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Control of Phase Separation Temperature of Polymer Blends by Copolymer Blending Method

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ABSTRACT: This study was performed to justify experimentally a copolymer blend model, which is based on the Prigogine-Flory-Patterson's equation of state theory. The blend of poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) is selected as model blend system: *n*-butyl acrylate (*n*BA) as comonomer is incorporated into PMMA. The cloud point of PVC/PMMA blend first increases with the *n*BA content, goes through a maximum and then decreases to the cloud point of PVC/P*n*BA blend of 145 ℃. This means that the *n*BA units chosen as comonomers are effective in elevating the cloud point of PVC/PMMA blend. The effect of *n*BA content on the cloud point of PVC/PMMA blend was interpreted in terms of a copolymer blend model based on the Prigogine-Flory-Patterson's eguation of state theory. The elevation of the cloud points with the *n*BA content is mainly due to an increase of the strength of interaction, which is caused by the addition of *n*BA units in the MMA/*n*BA copolymers. The *n*BA units added are effective in reducing the difference in characteristic temperatures of blend component and thus favorably contribute to elevating the cloud points of PVC/PMMA blends.

Introduction

The phase separation temperature of polymer blends is an important factor in preparing commercially attractive polymer blends. When a miscible polymer blend has the phase separation temperature lower than its melt processing temperature, one cannot obtain a homogeneous morphology after melt processing. In this case one must elevate the phase separation temperature of the blend to the range of temperatures available for melt processing systems. Copolymer blends have been of considerable interest in recent years[1-5] as an effective way of controlling the phase separation temperature of polymer blends. Comonomers incorporated into one component of a miscible polymer blend can cause a significant change in the phase behavior of the blend. Especially, the temperature at which polymer blends phase separate on heating, that is, lower critical solution temperature (LCST), changes dramatically with the type and the content of comonomer. Since the phase separation temperature of polymer blends reflects the magnitude of the interaction between blend components, its elevation indicates an increase in the strength of the interaction.

The phase separation temperature of polymer blends has been viewed as a balance between an unfavorable free volume term and a favorable interaction term.[6] Thus, in order to change the phase separation temperature of polymer blends by copolymer blending method, one must understand the effect of comonomer on the two terms mentioned above. Interesting efforts for applying an

equation of state (EOS) theory to copolymer blends have been made by many workers. The formulations based on the Prigogine's EOS theory,[7-9] the lattice-fluid theory,[5,10] modified Flory's EOS theory[11-13] have appeared in the literature. Recently, Jo and Lee suggested a model to interpret the LCST behavior of copolymer blends.[14-16] It was developed by combining the Prigogine-Flory-Patterson's equation of state theory and a binary interaction model. It has the advantage of describing separately the effect of comonomers on the interaction and the free volume terms of copolymer blends. Thermodynamic factors for affecting the LCST behavior of copolymer blends are as follows: (a) the intramolecular interaction within copolymers, (b) the relative magnitude of the characteristic parameters of comonomer selected, (c) the segmental interaction between monomeric units in copolymer blends, etc.

The objective of this study is to justify experimentally the copolymer blend model suggested by Jo and Lee. The blend of poly(vinyl chloride) (PVC) and poly(methyl methacrylate) (PMMA) is selected as model blend system. It is well known that the blends of PVC and PMMA are miscible at a molecular level and have an LCST of about 190 ℃[17]; *n*-butyl acrylate (*n*BA) as comonomer is incorporated into PMMA. Poly(*n*-butyl acrylate) (P*n*BA) is miscible with PVC but immiscible with PMMA.[18] The LCST of PVC/P*n*BA blends is about 125 ℃.[19] Since P*n*BA is miscible with PVC, the MMA/*n*BA copolymers will be miscible with PVC over the entire copolymer composition range. However, another study on the blends of PVC and P*n*BA has reported the immiscibility between PVC and P*n*BA.[20]

Theoretical Background

The lower critical solution temperature (LCST) behavior of polymer blends can be easily interpreted using Patterson's equation of state theory. Using the corresponding state theory and the van der Waals model, Patterson and Robard[21] have derived an expression for the Flory-Huggins interaction parameter χ_{AB} normalized to a reference molecule A:

