Phase Behavior of Ternary Polymer Blends of Poly(styrene-co-acrylic acid), Poly(ethylene oxide), and Poly(methyl methacrylate)

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ABSTRACT: The phase behavior of ternary polymer blends of poly(styrene-co-acrylic acid) (SAA), poly(ethylene oxide) (PEO), and poly(methyl methacrylate) (PMMA) was investigated as a function of the acrylic acid content in SAA. The immiscible region was decreased as the acrylic acid content in SAA increases. Six segmental interaction energy densities in the ternary blend were evaluated by combining melting point depression and a more extended binary interaction model.

Introduction

Some miscible ternary polymer blends were developed with the concept that polymer A, which is miscible with each of polymers B and C, can compatibilize the immiscible binary pair B and C. However, few miscible ternary polymer blends have been reported although many miscible binary blends have been found over the last decade. Prior to 1989, about 10 miscible polymer blends were reported in the literature.[1-13] Kwei et al.[1] have reported ternary polymer blends of poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA), and poly(vinylidene fluoride) (PVDF), in which the binary pair of PMMA and PEMA is immiscible; however, the addition of PVDF to the immiscible binary blend PMMA/PEMA can form a miscible ternary blend. Wang et al.[2] have also reported another blend system of poly(vinylidene chloride-co-vinyl chloride) (PVDC/VC), poly(acrylonitrile-co-butadiene) (NBR), and poly(vinyl chloride) (PVC), where PVC acts as a common solvent for an incompatible blend of PVDC/VC and NBR.

Recently, Paul et al.[3,5] have reported two other systems. One is a blend of polycarbonate (PC), poly(styrene-co-acrylonitrile) (SAN), and poly(ε-caprolactone) (PCL).[3] They found miscibility at PCL concentrations higher than 29 wt % whatever the PC/SAN ratio is. The other is a blend of PC, phenoxy, and PCL.[5] In the system, they also found that the blends are miscible at PCL levels greater than 60 wt %. Nishi et al.[12] have investigated the phase behavior of ternary polymer blends and analyzed their phase diagrams according to the Flory-Huggins-Scott theory. It was also reported that the ternary blends of PMMA, poly(epichlorohydrin), and PEO were miscible, where all three binary pairs are miscible.[8] More recently, the temperature dependence of the phase behavior of ternary blends has been examined by the extended version of Flory's equation-of-state theory.[13]

In the classical Flory-Huggins theory, the specific interaction between two chemical species can be described by the thermodynamic interaction energy density B.[14] According to the usual sign convention, a positive value indicates unfavorable interactions and a negative value does favorable interactions. The more negative B is, the stronger the interaction is. Several methods have been used to evaluate B values of miscible polymer pairs, viz., melting point depression,[15] vapor sorptions,[16] inverse gas chromatography,[17] and neutron[18] and small-angle X-ray scattering.[19] Among them, the melting point depression method has been used for blends where one of the components is semicrystalline. The melting point depression of a semicrystalline polymer in a mixture is due to a decrease of the chemical potential of the amorphous phase of the blend.

In the present study, it is attempted to examine the phase behavior of ternary polymer mixtures containing one copolymer, poly(styrene-co-acrylic acid) (SAA), PEO, and PMMA, as a function of copolymer composition and also to evaluate the thermodynamic interaction energy densities of all pairs between segmental units in the ternary blends by combining melting point depression and a more extended binary interaction model.

Experimental Section

Materials. PEO ($\bar{M}_w = 2 \times 10^5$, $T_g = -56$ °C, $T_m = 65$ °C) was purchased from the Aldrich Chemical Co. and PMMA ($\bar{M}_w = 1.5 \times 10^5$, $T_g = 110$ °C) was obtained from the Lucky Chemical Co., Korea. SAA was synthesized at 60 °C by bulk polymerization in a sealed glass ampule using benzoyl peroxide as an initiator. The maximum degree of conversion was controlled to less than 15%. The acrylic acid (AA) content in the copolymer was determined by titration in benzene/methanol (9/1, v/v) with a standardized methanolic NaOH solution using phenolphthalein as an indicator. The molecular weight of SAA was determined by GPC. The copolymer composition and other properties are listed in Table I.

