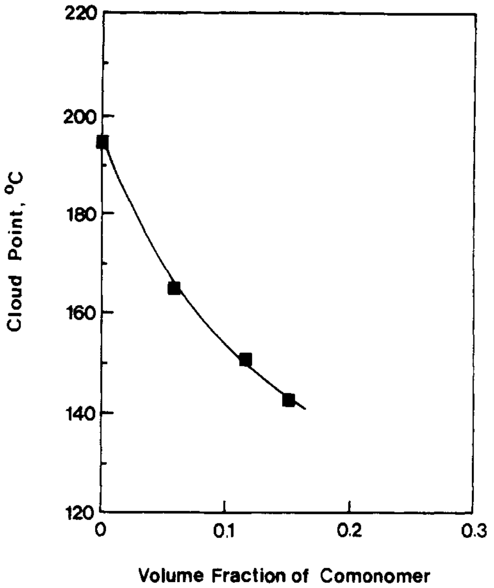

Figure 2. Cloud points for 50/50 PMMA/VC–VAc copolymer blends as a function of the VAc content in the copolymer.

Table II
Characteristic Parameters of Pure Polymers

polymer	v^*, cm^3/g	P^*, J/cm^3	T^*, K
PVC[a]	0.6250	646	8172
PVAc[b]	0.7210	561	6962
PMMA[a]	0.7343	562	8474
PnBMA[c]	0.8176	567	7146

[a] Reference 6. [b] Reference 7. [c] Reference 8.

refractive indices of component polymers is greater than a critical value, the turbidity of blend samples has also been used as an additional means of detecting phase separation to reinforce glass transition results. The refractive indices are different enough in all cases considered.[3] In all cases, as-cast films were clear. From the results of T_g measurements and optical clarity of blend samples, it is concluded that the copolymers of VC–VAc containing at least 16 vol % VAc units are miscible with both PMMA and PnBMA. Since the copolymers containing higher VAc units are not available at this time, it is not possible to evaluate the miscibility window with any certainty.

Phase Behavior of Blends Containing PMMA. Figure 2 shows how the cloud points of blends containing 50% PMMA vary with the VAc content in the VC–VAc copolymer. These blends show phase behavior of the LCST type because the blends became cloudy upon heating. As the VAc content in the copolymer increases, the cloud points decrease, showing a negative deviation from linearity. Therefore, assuming that the phase separation temperature reflects the strength of the interaction between blend components, an effective contact energy parameter X_{AB} at a given copolymer composition can be calculated by eq 5 from the cloud-point data shown in Figure 2. An iterative method introduced in ref 2 was used for the calculation. The characteristic parameters of pure polymers are listed in Table II. In this study, the characteristic parameters of the copolymer components are assumed to be equal to those of the corresponding homopolymers. Using the X_{AB} values which depend on the copolymer composition, segmental contact energy parameters X_{ij} are calculated from a nonlinear least-squares fit of eq 10. The results are listed in Table III.

The X_{AB} value is plotted against the copolymer composition in Figure 3, where the broken line represents eq 10 with $X_{23} = 0$. The monomeric units are designated as 1, 2, and 3 for methyl methacrylate (MMA), vinyl chloride (VC), and VAc, respectively. As shown in Figure 3, the X_{AB} values decrease with an increase of the VAc content and show a positive deviation from linearity. The difference between the calculated and additive values of X_{AB} is a measure of the type of intramolecular interaction, i.e., attractive or repulsive (see eq 10). The positive deviation in Figure 3 results from the attraction between VC and VAc units in the copolymer.