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

where C_A is the number of the external degrees of freedom of component A, $\tilde{v}_A^{1/3}$ is the reduced volume, and X_{AB} is the contact energy parameter. The starred quantities denote the molecular characteristics of the chain molecules. Since the reduced volume is related with the reduced temperature by the equation of state, eq 1 is a function of temperature. The first term on the right side of eq 1 is an interaction term, which arises from the difference in interaction energy between like and unlike segment pairs. The second term on the right side of eq 1 is the free volume term caused by a mismatch of thermal expansivities of blend components. This term is proportional to the difference in characteristic temperatures of components (ΔT^*). The larger ΔT^* makes the free volume term more positive, and thus leads to more unfavorable mixing. Eq 1 says that a blend pair is miscible at a given temperature provided the normalized χ_{AB} parameter is less than a critical value or zero in the limit of high molecular weight. Eq 1 is effective for qualitatively explaining the phase behavior of polymer blends. However, as pointed by Patterson, eq 1 has some limitations in the quantitative discussion because the phase separation behavior of polymer blends is controlled by the spinodal inequality condition.

In order to apply Patterson's theory expressed by eq 1 to copolymer blends, the effective contact energy parameter X_{AB} and the characteristic temperature of copolymers should be formulated in terms of segmental contact energy parameter X_{ij}, copolymer composition and the characteristic parameters of comonomers. According to Flory's treatment for mixtures, we have formulated these parameters in a previous paper.[14] For the blends of homopolymer A of monomer 1 and copolymer B of monomers 2 and 3, the effective contact energy parameter for the blends (X_{AB}) and the characteristic temperature for copolymers (T_B^*) can be expressed as follows:

$$X_{AB}=x\,X_{12}+(1-x)X_{13}-x(1-x)X_{23} \quad (2)$$

$$T_B^* = \frac{xP_2^* + (1-x)P_3^* - x(1-x)X_{23}}{x\frac{P_2^*}{T_2^*} + (1-x)\frac{P_3^*}{T_3^*}} \quad (3)$$

where X_{ij}, i, j=1, 2, or 3, is the segmental contact energy parameter between monomeric units i and j and x is the copolymer composition. In the development, it is assumed that the external degrees of freedom for copolymers follow the simple additive rule of the copolymer components and the number of contact sites per segment is the same for all segments. One can realize from eqs 2 and 3 that the intramolecular interaction within copolymers (X_{23}) contributes to the free volume term (proportional to T_A^*/T_B^*) of copolymer blends as well as to the interaction term (proportional to X_{AB}). It is noteworthy that eq 2 is identical to a binary interaction model for homopolymer/copolymer blends[2,22] and eq 3 is identical to an equation for binary mixture.[23]

Schematic diagram of Figure 1 shows some interesting possibilities for the variation of X_{AB} with copolymer composition. The negative deviation from linearity results from the repulsion between comonomers. The positive X_{23} contributes favorably to making X_{AB} more negative. Therefore, more strong repulsion within copolymers makes the interaction term more negative. This explanation is very similar to the binary interaction model in reference 2. However, the X_{ij} parameters are free from the free volume effect. The other factor for determining the magnitude of the X_{AB} parameter is the X_{13} parameter because it arises from the introduction of comonomer. A negative value of X_{13} is effective to making X_{AB} more negative. Thus, the comonomers, which interact fa-

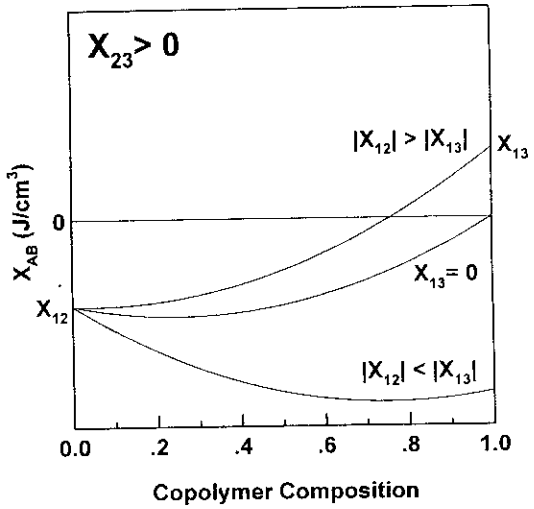

Figure 1. Schematic effective contact energy parameter X_{AB} for blends of a homopolymer (monomer 1) with a copolymer (monomers 2+3) as a function of copolymer composition.