Preparation of Blends. The blends were prepared by dissolving the component polymers in benzene/methanol (9/1, v/v). The solutions were cast on an aluminum dish, and most of the solvent was allowed to evaporate in the air at room temperature for at least 3 days and then completely dried in a vacuum oven at 45 °C for an additional several days.

Thermal Analysis. Thermal analysis was performed on a Du Pont 910 differential scanning calorimeter equipped with a mechanical cooling accessory. For the measurement of the glass transition temperature the sample was heated to 140 °C to eliminate the thermal history, quenched to −60 °C, and then heated at a heating rate of 20 °C/min. For the measurement of the equilibrium melting point, the sample was heated to 90 °C, maintained for 5 min to ensure complete melting of PEO crystals, quenched to the crystallization temperature T_c, kept at T_c for at least 30 min, and then heated at a heating rate of 20 °C/min.

Cloud-Point Measurement. The sample film was placed between two slide glasses and heated with a hot plate at a heating rate of 5 °C/min. The temperature at which, by visual inspection, the transparent film became opaque was taken as the cloud point.

Results and Discussion

Binary Blends. It has been reported that PMMA is miscible with SAA containing above 6 mol % of AA and that the miscibility of SAA/PMMA blends comes from the specific interaction between methyl methacrylate and acrylic acid units and the relatively strong repulsion

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Table I
Properties of Copolymers

sample	copolymer composn,[a] AA mol % in SAA	M_w[b]	T_g, °C
SAA12	12.2	5.6×10^4	117
SAA21	20.8	3.7×10^4	121
SAA33	33.1	2.2×10^4	145

[a] The copolymer compositions were determined by titration. [b] The weight-average molecular weights were determined by GPC.

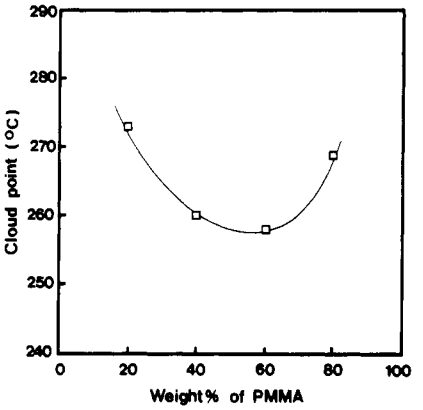

Figure 1. Cloud-point curve for SAA12/PMMA blends.

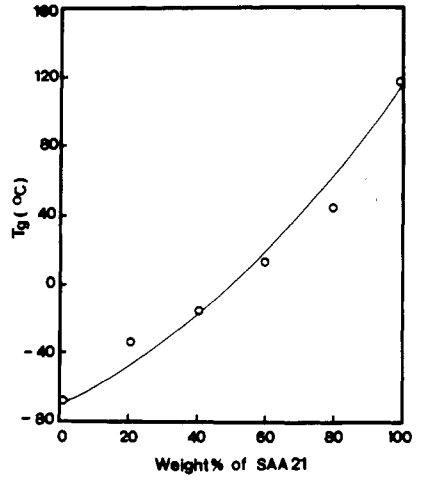

Figure 2. Glass transition behavior obtained by DSC for SAA21/PEO blends.

between styrene and acrylic acid units in the copolymer.[20] Since the glass transition temperatures of SAA and PMMA are so close that the resolution of T_g's for a blend is rather difficult, the existence of a single glass transition temperature as a miscibility criterion is not adequate for the system; however, lower critical solution behavior has been detected for the system of SAA12/PMMA (Figure 1) and has been taken as proof that the polymers are miscible at ambient conditions.

For SAA/PEO binary blends, it was found that PEO is miscible with SAA containing above 15 mol % of AA and that both the specific interaction between ethylene oxide and acrylic acid units and the intramolecular repulsive force in a SAA copolymer are responsible for the miscibility of the blends.[21] As shown in Figure 2, SAA21/PEO blends have a single glass transition temperature at all the compositions examined, and films were clear on heating above the melting point of PEO. Therefore, it is concluded that SAA21/PEO is completely miscible. In the blends of SAA12/PEO, the T_g's of PEO-rich blends do not show a single transition (Figure 3) and films are not always clear. Consequently, the blend of SAA12 and PEO is judged to be partially miscible.