Table III
Segmental Contact Energy Parameters

segment pair	X_{ij}, J/cm^3	segment pair	X_{ij}, J/cm^3
VC/MMA	−0.11	VC/nBMA	−1.74
VAc/MMA	−3.05	VAc/nBMA	1.41
VC/VAc	−2.28		

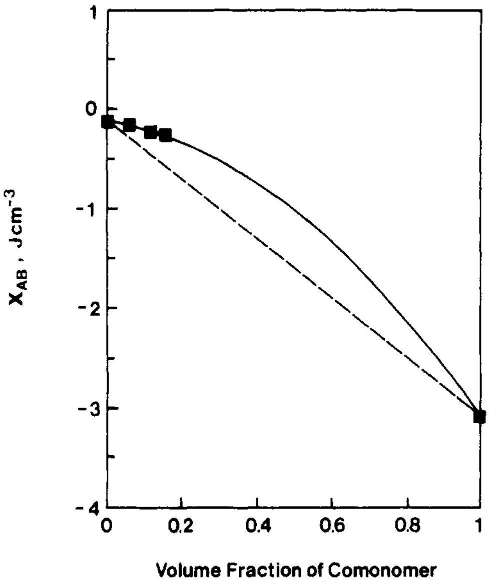

Figure 3. Variation of effective contact energy parameters of PMMA/VC–VAc copolymer blends with the volume fraction of comonomer (VAc) in the copolymer. The broken line represents the additive case in which $X_{23} = 0$.

The cloud points in Figure 2 may be slightly higher than true spinodals due to the heating rate dependence. The small difference between the cloud point and the spinodal results in a slight overestimation of the X_{AB} parameter. However, in the case of 10 °C difference which is acceptable at a relatively low heating rate,[9] the difference in the X_{AB} parameters does not exceed 1%. The method to determine the X_{AB} parameter from cloud-point data has been reported by several workers:[10,11] the spinodal curve can be made to fit closely to the cloud-point curve by using a proper X_{AB} parameter.

As listed in Table III, the contact energy parameter for the MMA and VC pair is estimated to be −0.11 J/cm^3, which is comparable to the value of −0.42 J/cm^3 reported by Vorenkamp et al.[11] If one considers that specific interactions between the acetate carbonyl group and the –CHCl– group of PVC have been identified,[12] the sign and magnitude of −2.28 J/cm^3 for X_{23} are reasonable. Detailed studies[13,14] for blends involving PVC, PVAc, and various copolymers that include a third comonomer have reported the immiscibility of PVC/PVAc. However, Bhagwagar et al.[15] recently pointed out that blends of PVC and PVAc are very sensitive to the type of solvent used in solution blending and that the blends prepared from THF are immiscible due to the $\Delta\chi$ effect. In a ternary system of polymers 1 and 2 and a solvent the $\Delta\chi$ effect arises when the difference between affinities of the two polymers to the solvent is considerably large.[16] Phase diagrams with a closed loop have been observed due to this effect:[17] two coexisting phases have the same concentration of total polymers, but one is rich in polymer 1 and the other in polymer 2. By the use of a different solvent, i.e., MEK, Bhagwagar et al.[15] could prepare a miscible blend of PVC and PVAc. Our result for the miscibility of PVC/PVAc is consistent with their experimental result. The LCST of blends of PVC and PVAc is predicted to be about 130 °C from eq 5 when the X_{23} value of -2.28 J/cm^3 is used. For the MMA and VAc pair, the value of $X_{13} = -3.05$ J/cm^3 is obtained. This result indicates that blends of PMMA and PVAc are miscible and the LCST is predicted to be 145 °C. Recent studies[18,19] have reported that PMMA is miscible with PVAc and the LCST of PMMA/PVAc blends is about 150 °C, depending on the molecular weights of the components. In spite of the experimental results, the miscibility of PMMA and PVAc is still a matter of controversy.[20,21] The results obtained here are still insufficient to draw conclusions about the miscibility of a PMMA and PVAc blend and its LCST because the available copolymer compositions are limited to low VAc levels. Consequently, more experimental work is needed for this system.