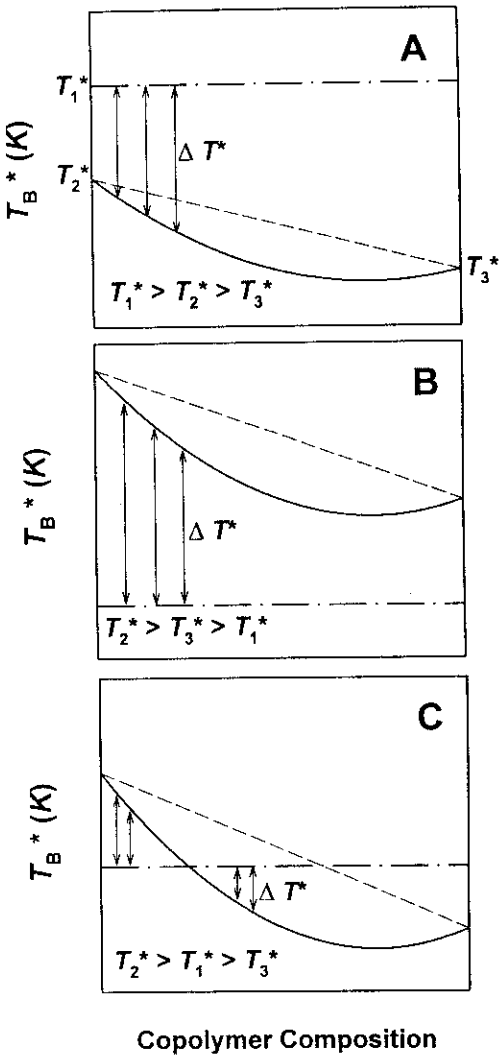

Figure 2. Schematic illustrations of various theoretical possibilities that the difference in T^* may depend on the relative magnitudes of T_i^* of blend components. The dashed lines show the additive case. The horizontal dot and dashed lines correspond to the T^* of homopolymer.

vorably with monomer 1, are desirable for elevating the phase separation temperature of polymer blends.

As deduced from eq 3, schematic understanding for the effect of comonomer on the free volume term is rather complex. This comes from the fact that ΔT^* depends on the magnitude of the characteristic parameters (P_i^* and T_i^*) of selected comonomer as well as X_{23}. Some possibilities for ΔT^* are schematically illustrated in Figure 2. The negative deviation from additivity in T_B^* is due to the intramolecular repulsion. It is noteworthy that T_B^* is dependent on the magnitude of the characteristic parameters of the comonomers. One can see that on the contrary to the interaction term, a positive X_{23} is not always favorable to the free volume term, that is, ΔT^*. In Figure 2C, ΔT^* first decreases and then increases. A copolymer composition at which T_B^* is the same as T_1^* exists. This is the most desirable situation to reduce the unfavorable free volume term and raise the LCST of a blend system.

From the theoretical consideration mentioned above, one can obtain a prior guidance on how to select comonomers that will give the desirable effect of raising LCST of a blend system. In terms of the interaction term, the comonomers that make X_{AB} more negative are favorable for raising the LCST. This is possible when X_{13} is more negative than X_{12}. A positive value of X_{23} is also required. This means that the polymer of monomer 3 must be miscible with the polymer of monomer 1 and immiscible with the polymer of monomer 2. In terms of the free volume term, the comonomers that reduce the difference in T^* are favorable. To select these comonomers one must simultaneously consider the following factors: the intramolecular interaction within copolymers (X_{23}) and the relative magnitude of the characteristic parameters of comonomers selected.

Experimental

All polymers, except PVC, were synthesized in a sealed glass ample by bulk polymerization at 65 ℃ using AIBN as initiator. The maximum degree of conversion was controlled to about 10 wt %. The *n*BA contents in the MMA/*n*BA copolymers were determined using 300 MHz ^{1}H-NMR (Bruker AMX-R300). The intrinsic viscosity of the polymers synthesized was measured using an Ubbelodhe viscometer. The characteristics for the polymers

Table I. Polymers Used in This Study

polymer	source	copolymer compositon (mole % of *n*BA)	intrinsic viscosity[a] (mL/g)	T_g(℃)[b]
PVC	Junsei Chem. Co.	-	1,100[d]	84.2
PMMA	Synthesized	-	39.1	118.0
P*n*BA	Synthesized	-	42.3	-45.6
M*n*BA4[c]	Synthesized	4.1	36.7	112.6
M*n*BA6	Synthesized	5.8	41.2	108.6
M*n*BA10	Synthesized	9.6	33.8	97.6
M*n*BA15	Synthesized	15.3	49.9	83.7
M*n*BA19	Synthesized	19.1	41.7	59.9
M*n*BA31	Synthesized	31.2	56.3	38.2
M*n*BA43	Synthesized	43.1	44.2	22.9
M*n*BA57	Synthesized	57.6	51.6	-0.6
M*n*BA69	Synthesized	68.5	32.3	-17.4
M*n*BA79	Synthesized	79.2	41.4	-29.4
M*n*BA85	Synthesized	85.4	36.6	-35.4
M*n*BA97	Synthesized	96.9	44.7	-45.2

