The Effects of Intramolecular Interactions of Random Copolymers on the Phase Behavior of Polymer Mixtures[†]

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Abstract : To explore the effects of intramolecular interactions within the copolymer on the phase separation behavior of polymer blends, copolymers having two different types of intramolecular interactions, i.e., intramolecular repulsion and intramolecular attraction were prepared. In this study, poly(styrene-*co*-methylmethacrylate) (P(S-MMA)) having intramolecular repulsion caused by positive interaction between styrene and MMA and poly(styrene-*co*-ethyl-methacrylate) (P(S-EMA)) and poly(styrene-*co*-cyclohexylmethacrylate) (P(S-CHMA)) having intramolecular attraction caused by negative interaction between styrene and methacrylate were blended with tetramethyl polycarbonate (TMPC). The phase behavior of blends was examined as a function of copolymer composition and blend composition. TMPC formed miscible blends with styrenic copolymers containing less than certain amount of methacrylate. The phase separation temperature of TMPC blends with copolymer such as P(S-MMA) and P(S-EMA), first increases with methacrylate content, goes through a maximum and then decreases just prior to the limiting content of methacrylate for miscibility, while that of TMPC blends with P(S-CHMA) always decreases. The calculated interaction energy for TMPC-P(S-EMA) pair is negative and monotonically increases with EMA content of the copolymer. Such behavior contradicted the general notion that systems with more favorable energetic interactions have higher LCST. The detailed inspection of the lattice-fluid theory related to the phase behavior was performed to explain such behavior.

Keywords : intramolecular interactions, styrene-methacrylate copolymers, TMPC, LCST-type phase behavior, equation-of-state effects, interaction energy.

Introduction

The phase behavior of polymer blends is a function of component molecular weight, the free volume of equation-of state effects, and especially the polymer-polymer interactions.[1-11] When the pair interactions are strongly favorable, miscibility exists at all temperature range and compositions in spite of potentially unfavorable equation-of-state contributions; whereas, strongly unfavorable interactions lead to immiscibility regardless molecular weights. Polymer-polymer mixtures having weak favorable interaction, which generally exhibit LCST behavior under the melt processing temperature, become sensitive to modification in component molecular structure. Homopolymer pairs with weak favorable interaction are of considerable interest because there are avenues to make their blends usefully miscible. Incorporation of a comonomer into one of the polymers can be an attractive possibility for making an immiscible pair or a pair showing

LCST behavior into a miscible pair or for altering the phase diagram enough to allow formation of homogeneous mixtures by melt processing.[5-7]

To understand the potential effects of copolymerization on the blend phase behavior, copolymers having two different types of intramolecular interactions were prepared. One type was that each component composed of copolymer has unfavorable interactions, i.e., positive interaction energy; whereas the other type was that each component composed of copolymer has favorable interactions, i.e., negative interaction energy. For this examination, blends of tetramethyl bisphenol-A polycarbonate (TMPC) and polystyrene (PS) that showed LCST-type phase behavior below the melt processing temperature[12,13] were selected as a homopolymer pair. Styrenic copolymers containing various methacrylates were prepared and then phase behavior of their blends with TMPC was studied to explore the effects of intramolecular interactions on the phase diagram.

Experimental

Tetramethyl polycarbonate was supplied by Bayer AG, and its weight average molecular weight determined by

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Table I. Copolymers Synthesized for this Study

Abbreviation	Methacrylate Content (wt%)[a]	$\overline{M}_w$[b]	$\overline{M}_w/\overline{M}_n$[b]
P(S-MMA) 5	4.5	120,000	1.80
P(S-MMA) 10	10.2	155,000	2.05
P(S-MMA) 15	14.7	135,000	1.68
P(S-MMA) 20	20.0	117,000	2.10
P(S-MMA) 30	39.5	150,000	1.80
P(S-MMA) 35	34.0	110,000	2.07
P(S-MMA) 40	39.0	145,000	1.95
P(S-EMA) 12	12.0	115,000	1.95
P(S-EMA) 13	13.5	135,000	1.78
P(S-EMA) 15	14.8	125,000	1.75
P(S-EMA) 17	16.8	130,000	2.25
P(S-EMA) 19	19.4	114,000	1.85
P(S-EMA) 25	24.0	124,000	2.05
P(S-CHMA) 10	7.8	60,000	1.79
P(S-CHMA) 15	11.6	68,000	1.91
P(S-CHMA) 25	22.8	70,300	1.92
P(S-CHMA) 35	36.7	68,000	1.82
P(S-CHMA) 45	44.5	87,000	1.90