Comparing the cloud points of PMMA/PVC and PMMA/PVAc blends, one may infer that the strength of the interaction between PMMA and PVC must be larger than that between PMMA and PVAc. However, in the above calculation, X_{13} is more negative than X_{12}. This result comes from the fact that the contact energy parameter X_{ij} does not account for the free volume effect. At a temperature where the favorable interaction term can no longer outweigh the unfavorable free volume term to give a negative value of χ_{AB}, a LCST occurs. The large difference of the free volume between components in blends results in an unfavorable condition for mixing. Therefore, if the free volume term of a blend is a large positive number, the interaction term must be a large negative number to give miscibility. One can see in Table II that the difference in characteristic temperatures (ΔT^*) between PMMA and PVAc is much larger than that between PMMA and PVC, suggesting that the free volume term of the latter pair does not oppose mixing as much as that of the former one. The higher cloud point for a PMMA/PVC blend comes from the fact that the unfavorable free volume contribution of a PMMA/PVC blend is smaller than that of a PMMA/PVAc blend.

Figure 4 shows the characteristic pressure and temperature of a VC–VAc copolymer calculated from eqs 11 and 12. P_B^* of the copolymer does not exhibit a large deviation from linearity. This arises from the fact that the contribution of X_{23} to P_B^* is very small as compared to P_i^* of the copolymer components. Analogously, T_B^* of the copolymer is governed by the relative magnitude of the characteristic parameters, mainly T_i^* of the copolymer components. This means that the free volume term of blends containing a VC–VAc copolymer is not significantly affected by the intramolecular interaction within the copolymer. As shown in Figure 4B, ΔT^* between PMMA and a VC–VAc copolymer linearly increases as the VAc content in the copolymer increases. This results in an unfavorable increase of the free volume term of the copolymer blends.

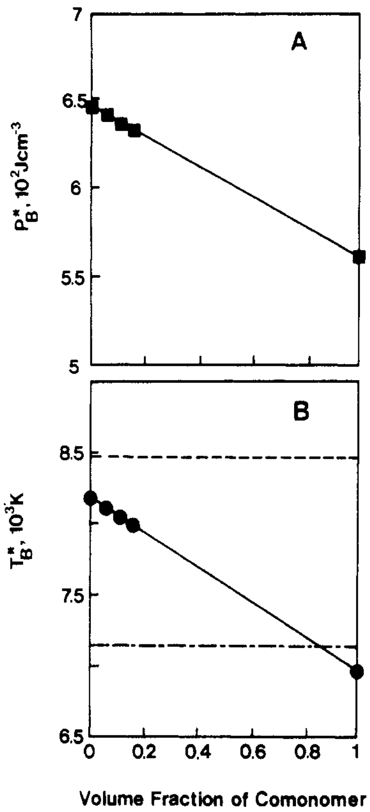

Figure 4. Characteristic parameters of VC–VAc copolymers: (A) characteristic pressure and (B) characteristic temperature. In B, the broken and dot and dashed lines represent the characteristic temperatures of PMMA and PnBMA, respectively.

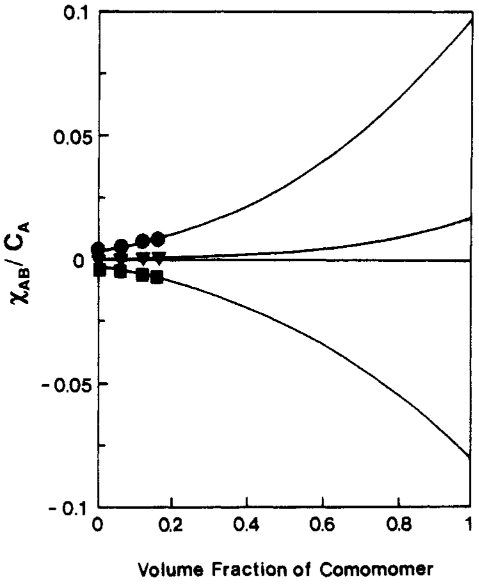

Figure 5. Variation of the interaction (■) and free volume (●) contributions to the Flory–Huggins χ_{AB}/C_A parameter (▼) at the cloud point of the PMMA/PVC blend with the VAc content in the copolymer.