[a] In acetone at T=25 ℃.
[b] T_g was determined by DSC with the heating rate of 20 ℃.
[c] The numbers following M*n*BA are the mole percentages of *n*BA units in the copolymers.
[d] Degree of polymerization.

used in this study are listed in Table I.

All blend solutions were prepared by dissolving the component polymers in methyl ethyl ketone (MEK) at 65 ℃. The solutions were cast on a petri dish for cloud point measurement or poured into methanol to obtain precipitates for thermal analysis. The resulting samples were dried under ambient conditions for about 5 days and then further dried under vacuum at 60 ℃ for 2 days.

Thermal analysis was performed on Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) equipped with a mechanical cooling accessory. Samples were first heated from room temperature to 150 ℃ at a rate of 20 ℃/min and maintained at final temperature for 5 min. After rapidly cooled to about -70 ℃ they were heated to 150 ℃ at the same heating rate. The glass transition temperature was taken as the midpoint of the heat capacity change in the second scan.

Cloud points were determined as follows. The sample films prepared was placed between two slide glasses and heated onto a hot plate at a heating rate of about 1 ℃/min. The temperature at which, by visual inspection, transparent film became opaque was designated as cloud point.

Results and Discussion

The existence of composition-dependent single T_g between those of blend components is a widely used criterion in determining the miscibility of polymer blends. Figure 3 shows the representative DSC thermograms of the blends of PVC and the MMA/*n*BA copolymers (5/5, wt/wt) and the T_g's as a function of the *n*BA content in the copolymers are summarized in Figure 4. For blends with copolymers containing *n*BA contents of less than 40% by mole, single glass transitions are observed between the glass transition temperatures of the blend components. On the other hand, blends of PVC and the MMA/*n*BA copolymer containing 50 mole % or more *n*BA show two distinct glass transitions. From these results, we conclude that the M*n*BA57 copolymer is just beyond a critical limit to form completely miscible blends with PVC at the annealing temperature of 150 ℃. Since the blends of PVC and P*n*BA have an LCST of about 125 ℃, we suppose that the blends with two distinct T_g's are miscible but have the LCST's lower than the annealing temperature of 150 ℃. As prepared films were clear at room temperature.

The blends with two different T_g's are phase-separated into two distinct phases, PVC-rich (higher T_g) and copolymer-rich (lower T_g) phases. As shown in Figure 4, the higher T_g's remain in-