[a]Methacrylate content in copolymer was determined by elemental analysis.
[b]Molecular weights were determined by GPC using polystyrene standards.

light scattering measurements is 33,000 g/mole. Synthesis of copolymer was performed in bulk at 70 °C with AIBN as the initiator and ethyl benzene as a chain transfer agent. Conversion for the synthesis of copolymers was kept about 10% to avoid composition drift. Molecular weight information of copolymers was obtained using GPC calibrated with polystyrene standards. The monomer content of copolymers was determined by element analysis. Hompolymers and copolymers used in this study were listed in Table I. The numerical value included as a part of the code for these copolymers indicates the weight percent of methacrylate.

Blends prepared by solution casting from tetrahydrofuran (THF) at 60 °C were dried in an air circulating oven for a day, then finally dried under vacuum at 120 °C for a week. Glass transition temperatures of blends were examined using a Perkin-Elmer DSC-7 at a scanning rate of 20 °C/min. The temperature at which phase separation caused by LCST-type phase behavior was measured by an annealing technique[14,15] to access the closest true equilibrium temperature.

Results and Discussion

Phase Behavior. TMPC blends with various PMMA, PEMA, PnPMA, PnBMA, PCHMA, and PphMA were not miscible. It was well-known that TMPC blend with PS is miscible and shows LCST-type phase behavior at around 240 °C.[12,13] In the previous study,[15] we have examined misci-
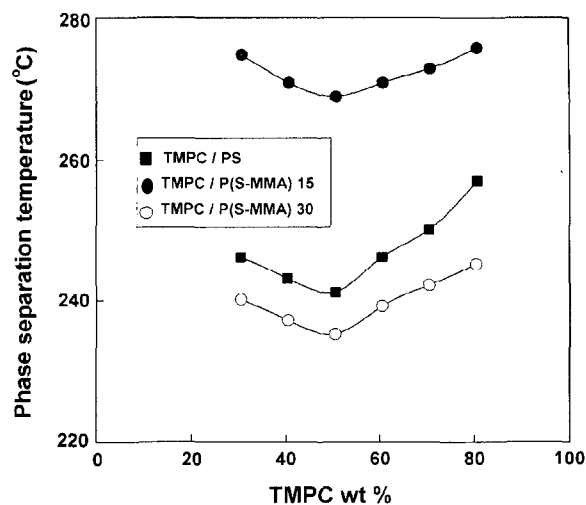

Figure 1. Phase separation temperatures of TMPC blends with P(S-MMA) copolymers.

bility of PS blends with various polymethacrylates by changing molecular weight of PS and then calculated interaction energy of each binary pair from the LCST-type phase boundary using lattice-fluid theory. Binary interaction energies between styrene and various methacrylates were in the order of PnPMA < PEMA < PCHMA < PnBMA < PMMA and their values were negative except styrene-MMA binary pair. Based on the miscibility information related to the pairs mentioned above, styrene-methacrylate copolymers such as styrenic copolymers containing MMA, EMA, or CHMA were synthesized at various compositions. Among these blends, styrene-methacrylate copolymers containing less than certain amount of methacrylate form miscible blends with TMPC. For example, TMPC blends with P(S-EMA) copolymers form miscible blends when copolymers contains less than 20 wt% EMA. Miscible blends observed here exhibited LCST-type phase separation behavior as shown in Figures 1-3. The phase separation curves are very similar with one another showing a minimum at about 50 wt% TMPC.