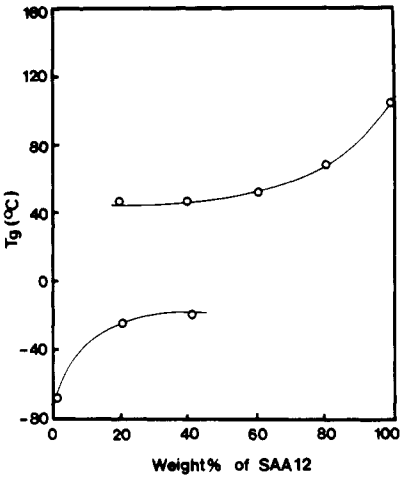

Figure 3. Glass transition behavior of SAA12/PEO blends showing miscibility over only a portion of the composition spectrum.

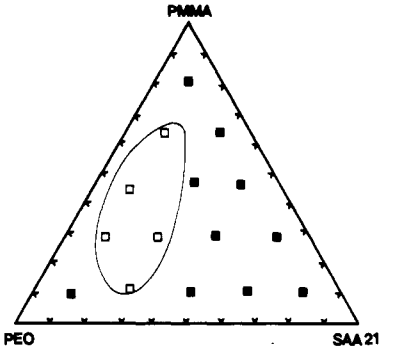

Figure 4. Phase behavior of ternary blends of SAA21/PMMA/PEO at room temperature. In the Figure, ■ indicates that the blend film shows single T_g and clear melts, and □ indicates that the blend film shows cloudy and multiphase behavior.

The PEO/PMMA pair has been known to be miscible.[22,23] Martuscelli and Demma[23] reported that blends of PEO with PMMA show a unique morphology, a depression of spherulite growth rate and melting temperature of PEO with increasing PMMA concentration, and a glass transition temperature intermediate between those of the pure components.

Ternary Polymer Blends. In the SAA21/PMMA/PEO blend, all three binary pairs are miscible, as discussed in the previous section. To our knowledge, only one example of the case has been reported.[8] Figure 4 shows the ternary phase diagram of a SAA21/PMMA/PEO system at room temperature. The miscibility was determined from the cloud point and glass transition temperature. More specifically, for the blends of high PEO content, the blend is judged to be miscible when the cloud point was observed at temperatures higher than the melting point of PEO or/and when a single glass transition temperature was observed. For the blends of low PEO content, the blends are judged to be miscible when the blend film was transparent at room temperature or/and when a single glass transition temperature was observed. In any case, the blends are judged to be immiscible whenever two T_g's are observed. However, since the use of the single T_g criterion for judging the absence of multiple amorphous phases in the SAA21/PMMA/PEO ternaries will be difficult for regions of composition where the T_g's of the binary combinations tend to overlap,[3] the optical clarity was mainly used for determining the miscibility of ternary blends.

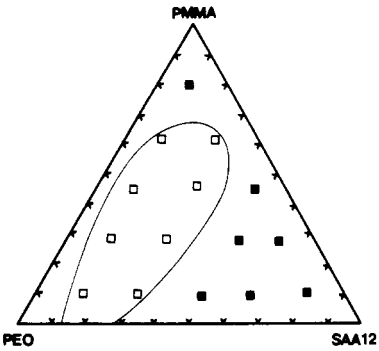

Figure 5. Phase diagram for ternary blends of SAA12/PMMA/PEO at room temperature ■ indicates that the blend film shows single T_g and clear melts, and □ indicates that the blend film shows cloudy and multiphase behavior.