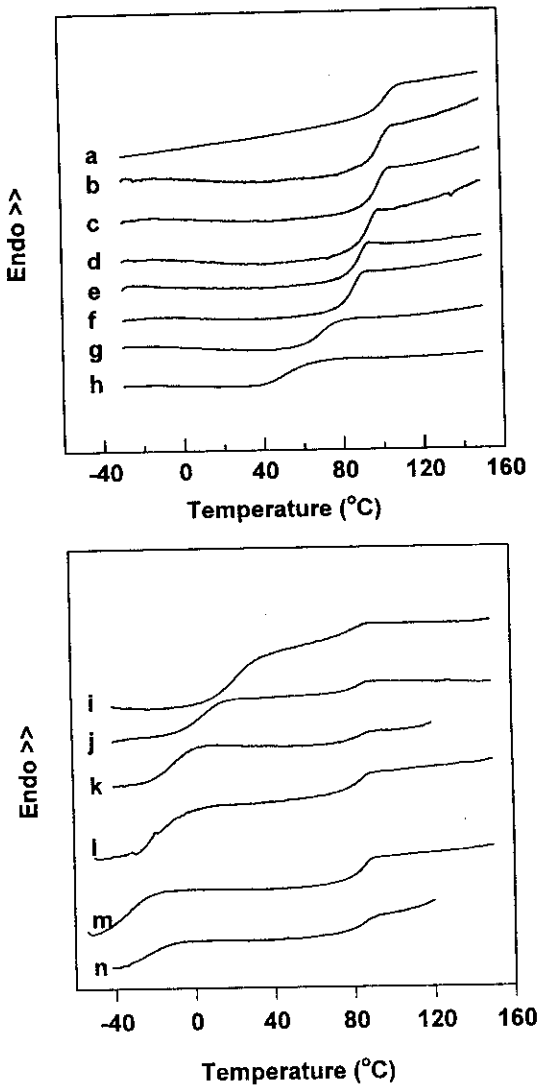

Figure 3. Representative DSC thermograms of the blends of PVC and MMA/*n*BA copolymers (5/5, wt/wt), annealed at 150 ℃ for 5 min: (a) PMMA; (b) M*n*BA4; (c) M*n*BA6; (d) M*n*BA10; (e) M*n*BA15; (f) M*n*BA19; (g) M*n*BA31; (h) M*n*BA43; (i) M*n*BA57; (j) M*n*BA69; (k) M*n*BA79; (l) M*n*BA85; (m) M*n*BA97; (n) P*n*BA, respectively.

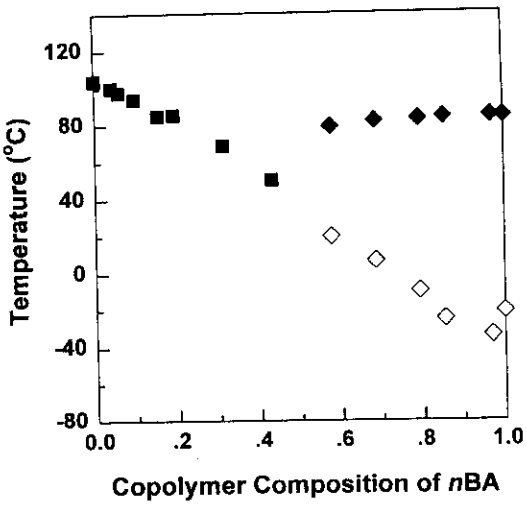

Figure 4. Glass transition temperatures of the blends of PVC and MMA/*n*BA copolymers (5/5, wt/wt): (■) single T_g; (◆) T_g of PVC-rich phase; (◇) T_g of copolymer-rich phase. This is a summary of DSC results shown in Figure 3.

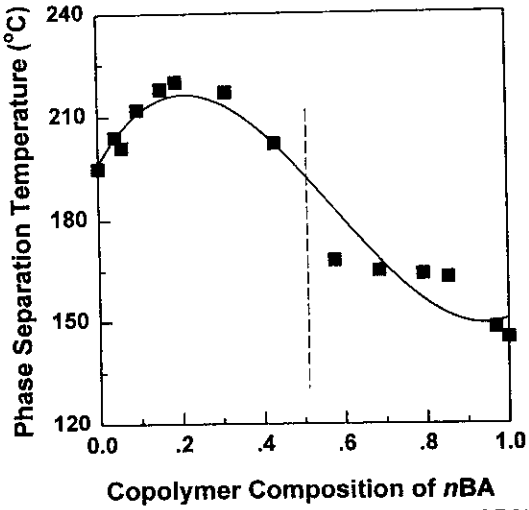

Figure 5. Cloud points for the blends of PVC and MMA/*n*BA copolymers (5/5, wt/wt) as a function of the *n*BA content in the copolymers.

variant indicating that the copolymers are not dissolved in the PVC-rich phases. However, the lower T_g's of copolymer-rich phases are slightly higher than those of the pure copolymers. From the extent of the T_g elevation of the copolymer-rich phases, we can calculate the fraction of PVC dissolved in each phase using the Fox equation. For the blend of PVC and M*n*BA57, T_g of the copolymer-rich phase is 20 ℃. The fraction of PVC dissolved in the M*n*BA57 copolymer-rich phase is calculated to be about 30% by weight.

Figure 5 shows how the cloud points of the blends of PVC and the MMA/*n*BA copolymers (5/5, wt/wt) vary with the *n*BA content in the copolymers. This figure clearly shows the effect of *n*BA content on the cloud point of PVC/PMMA blends. The cloud point first increases with *n*BA content, goes through a maximum and then decreases to the cloud point of the PVC/P*n*BA blend of 145 ℃. The maximum rise in the cloud points occurs at about 20 mole % of *n*BA. It is clear that the *n*BA units chosen as comonomers are effective in elevating the cloud point of PVC/PMMA blend.