The effect of methacrylate content can be more easily exhibited by plotting the phase separation temperature for a fixed TMPC content of the blend versus the methacrylate content of the copolymer, as shown in Figures 4-6. The phase behavior depends on the copolymer composition. In the cases of TMPC/P(S-MMA) and TMPC/P(S-EMA) blends, the phase separation temperature of miscible blends first increases gradually with methacrylate content, goes through a maximum and then decreases just prior to the limiting content of methacrylate for miscibility with TMPC. On the other hand, the phase separation temperature of TMPC/P(S-CHMA) monotonically decreases with methacrylate content and then miscibility and the LCST behavior shift to the immiscibility. It has been shown previously that
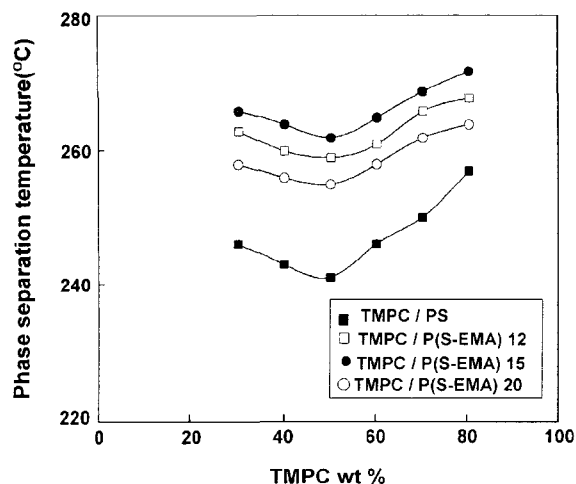
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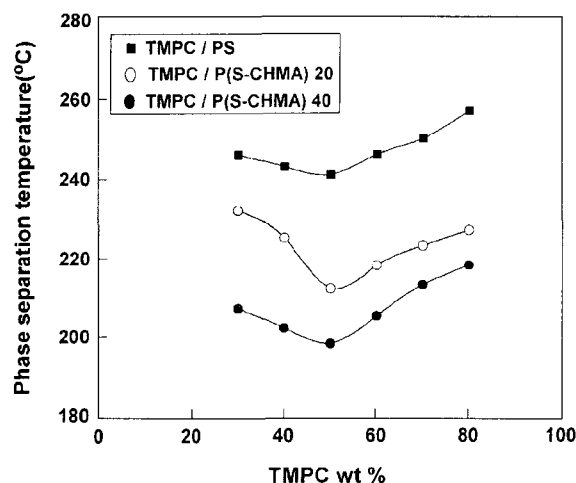**Figure 2.** Phase separation temperatures of TMPC blends with P(S-EMA) copolymers.

Legend (Figure 2):
■ TMPC / PS
□ TMPC / P(S-EMA) 12
● TMPC / P(S-EMA) 15
○ TMPC / P(S-EMA) 20

Figure 3. Phase separation temperatures of TMPC blends with P(S-CHMA) copolymers.

Legend (Figure 3):
■ TMPC / PS
○ TMPC / P(S-CHMA) 20
● TMPC / P(S-CHMA) 40

Figure 4. Phase separation temperatures of TMPC blends with P(S-MMA) copolymers at 50 wt% TMPC in blends. Note that P(S-MMA) copolymers containing more than 35 wt% MMA did not form miscible blends with TMPC.

Figure 4 regions: Immiscible region / Misible region

Figure 5. Phase separation temperatures of TMPC blends with P(S-EMA) copolymers at 50 wt% TMPC in blends. Note that P(S-EMA) copolymers containing more than 19 wt% EMA did not form miscible blends with TMPC.

