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Phase Equilibrium of the Ternary System Composed of Polystyrene/Poly(n-butyl methacrylate)/Cyclohexane

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ABSTRACT: The phase behavior of three component system composed of well fractionated polystyrene, poly(n-butyl methacrylate), and cyclohexane was investigated by means of turbidimetry and gel permeation chromatography. Variations of the polymer concentration and the temperature lead the ternary system to be separated into two phases. Cloud point curves were determined as the function of mixing ratio of the two polymers, molar mass, temperature, and concentration. Equilibrium phase diagrams and tie lines for a number of partially miscible systems were constructed for the temperature range of 10.9∼26.7 ℃ under atmospheric pressure. The polymer-polymer interaction parameters calculated based on the Flory-Huggins theory by using the experimentally obtained phase composition data and the polymer-solvent interaction parameters of binary systems, were found to be in the range of −0.0761∼0.1900. All the experimental results lead to a conclusion that the difference of the molar mass between the two polymers is the most important factor in enhancing the miscibility of the incompatible polymers.

Introduction

Since the pioneering work of Flory-Huggins,$^{1-3}$ numerous studies have been made on the phase behavior of binary or multicomponent systems.$^{4-8}$ This is because the phase composition relationship of the conjugated phases at equilibrium for a system containing polymers can provide various informations on the phenomenon of phase separation or the interaction parameter of polymer-solvent or polymer-polymer.

As is known well, the immiscibility between components in a system usually leads to phase separation. This phenomenon takes considerable importance not only for thermodynamics of polymer solution but also for the practical purposes of the material investigation. In particular, partial miscibility of polymer-solvent or polymer-polymer system plays a significant role in the theory of polymer fractionation, in the preparation of membranes, films, and coatings, and in the determination of service properties of polymer blends. Thus, the knowledge about the factors affecting the phase behavior of multicomponent polymer system and the interactions acting between components becomes fundamental and imperative.

The present paper is concerned with the phase behavior of incompatible polystyrene(PS) and poly(n-butyl methacrylate)(PnBMA) in the presence of cyclohexane(CH). The principal motivation of selecting this combination lies in the fact that the system given is thermodynamically intriguing. In fact, no specific interactions between the two polymers being expected, cyclohexane is known as a poor solvent for PS but shows good solubility for PnBMA in the temperature range studied here. In addition, no detailed description on the phase behavior can be found for systems containing PnBMA. Attentions are paid to the evaluation of polymer-polymer interaction parameter.

Experimental

Materials. PS was synthesized by bulk polymerization with AIBN at 70 ℃. PnBMA was purchased from Aldrich. Both polymers were purified and fractionated carefully by successive precipitation method with toluene and methanol as solvent and non-solvent, respectively. The results are summarized in Table I. Solvents were purified by standard methods.^{9}

Viscometry. Solution viscosity was measured by employing the suspended level type of Ubbelohde viscometer at 34.1± 0.05 ℃. The intrinsic viscos-

Table I. Fractionation Results of Polystyrene and Poly(n-butyl methacrylate)

Fractions	Weight(g)	Fractions	Weight(g)
PS1-1	0.1300	PnBMA2	0.7546
PS1-2	0.3751	PnBMA3	0.8157
PS1-3	0.1259	PnBMA4	0.6426
PS2	0.4400	PnBMA5	0.8287
PS3-1	0.1793	PnBMA6	0.3181
PS3-2	0.0906	PnBMA7	0.3126
PS3-3	0.0524	PnBMA8	0.1891
PS3-4	0.2150	PnBMA9	0.1582
PS4-1	0.1056		
PS4-2	0.5334		
PS4-3	0.3495		
PS4-4	0.1692		
PS5-1	0.5007		
PS5-2	0.0591		
PS6-1	0.3114		
PS6-2	0.1607		
PS6-3	0.3468		
PS6-4	0.3063		
PS7-1	0.1207		
PS7-2	0.1525		
PS7-3	0.4574		
PS7-4	0.4341		
PS8	2.0283		
PS9	1.5087		
PS10	1.5275		

Table II. Molecular Characteristics of Polystyrene

Sample Code	$\bar{M}_n/10^5$	$\bar{M}_w/10^5$	$\bar{M}_z/10^5$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_z/\bar{M}_w$	$[\eta]^a$
PS2	10.2433	16.4465	25.9523	1.606	1.578	86.97
PS3-1	2.3536	3.0481	4.1673	1.295	1.367	46.56
PS3-2	2.0704	2.6031	3.2582	1.257	1.252	
PS4-3	1.1017	1.2650	1.4400	1.148	1.138	
PS5-1	1.4730	1.6609	1.8475	1.128	1.112	
PS6-1	1.1251	1.2535	1.3789	1.114	1.100	30.38
PS7-3	0.9374	1.0184	1.0940	1.087	1.074	
PS7-4	0.6829	1.0103	1.2128	1.479	1.206	
PS8	0.6255	0.7105	0.7874	1.136	1.108	20.66
PS9	0.5376	0.6008	0.6569	1.118	1.093	

[a] Intrinsic viscosity [cm^3/g] in cyclohexane at 34.1 ℃.

ity was obtained by a conventional method.[10]

Table III. Molecular Characteristics of Poly(n-butyl methacrylate)

Sample Code	$\bar{M}_n/10^5$	$\bar{M}_w/10^5$	$\bar{M}_z/10^5$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_z/\bar{M}_w$	$[\eta]^a$
RAW	0.7692	1.4429	2.8247	1.876	1.958	30.62
PnBMA2	2.1779	3.0477	4.4186	1.399	1.450	53.70
PnBMA3	1.7566	2.1643	2.6109	1.232	1.206	
PnBMA4	1.5593	1.8052	2.0748	1.158	1.121	30.67
PnBMA5	1.3066	1.4930	1.6722	1.143	1.120	
PnBMA6	1.1136	1.2470	1.3916	1.120	1.116	
PnBMA7	1.0415	1.1412	1.2439	1.096	1.090	26.49
PnBMA8	0.8422	0.9225	1.0052	1.095	1.090	24.78
PnBMA9	0.8142	0.8767	0.9363	1.077	1.068	22.11

[a] Intrinsic viscosity [cm^3/g] in cyclohexane at 34.1 ℃.