The result shown in Figure 5 is slightly different to the DSC results of Figures 3 or 4; blends with the copolymers containing 50 mole % or more *n*BA is phase-separated at 150 ℃. The discrepancy may

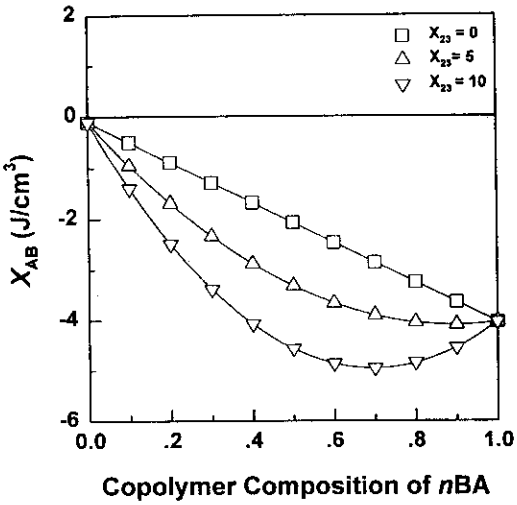

Figure 6. Variation of effective contact energy parameters X_{AB} with the magnitude X_{23}. This is calculated from eq 2.

be explained in terms of the following two reasons. First, from the turbidity measurement homogeneity is present down to a level of approximately 1000A.[24] However, glass transition phenomenon is not sensitive to dimensions which are much smaller than 100A.[25] The determination of the miscibility by cloud points may not be confirmed by thermal analysis. Second, the cloud points in Figure 5 may be slightly higher than the

true phase separation temperatures due to the heating rate dependence. More precise cloud points must be determined by using other experiments such as light scattering technique.

The monomeric units are designated as 1, 2, and 3 for vinyl chloride (VC), methyl methacrylate (MMA), and *n*-butyl acrylate (*n*BA), respectively. From the cloud points of PVC/PMMA and PVC/P*n*BA blends, the values of X_{13} and X_{12} were estimated to be -0.12 and -4.02 J/cm^3, respectively. The value of X_{12} = -0.12 J/cm^3 is comparable with that of -0.42 J/cm^3 reported by Vorenkamp *et al.*[17] The value of X_{13} = -4.02 J/cm^3 is comparable with that of -12.82 J/cm^3 by Sham and Walsh.[26] They reported that the value of X_{13} is estimated to be -12.82 J/cm^3 from the experimental heat of mixing of PVC/P*n*BA blends. From the immiscibility of PMMA/P*n*BA blends, we can expect a positive value X_{23}. Figure 6 illustrates how the X_{AB} parameters vary with the copolymer composition of *n*BA and the magnitude of X_{23}. The X_{AB} parameters are very sensitive to the magnitude of X_{23}. The value of X_{23} = 10 J/cm^3 is so large as to make the X_{AB} more negative and show a minimum. The characteristic parameters of pure polymers are listed in Table II. In this calculation, the characteristic parameters of the copolymer components are assumed to be equal to those of the corresponding homopolymers.

Table II. Characteristic Parameters of the Polymers Used in This Study

polymer	v_{sp}*(cm^3/g)	T*(K)	T*(Pa)
PVC[a]	0.6250	8172	646
PMMA[a]	0.7343	8474	562
P*n*BA[b]	0.8176	6618	411

[a]Determined from *P-V-T* data of reference 27.
[b]Determined from data (α, γ, v_{sp}) of reference 26.

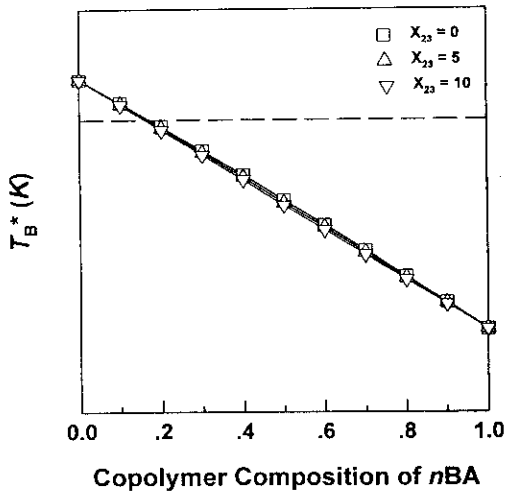

Figure 7. Variation of T_B* for the MMA/*n*BA copolymers with the magnitude of T_{23}. The broken line represents the characteristic temperature of P*n*BA. This is calculated from eq 3.