Figure 5 regions: Immiscible region / Miscible region

addition of comonomer units like acrylonitrile and maleic-anhydride to styrene may be an effective way of raising the phase separation temperatures of TMPC blends.[5,16,17] It has been attributed to the intramolecular repulsion between styrene and comonomer caused by relatively large positive interaction energies. Since blends of PS/PMMA are immiscible and their interaction energies might be positive, phase behavior of TMPC/P(S-MMA) blends shown in Figures 1 and 4 might be explained with the intramolecular repulsion between comonomer. However, since PS blends with PEMA or PCHMA are miscible and their interaction energy is negative, intramolecular repulsion between styrene and comonomer cannot be expected. Because of this, it might be expected that addition of such monomer to the styrene always decreased the LCST. Phase behavior of TMPC blends with P(S-CHMA) shown in Figures 3 and 6 well
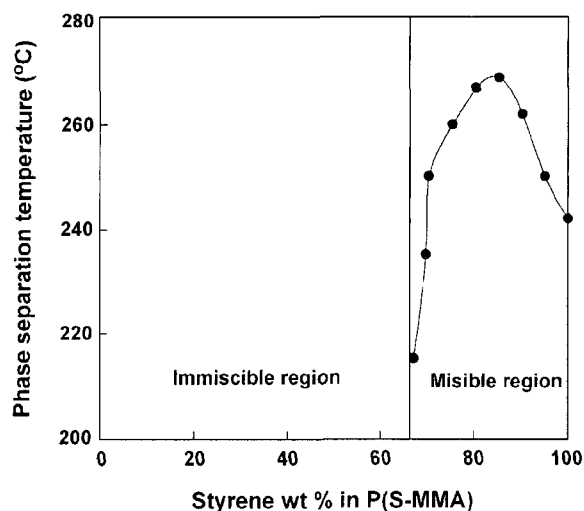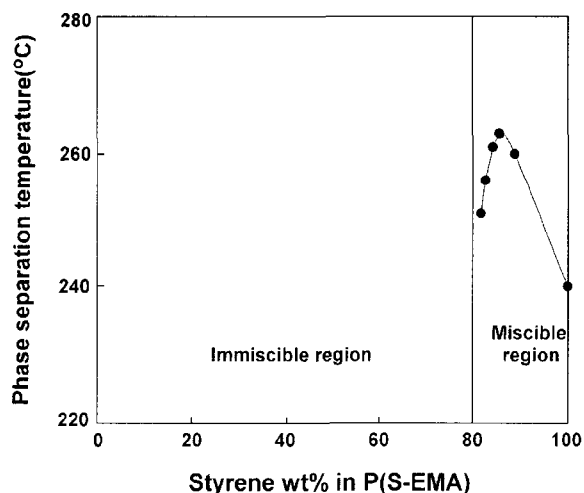
matched with general notions of binary interaction model while that of TMPC blends with P(S-EMA) shown in Figures 2 and 5 contradicts with expectation. To understand phase behavior of these blends, interaction energies of binary pairs involved in the miscible blends were calculated from the observed phase separation temperature using the lattice-fluid theory. The equation-of-state effects of these blends cause such behavior as explained next.

Interaction Energies. The binary interaction energies involved in the miscible blends were calculated from phase boundaries observed here using the lattice-fluid theory[5,6,18-20]
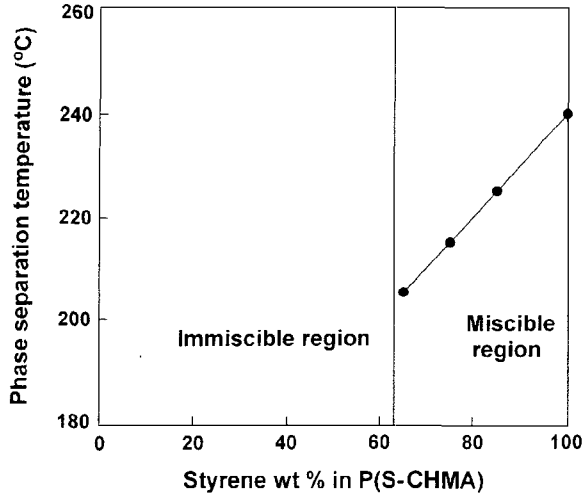
Figure 6. Phase separation temperatures of TMPC blends with P(S-CHMA) copolymers at 50 wt% TMPC in blends. Note that P(S-CHMA) copolymers containing more than 35 wt% CHMA did not form miscible blends with TMPC.

combined with binary interaction model.[21-23] The temperature at which phase separation caused by lower critical solution temperature, LCST, occurred, was measured by an annealing technique to access the closest true equilibrium temperature. To extract information about interaction energy from the liquid-liquid phase boundaries shown in Figures 1-6, it is assumed that to a good approximation these data correspond to the spinodal curve. As described in the previous research,[14,15] the morphology of blend observed at a reported phase separation temperature could be characterized by a high level of phase interconnectivity in both the minor and major phase caused by spinodal decomposition.[24,25]