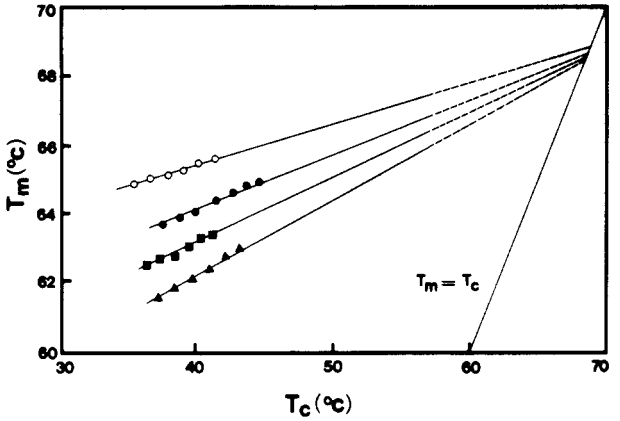

Figure 6. Hoffman-Weeks plot for PEO/PMMA blends: (○) 100, (●) 90, (■) 80, (▲) 70 wt % PEO.

In the SAA12/PMMA/PEO system, binary blends of SAA12/PEO have been shown to be partially miscible, while both systems of SAA12/PMMA and PEO/PMMA are miscible. Figure 5 shows the ternary phase diagram of a SAA12/PMMA/PEO system at room temperature. As compared with Figure 4, the result shows that the lower the AA content in SAA copolymer, the larger the size of the immiscible region in the ternary phase diagram. In other words, the acrylic acid unit in SAA gives a favorable effect on the miscibility of ternary polymer blends.

Analysis of Melting Point Depression of PEO in the Blends. The relation between the melting point depression and the interaction energy parameter in the blend was derived by Nishi and Wang[15]

$$T_m^\circ - T_{mb}^\circ = -B\frac{V_{iu}}{\Delta H_{iu}} T_m^\circ (1-\phi_i)^2 \quad (1)$$

where T_m° and T_{mb}° are the equilibrium melting points of a pure crystalline polymer and blends, respectively, $\Delta H_{iu}/V_{iu}$ is the heat of fusion of a pure crystalline component per unit volume, $1-\phi_i$ is the volume fraction of the amorphous phase, and B is the interaction energy density in polymer blends. When $T_m^\circ - T_{mb}^\circ$ is plotted against $(1-\phi_i)^2$, the overall interaction density is obtained from the slope of the plot.

The equilibrium melting points of pure PEO and PEO/PMMA blends were obtained by using Hoffman-Weeks plots (Figure 6) and are listed in Table II. Figure 7 shows the melting point depression of PEO in PEO/PMMA blends. According to eq 1, the B value for PEO/PMMA was determined from the slope of the straight line of Figure 7. When the values of 41.4 cm³/mol and 1980 cal/mol were used for V_{iu} and ΔH_{iu}, respectively, in eq 1, B was

Table II
Equilibrium Melting Temperatures for PEO and PEO/PMMA Blends

sample	T_{mb}°, °C	sample	T_{mb}°, °C
PEO[a]	68.9	PEO/PMMA (80/20)	68.6
PEO/PMMA (90/10)	68.7	PEO/PMMA (70/30)	68.5

[a] Equilibrium melting temperature (T_m°) of pure PEO.

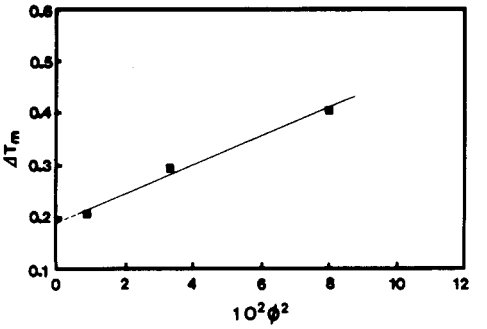

Figure 7. Plot of the equilibrium melting point of PEO/PMMA blends vs the square of the volume fraction of PMMA.

estimated to be −0.40 cal/cm³, indicating the fact that PEO/PMMA is miscible.

Application of Binary Interaction Model to Ternary Polymer Blends. The heat of mixing, ΔH_{mix}, of a multicomponent system can be described in terms of binary interaction parameters by

$$\Delta H_{mix} = V\sum_i \sum_{i\neq j} B_{ij}\phi_i\phi_j \quad (2)$$

where V is the system volume, B_{ij} is the interaction energy density, and ϕ_i and ϕ_j are the volume fractions of components i and j in the mixture, respectively. As in the case of binary mixtures, $\Delta H_{mix} = 0$ becomes the criterion for predicting a boundary between single-phase and multiphase behavior.