Figure 7 shows the characteristic temperatures of the MMA/*n*BA copolymers calculated from eq 3. When the same values of X_{23} as those used in Figure 6 are used for the calculation, T_B* is not affected by the magnitude of X_{23} although that it is critical to X_{AB}. This is because the contribution of X_{23} to T_B* is very small as compared to P_i* of the copolymer components. This means that the free volume term of the blends containing the MMA/*n*BA copolymers is not significantly affected by the intramolecular interaction within copolymers. As shown in Figure 7, T_B* of the copolymers is governed by the magnitude of T_i* of the copolymer components. Recalling the order in the magnitude of the characteristic temperatures T_i* , this is the same case as suggested for Figure 2C. One can ex-

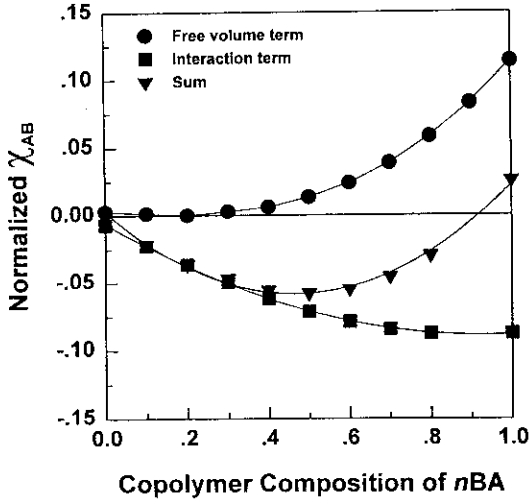

Figure 8. Variation of the interaction (■) and free volume (●) contributions to the normalized Flory-Huggins interaction parameter (▼) at the cloud point of the PVC/PMMA blend with the *n*BA content in the MMA/*n*BA copolymers.

pect a copolymer composition at which ΔT^* is zero. This is the most desirable case for elevating cloud points of polymer blends in terms of the free volume term.

In Figure 8, normalized χ_{AB} (χ_{AB}/C_A), calculated at the cloud point of PVC/PMMA blend, is plotted against the *n*BA content in the copolymers. The value of X_{23}=5 J/mol was used for the calculation. The value of normalized χ_{AB} for PVC/PMMA is zero since the unfavorable free volume term cancels the favorable interaction term at the cloud point. The effect of *n*BA units on the free volume term of the blends of PVC and MMA/*n*BA copolymer as well as on the interaction term is well shown in Figure 8. The interaction term increases favorably with increasing the *n*BA content in the copolymers. The positive value of X_{23} makes the interaction term more favorable. However, although X_{23} is zero, the interaction term will increase favorably because the absolute value of X_{13} is larger than that of X_{12}. As expected from Figure 7, first, the free volume term first favorably decreases with the *n*BA content, becomes zero, and then unfavorably increases. This is possible because T_{PVC}^* is between T_{PMMA}^* and T_{nBA}^*. However, the free volume term does not vary with the *n*BA content as dramaticaly as the interaction term. The magnitude of X_{23} does not contribute largely to the free volume term (or ΔT^*), unlike its contribution to the interaction term. Normalized χ_{AB} parameters are sum the of the two terms mentioned above. As shown in Figure 8, normalized χ_{AB} becomes negative, goes through a minimum, and then eventually goes positive as the comonomer content increases from zero. Thus, in a qualitative sense, the normalized χ_{AB} parameters parallel the experimental results shown in Figure 5. Since Figure 8 is calculated at the cloud point of PVC/PMMA blend, blends with the positive χ_{AB} values have the phase separation temperature lower than that of PVC/PMMA blend.

Figure 8 does not predict the copolymer composition at which the maximum rise in the cloud points occurs. However, it may be possible to predict the composition if more precise cloud points are determined by using other experiments such as light scattering technique. Also, it is possible to analyze more quantitatively the effect of *n*BA units on the LCST behavior of the blends of PVC and MMA/*n*BA copolymers. More experimental work is needed for this system.

Conclusions

We investigated the effect of comonomer on the LCST behavior of copolymer blends using PVC/PMMA blend as a model system. The *n*BA was chosen as comonomer and incorporated into PMMA. The cloud point of PVC/PMMA blend first increases with the *n*BA content, goes through a maximum and then decreases to the cloud point of PVC/P*n*BA blend. The maximum rise in the cloud points occurs at about 20 mole % of *n*BA. As expected, it is clear that the *n*BA units chosen as comonomer are effective in elevating the LCST of PVC/PMMA blend.