There are several equation-of-state theories for mixtures; however, the following discussion is limited to the lattice-fluid theory. This theory expresses thermodynamic functions in terms of reduced variables $\tilde{P} = P/P^*$, $\tilde{T} = T/T^*$, $\tilde{\rho} = 1/\tilde{v}^* = \rho/\rho^*$ where the asterisks denote characteristic parameters. The characteristic parameters are related to v^*(mer close-packed volume) and r(chain length) as follows.

$$kT^* = P^* v^* \tag{1}$$

$$\rho^* = \frac{M}{rv^*} \tag{2}$$

$$r = P^* M/kT^* \rho^* \tag{3}$$

Where M is the molecular weight (weight average should be used for polydisperse components). The following simple reciprocal mixing rules are used for mixtures and for copolymers

$$\frac{1}{v^*} = \sum_i \frac{\phi_i}{v_i^*} \tag{4}$$

$$\frac{1}{\rho^*} = \sum_i \frac{w_i}{\rho_i^*} \tag{5}$$

$$\frac{1}{r} = \sum_i \frac{\phi_i}{r_i} \tag{6}$$

Where w_i and ϕ_i are the weight fraction and the hard core volume fraction, respectively. The characteristic pressure of a mixture, P^*, is related to those of the pure components and the interaction energy, $\Delta p^*_{(ij)}$, by[6]

$$P^* = \sum_i \phi_i P_i^* - \sum_{i<j} \sum \phi_i \phi_j \Delta p^*_{(ij)} \tag{7}$$

For a binary blend of a random copolymer composed of units 1 and 2 units and a homopolymer of 3, the interaction energy between copolymer and homopolymer ($\Delta p^*_{(ij)} = \Delta p^*$) is given by in terms of monomer unit pair interactions, Δp^*_{ij}:[6,21-23]

$$\Delta p^* = \Delta p^*_{13} \phi_1' + \Delta p^*_{23} \phi_2' - \Delta p^*_{12} \phi_1' \phi_2' \tag{8}$$

Where ϕ_i' indicates the close packed volume fraction of component i in copolymer. The free energy of mixing per unit volume, g, is given by

$$g = g_{nc} + g_c \tag{9}$$

where g_c is the combinatorial entropy

$$g_c = RT \sum_i \frac{\phi_i}{v_i^* r_i} \ln \phi_i \tag{10}$$

and g_{nc} is the non-combinatorial free energy represented by

$$g_{nc} = -\tilde{\rho} P^* + P\tilde{v} + \frac{RT}{v^*} \left(\frac{1-\tilde{\rho}}{\tilde{\rho}} \ln(1-\tilde{\rho}) + \frac{\ln\tilde{\rho}}{r} \right) \tag{11}$$

Finally, the spinodal condition for a compressible mixture can be written

$$\frac{d^2 g}{d\phi^2} = g_{\phi\phi} - \frac{(g_{\tilde{\rho}\phi})^2}{g_{\tilde{\rho}\tilde{\rho}}} = 0 \tag{12}$$

where the subscripts ϕ and $\tilde{\rho}$ indicate partial derivatives with respect to ϕ or $\tilde{\rho}$. In terms of the Sanchez-Lacombe theory, the indicated derivatives for binary mixture are given by[6]

$$g_{\phi\phi} = -2\tilde{\rho}\Delta P^* + RT \left(\frac{1}{\phi_1 r_1 v_1^*} + \frac{1}{\phi_2 r_2 v_2^*} \right) \tag{13}$$

$$g_{\tilde{\rho}\phi} = -(p_1^* - p_2^* - (1-2\phi_1)\Delta P^*) + \frac{RT}{\tilde{\rho}} \left(\frac{1}{r_1 v_1^*} - \frac{1}{r_2 v_2^*} \right)$$