Figure 5 shows the dependence of χ_{AB}/C_A for blends of PMMA and a VC–VAc copolymer on the VAc volume fraction in the copolymer. This figure was calculated at 190 °C, corresponding to the cloud point of PMMA/PVC. The value of χ_{AB}/C_A for PMMA/PVC is zero, since the unfavorable free volume term cancels the favorable interaction term at the cloud-point temperature. The effect of a VAc unit on the free volume term as well as on the interaction term is shown in Figure 5. The interaction term increases favorably with the number of VAc units, although it exhibits a positive deviation from linearity due to the attraction between VC and VAc units. On the other hand, the free volume term is closely related to ΔT^* which is dependent upon the copolymer composition. The χ_{AB}/C_A parameters, given by the sum of the interaction and free volume terms, slightly increase with an increase

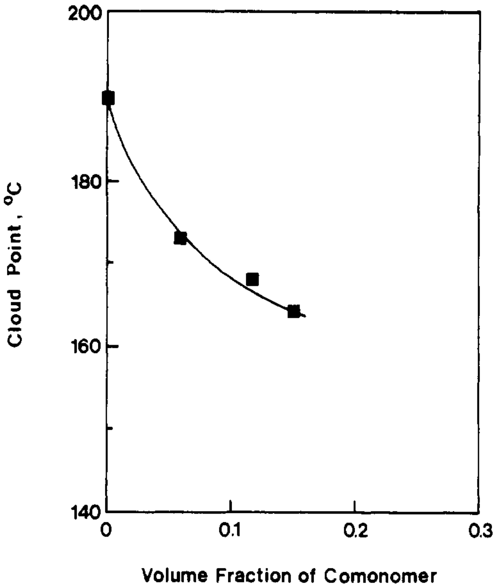

Figure 6. Cloud points for 50/50 PnBMA/VC–VAc copolymer blends as a function of the VAc content in the copolymer.

of the VAc content in the copolymer.

The χ_{AB}/C_A values must be regarded as the level of interaction at a given temperature. If the value of χ_{AB}/C_A calculated at a given copolymer composition and temperature is positive, the interaction for the copolymer blend is less attractive than that of the reference blend. This implies that a blend having a positive value of χ_{AB}/C_A has lower cloud point than that of the reference. As shown in Figure 5, an increase in the free volume term with the copolymer composition leads to an unfavorable increase in χ_{AB}/C_A. This results in a lower cloud point. Therefore, the variation in χ_{AB}/C_A with the copolymer composition is in good agreement with the trend of the LCST behavior shown in Figure 2.

LCST Behavior of Blends Containing PnBMA. Figure 6 shows how the cloud points of 50/50 PnBMA/VC–VAc copolymer blends vary with the VAc content in the VC–VAc copolymer. Similarly to Figure 2, the cloud points decrease as the number of VAc units in the copolymer increases. However, unlike PMMA, PnBMA is immiscible with PVAc.[22]

Figure 7 shows the dependence of X_{AB} on the volume fraction of VAc in the copolymer. The X_{AB} values decrease with an increase of the VAc content. This result is the opposite to that for the blends containing PMMA (see Figure 3). The immiscibility of PnBMA/PVAc is the main reason for the difference. The value of -2.28 J/cm^3 for X_{23} determined from the previous section was used for this calculation. The segmental X_{ij} values are also listed in Table III. The signs of the X_{ij} values are reasonable, considering the miscibility of the corresponding homopolymer pairs.

The variation of ΔT^* between PnBMA and a VC–VAc copolymer with the copolymer composition is also illustrated in Figure 4B. The incorporation of VAc units into the VC polymer contributes favorably to narrowing ΔT^* because the magnitude of T^* of the VAc unit is similar to that of PnBMA.