The LCST behavior of this system was interpreted in terms of the model for copolymer blends and was proposed by Jo and Lee. The interaction term of this blend system increases with increasing the *n*BA, irrespective of the magnitude of intramolecular interaction between MMA and *n*BA (X_{23}). This is because the interaction between VC and *n*BA is much stronger than that between VC and MMA. The interaction term is very sensitive to the magnitude of X_{23}.

The free volume term of this system, first, favorably decreases with the *n*BA content, becomes zero, and then unfavorably increases. This is possible because T_{PVC}^* is between T_{PMMA}^* and T_{nBA}^*. The magnitude of X_{23} does not contribute largely to the free volume term (or ΔT^*) unlike its contribution to the interaction term.

From these results, it is clear that the phase separation temperature of polymer blends can be controlled effectively by copolymer blending method. This is possible from the systematic understanding for the thermodynamic factors, which contribute to the normalized Flory-Huggins χ_{AB} parameter.

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References

(1) G. ten Brinke, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, **16**, 1827 (1983).
(2) D. R. Paul and J. W. Barlow, *Polymer*, **25**, 487 (1984).
(3) Y. Y. Chien, E. M. Pearce, and T. K. Kwei, *Macromolecules*, **21**, 1616 (1988).
(4) M. Nishimoto, H. Keskkula, and D. R. Paul, *Macromolecules*, **23**, 3633 (1990).
(5) C. K. Kim and D. R. Paul, *Polymer*, **33**, 4929 (1992).
(6) I. C. Sanchez, in *Polymer Compatibility and Incompatibility: Principles and Practices*, K. Solc, Ed., MMI Symposium Series Vol. 2, Harwood, New York, 1982.
(7) H. W. Kammer, *Acta Polym.*, **37**, 1 (1986).
(8) H. W. Kammer, J. Kressler, B. Scheller, H. Kroschwite, and G. C. Naake, *Acta Polym.*, **40**, 75 (1989).
(9) H. W. Kammer, T. Inoue, and T. Ougizawa, *Polymer*, **30**, 888 (1989).
(10) C. G. Panayiotou, *Makromol. Chem.*, **188**, 2773 (1987).
(11) T. Shiomi, H. Ishimatsu, T. Eguchi, and K. Imai, *Macromolecules*, **23**, 4970 (1990).
(12) T. Shiomi, T. Eguchi, H. Ishimatsu, and K. Imai, *Macromolecules*, **23**, 4978 (1990).
(13) T. Shiomi and K. Imai, *Polymer*, **32**, 73 (1991).
(14) W. H. Jo and M. S. Lee, *Macromolecules*, **25**, 842 (1992).
(15) M. S. Lee, S. C. Lee, S. H. Chae, and W. H. Jo, *Macromolecules*, **25**, 4339 (1992).
(16) M. S. Lee and W. H. Jo, *Polymer (Korea)*, **15**, 584 (1991).
(17) E. J. Vorenkamp, G. ten Brinke, J. G. Meijer, H. Jager, and G. Challa, *Polymer*, **26**, 1725 (1985).
(18) S. Krause, in *Polymer Blends*, D. R. Paul and S. Newman, Eds., Academic Press, New York, 1978, Vol. 1, Chapter 2.
(19) D. J. Walsh and C. K. Sham, *Macromolecules*, **22**, 3799 (1989).
(20) C. Tremblay and R. E. Prud'homme, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 1857 (1984).
(21) D. Patterson and A. Robard, *Macromolecules*, **11**, 690 (1978).
(22) D. R. Paul and J. W. Barlow, *Polymer*, **25**, 487 (1984).
(23) P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1833 (1965).
(24) L. A. Utracki, *Polymer Alloys and Blends: Thermodynamics and Rheology*, Oxford Univ. Press, New York, 1990, pp 64.
(25) J. E. Mark, A. Eisenberg, W. W. Graessley L. Mandelkern, E. T. Samulski, J. L. Koenig, and G. D. Wignall, *Physical Properties of Polymer*, 2nd Ed., ACS, Washington, DC, 1993 pp 88.
(26) C. K. Sham and D. J. Walsh, *Polymer*, **28**, 804 (1987).
(27) R. Simha, P. S. Wilson, and O. Olabisi, *Kolloid Z.Z. Polym.*, **251**, 402 (1973).