$$-RT \left(\frac{1}{v_1^*} - \frac{1}{v_2^*} \right) \left(\frac{\ln(1-\tilde{\rho})}{\tilde{\rho}^2} + \frac{1}{\tilde{\rho}} \right) \tag{14}$$
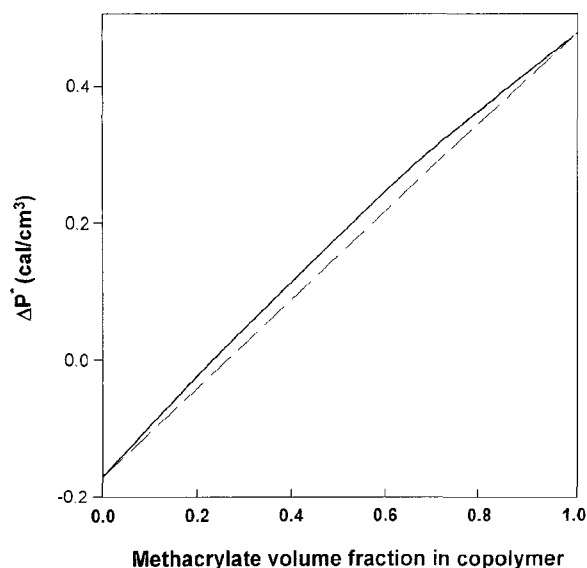
Figure 7. Effect of copolymer composition on the interaction energies for TMPC/P(S-EMA) blends.

$$g_{\tilde{\rho}\tilde{\rho}} = \frac{RT}{v^*}\left(\frac{2\ln(1-\tilde{\rho})}{\tilde{\rho}^3} + \frac{1}{\tilde{\rho}^2(1-\tilde{\rho})} + \frac{1}{\tilde{\rho}^2}\left(1-\frac{1}{r}\right)\right) \tag{15}$$

The ΔP^* values for blends of TMPC with specific sty-rene-methacrylate copolymers were calculated from phase boundaries shown in Figures 1-6 using equation (12).

The curve presenting interaction energy for TMPC/P(S-MMA) blends was down convex while those for TMPC/P(S-EMA) blends and TMPC/P(S-CHMA) blends exhibited opposite trend. Figure 7 shows the change in the interaction energies of TMPC/P(S-EMA) blends as a function styrene content in the copolymers. The curve shape for the interaction energies of TMPC-P(S-MMA) pairs might stem from the positive interaction energy between styrene and MMA. On the other hand, those for the interaction energies of TMPC-P(S-EMA) pairs and TMPC-P(S-CHMA) pairs might stem from the negative interaction energy between styrene and EMA or between styrene and CHMA. These curvatures of interaction energies for TMPC-copolymer blends coincided with those predicted with binary interaction model.[21-23] The curve presenting net interaction energy for TMPC/P(S-EMA) blends is up convex. Curve for TMPC/P(S-CHMA) blends was similar with that for P(S-EMA). As shown in Figure 6 the minimum phase separation temperature (this occurs around $\phi_{TMPC} \approx 0.5$) for TMPC/P(S-CHMA) blends monotonically decreases with CHMA content. This would seem to agree with the general notion that systems with less favorable interactions have lower LCST. On the other hand, phase separation temperature for a blend of TMPC with P(S-EMA) reaches a maximum when copolymer contains 13.5 wt% EMA (Figure 5). This would seem to contradict

the general notion that systems with more favorable ener-getic interactions have higher LCST. To understand such behavior of TMPC and styrene-methacrylate copolymer binary mixture, the phase stability condition of lattice-fluid theory was analyzed as exhibited next.

For the phase stability, the term in equation (12), i.e., $(d^2g/d\phi^2)$should be positive. The indicated derivatives in equation (13) are approximately given by[6]

$$\frac{d^2g}{d\phi^2} \approx -2\tilde{\rho}\Delta P^* - \left(\frac{R}{v^*}\right)^2 (T_1^* - T_2^*)^2 \kappa\tilde{\rho}^3 > 0 \tag{16}$$