In Figure 8, the χ_{AB}/C_A parameters calculated at 195 °C (corresponding to the cloud point of PnBMA/PVC) are plotted against the VAc volume fraction in the copolymer. As expected from the results in Figures 7 and 4B, the interaction term unfavorably increases as the VAc content in the copolymer increases, whereas the free volume term favorably decreases. The sum of these two terms χ_{AB}/C_A

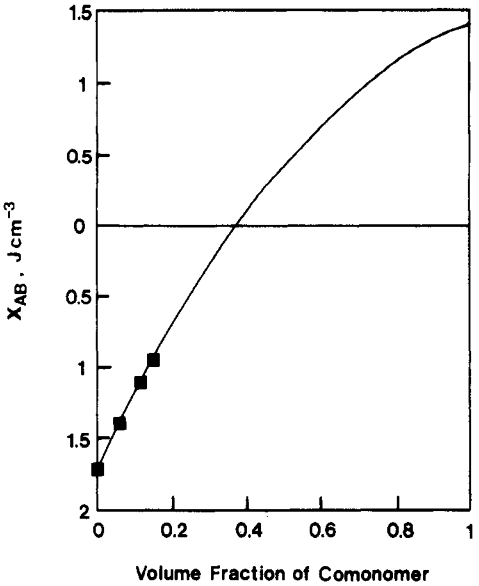

Figure 7. Variation of effective contact energy parameters of PnBMA/VC–VAc copolymer blends with the volume fraction of VAc in the copolymer.

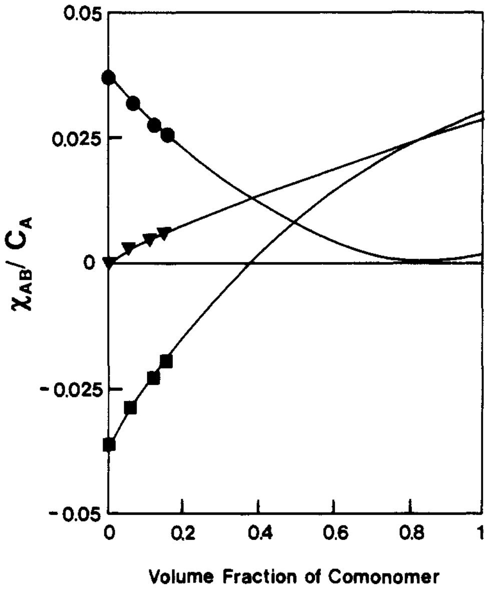

Figure 8. Variation of the interaction (■) and free volume (●) contributions to the Flory–Huggins χ_{AB}/C_A parameter (▼) at the cloud point of the PnBMA/PVC blend, with the VAc content in the copolymer.

slightly increases with an increase of the VAc content in the copolymer. This variation of χ_{AB}/C_A with the copolymer composition corresponds well to the variation of the cloud points. Because of the favorable effect of the VAc unit on the free volume term, the unfavorable increase in the interaction term is diminished and to a certain extent the miscibility window is enlarged.

Conclusions

The present results may confirm, at least in a qualitative manner, the importance of the effect of comonomer on the free volume term which we have introduced in our other recent paper[2] by applying Patterson's theory to copolymer blends.

Incorporation of a VAc unit into the VC polymer decreases the cloud points for blends with PMMA, even though the VAc unit has the favorable effect of making the interaction term of copolymer blends more negative. This is due to a large unfavorable free volume effect of the

VAc unit that compensates for the favorable change in the interaction term.

In the blends containing PnBMA, the situation appears to be the reverse. Although a VAc unit has a favorable effect on the free volume term, the cloud points of PnBMA/VC–VAc copolymer blends decrease with an increase of the comonomer content. This is the result of the unfavorable increase in the interaction term with the VAc content, which outweighs the favorable decrease in the free volume term.

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Registry No. (VC)(VAc) (copolymer), 9003-22-9; PMMA, 9011-14-7; PnBMA, 9003-63-8.