Let polymer A be a copolymer composed of monomers 1 and 2 with volume fractions denoted by ϕ_1' and ϕ_2' and polymers B and C be comprised of monomers 3 and 4, respectively. In the blend of A, B, and C, the volume fractions occupied by the various monomeric units are ϕ_1, ϕ_2, ϕ_3, and ϕ_4, while the volume fractions of A, B, and C are ϕ_A, ϕ_B, and ϕ_C. For a ternary mixture of A, B, and C, the heat of mixing is given by eq 3. The first term of the

$$\Delta H_{mix} = (V_A + V_B + V_C)\sum_{i\neq j}^{4} B_{ij}\phi_i\phi_j - V_A B_{12}\phi_1'\phi_2' \quad (3)$$

right-hand side is the heat of mixing A, B, and C, while the second term is the heat of mixing for the copolymer. Accordingly, the partial molar enthalpy of component 3, $\Delta\bar{H}_3$, was derived as eq 4 where $\psi_i = \phi_i/(1-\phi_3)$, V_3 is the

$$\Delta\bar{H}_3 = V_3(B_{13}\psi_1 - B_{14}\psi_1\psi_4 + B_{23}\psi_2 - B_{24}\psi_2\psi_4 + B_{34}\psi_4 - B_{12}\psi_1\psi_2)(1-\phi_3)^2 \quad (4)$$

molar volume of component 3, and ϕ_i is the volume fraction of component i in the mixture. Consequently, overall interaction energy density B in the blend is related with segmental interaction energy densities B_{ij}'s by the following relation:

$$B = B_{13}\psi_1 - B_{14}\psi_1\psi_4 + B_{23}\psi_2 - B_{24}\psi_2\psi_4 + B_{34}\psi_4 - B_{12}\psi_1\psi_2 \quad (5)$$

Equation 1 suggests that the parameter B for a ternary blend can be evaluated from the slope of T_m versus the

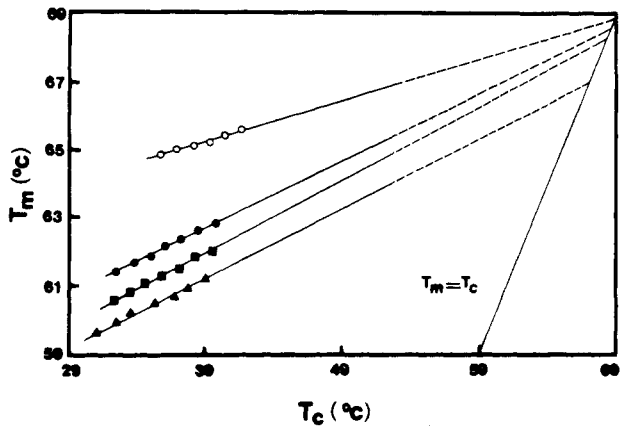

Figure 8. Hoffman–Weeks plot for SAA33/PMMA/PEO blends at a SAA33/PMMA ratio of $^1/_3$: (○) 100, (●) 90, (■) 80, (▲) 70 wt % PEO.

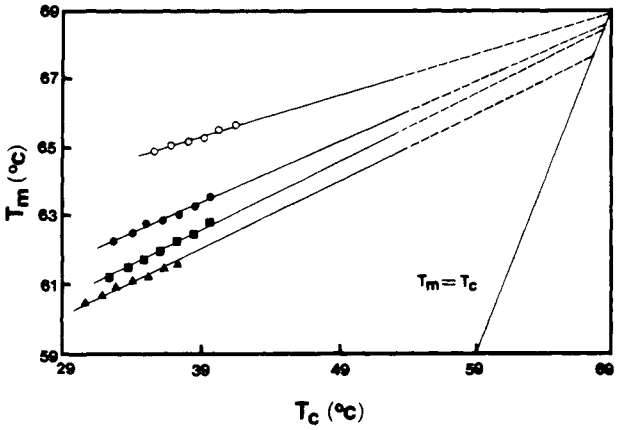

Figure 9. Hoffman–Weeks plot for SAA33/PMMA/PEO blends at a SAA33/PMMA ratio of 1: (○) 100, (●) 90, (■) 80, (▲) 70 wt % PEO.