where ΔP^* is interaction energy between TMPC and copolymer, T_1^* and T_2^* are characteristic temperature of copolymer and TMPC, respectively, and κ is the isothermal compressibility of the binary mixture. Note that the combi-natorial entropy terms are negligible at high molecular weight. The explanation for the observed phase behavior of blends reveals in the two terms of equation (16) comprising the stability condition. Since the characteristic temperature for PS is larger than that for methacrylate, the characteristic temperature for styrene-methacrylate copolymer (T_1^*) become smaller as methacrylate content increases. The difference in the characteristic temperature, $|T_1^* - T_2^*|$, becomes smaller as the methacrylate content of the copolymer increases (See Table II). The contribution of this term to the phase stability becomes more favorable as methacrylate content increases. Since the reduced density becomes smaller as methacrylate content increases, at a given temperature, a smaller reduced density results in a larger isothermal compressibility of the copolymer. The increased compressibility relative to that of PS and the increased interaction energy (ΔP^*), relative to that of TMPC-styrene pair, caused by introducing metha-crylate destabilizes the mixture and promotes phase separa-tion. In consequence, the energetic interaction and com-pressibility become less favorable for phase stability as methacrylate content increase, while the difference in the characteristic temperature becomes more favorable. It means that phase separation temperature is determined by the competition among these terms. To see this more clearly, $d^2g/d\phi^2$ was plotted as a function of temperature. Figure 8 shows the calculated $d^2g/d\phi^2$ of various binary pairs, as a function of temperature. It was suggested that the observed increase in blend phase separation temperature caused by

Table II. Characteristic Properties of Lattice-Fluid Theory

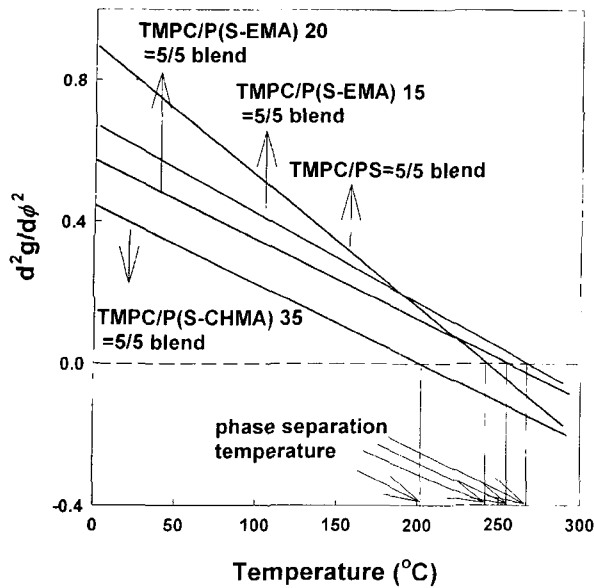| Polymer	T^* (K)	P^*(bar)	ρ^*(gcm^{-3})	Reference
TMPC	729	439.5	1.1854	[5]
PS	810	373.0	1.0920	[5]
PMMA	742	488.3	1.2498	[6]
PEMA	653	524.1	1.1927	[26]
PCHMA	735	442.9	1.1624	[26]

Figure 8. Effect of temperature on term for TMPC/PS, TMPC/ P(S-EMA)15, TMPC/P(S-EMA)20, and TMPC/P(S-CHMA)35 blends containing 50 wt% TMPC.

adding small amount of EMA to the styrenic polymer stems from equation-of-state effects, mainly reduction in $|T_1^* - T_2^*|$, rather than from energetic effects.

Conclusions

Copolymers having two different types of intramolecular interactions were prepared to examine the effects of copolymerization on the phase behavior of the polymer blend. One type of copolymer was that each component composed of copolymer has positive interaction energy; whereas, the other type of copolymer was that each component composed of copolymer has negative interaction energy. In this study, the former were P(S-MMA) copolymers and the latter were P(S-EMA) and P(S-CHMA) copolymers. These copolymers were blended with TMPC. Changes in the phase separation temperature caused by LCST-type phase behavior of these blends were examined as functions of copolymer and blend composition. TMPC formed miscible blends with styrenic copolymers containing less than certain amount of methacrylate. The phase separation temperature of TMPC blends with copolymer such as P(S-MMA) and P(S-EMA), first increases with methacrylate content, goes through a maximum and then decreases just prior to the limiting content of methacrylate for miscibility, while that of TMPC blends with P(S-CHMA) always decreases. The detail inspection of thermodynamic terms related to the phase separation suggested that the observed increase in blend phase separation temperature caused by adding small amount of EMA to the styrenic polymer stemmed from equation-of state-effects

rather than from energetic effects, i.e., a more negative interaction energy.

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