square of the amorphous volume fraction in exactly the same way as for a binary blend. To apply eq 5 to the present ternary blends, one denotes acrylic acid by 1, styrene by 2, ethylene oxide by 3, and methyl methacrylate by 4. There are six segmental interaction energy parameters in the present ternary blends. Among them, B_{12}, B_{13}, and B_{23} were determined in the previous study[21] by combining the equilibrium melting point depression and a binary interaction model. The values were B_{12} = 36.64 cal/cm^3, B_{13} = −15.46 cal/cm^3, and B_{23} = 1.78 cal/cm^3. The value of B_{34} corresponding to the interaction between ethylene oxide and methyl methacrylate was directly obtained from the melting point depression of PEO in the PEO/PMMA blend. The value was −0.40 cal/cm^3, as evaluated in the previous section.

Two parameters B_{14} and B_{24} still remain unknown. In order to evaluate the two unknown parameters, one can use eqs 1 and 5. The overall interaction parameter B has been evaluated from the equilibrium melting point depression at a given ψ_i, which corresponds to the SAA33/PMMA ratio. The equilibrium melting points were determined from the Hoffman–Weeks plots, as shown in Figures 8 and 9. Table III shows the equilibrium melting temperature of ternary blends of SAA33/PMMA ratios of 1 and $^1/_3$.

Figure 10 shows plots of the equilibrium melting point depression of PEO versus the square of the volume fraction of amorphous polymers at SAA33/PMMA ratios of 1 and $^1/_3$. From the slope of the line two overall interaction parameters in ternary blends are determined: B = −1.84 cal/cm^3 for a SAA33/PMMA ratio of 1 and B = −3.42

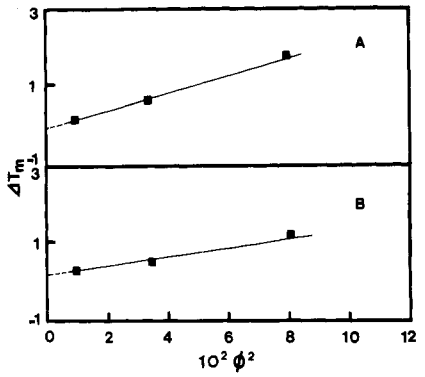

Figure 10. Equilibrium melting point depression of SAA33/PMMA/PEO blends vs the square of the volume fraction of amorphous polymers: A, the ratio of SAA33/PMMA is $^1/_3$; B, the ratio of SAA33/PMMA is 1.

Table III
Equilibrium Melting Temperature of SAA33/PMMA/PEO Blends

sample	$T_{mb}°$, °C	sample	$T_{mb}°$, °C
SAA33/PMMA/PEO (2.5/7.5/90)	68.7	SAA33/PMMA/PEO (5/5/90)	68.6
SAA33/PMMA/PEO (5/15/80)	68.3	SAA33/PMMA/PEO (10/10/80)	68.5
SAA33/PMMA/PEO (7.5/22.5/70)	67.0	SAA33/PMMA/PEO (15/15/70)	67.7

Table IV
Segmental Interaction Energy Densities

segment pair	B_{ij}, cal/cm^3	segment pair	B_{ij}, cal/cm^3
AA/EO	−15.46	EO/MMA	−0.40
ST/EO	1.78	ST/MMA	2.37
AA/ST	36.64	AA/MMA	12.50

cal/cm^3 for a SAA33/PMMA ratio of $^1/_3$. Upon substitution of two overall interaction parameters and the corresponding values into eq 5, the unknown parameters B_{14} and B_{24} can be evaluated by solving two simultaneous equations since the values of four parameters B_{12}, B_{13}, B_{23}, and B_{34} have been known. The estimated values were B_{24} = 2.37 cal/cm^3 and B_{14} = 12.50 cal/cm^3. Table IV lists six segmental interaction energy densities in the present ternary blends. The positive values of B_{14} and B_{24} suggest that poly(acrylic acid)/poly(methyl methacrylate) and polystyrene/poly(methyl methacrylate) blends are immiscible. The fact that poly(acrylic acid) is immiscible with PMMA has also been supported by Brannock and co-workers.[24]

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