Gel Permeation Chromatography. A Waters model 201 unit fitted with U6K injector, M6000A solvent delivery system, R401 differential RI detector, M730 data module, and linear columns packed with Styragel was used. The mobile phase, Tedia GPC grade tetrahydrofuran(THF), was filtered through Millipore 0.45 μm filter and degassed. The flow rate of THF was 1.0 mL/min. In Tables II and III are listed values of molecular characteristics obtained from PS and PnBMA, respectively.

Combination of Polymer Component for Ternary System. Three types of polymer combination were made : system A composed of PS5-1($\bar{M}_w=1.66\times10^5$) and PnBMA5($\bar{M}_w=1.49\times10^5$), system B of PS9($\bar{M}_w=1.44\times10^5$) and PnBMA5, and system C of PS9 and unfractionated PnBMA ($\bar{M}_w=1.44\times10^5$).

Preparation of Ternary Solution. A homogeneous THF solution of known weight ratio of PS (component 2) and PnBMA(component 3) was prepared, filtered, and evacuated to dryness at room temperature. The dried polymer mixture, then, dissolved again in a desired amount of the purified cyclohexane(component 1). After confirmation of the transparency of the solution by a turbidimeter, the solution was used for the further testing.

The total weight fraction of polymer w in the test solution and the volume fraction ξ_3 of the PnBMA in the polymer mixtures were determined gravimetrically. ξ_3 is expressed by

$$\xi_3=\left[1+\frac{\upsilon_2}{\upsilon_3}(w_3^{-1}-1)\right]^{-1} \tag{1}$$

with w_2 and w_3 the weight fraction of PS and PnBMA, respectively. The total volume fraction of polymer ϕ was calculated from w using the relation

$$\phi=\left[1+\frac{\upsilon_1}{(\upsilon_2 w_2+\upsilon_3 w_3)}(w^{-1}-1)\right]^{-1} \tag{2}$$

where υ_1 and υ_i(i=2, 3) are the specific volume of solvent and polymers, respectively. The specific volume was 1.2923 cm^{3}g^{-1} for cyclohexane, 0.9343 cm^{3}g^{-1} for PS, and 0.9536 cm^{3}g^{-1} for PnBMA at

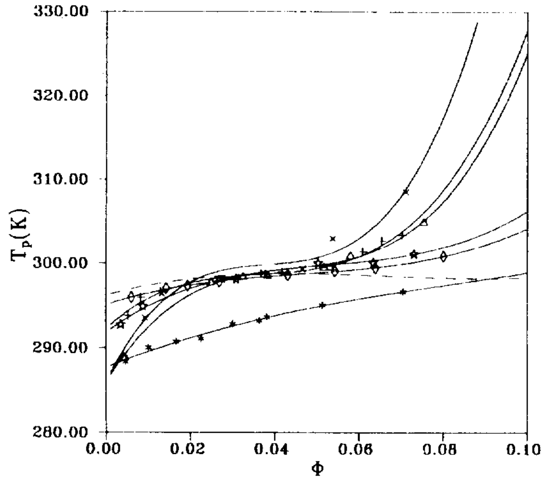

Figure 1. Cloud point curves of cyclohexane solutions of PS5-1(2) and PnBMA5(3) mixtures with different ξ_3 values ; *, 0.9834 ; ×, 0.7795 ; +, 0.5828 ; ☆, 0. 5091 ; ◇, 0.2695 ; △, 0.0695 ; – – –, 0.

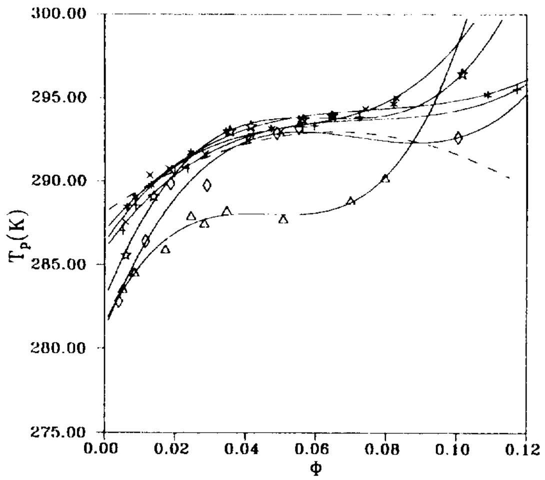

Figure 2. Cloud point curves of cyclohexane solutions of PS9(2) and PnBMA5(3) mixtures with different ξ_3 values ; △, 0.8028 ; ◇, 0.5715 ; ☆, 0.4120 ; +, 0.2517 ; ×, 0.2164 ; *, 0.1320 ; – – –, 0.

any temperature studied.

Cloud Point Measurement. Cloud point temperatures for a series of ternary solutions were measured in a thermostated water bath by monitoring the intensity of light transmitted through the test solutions. The turbidimeter employed is identical to that described elsewhere.[11] The sample cell, being suspended in the middle portion of the water bath, warmed up to 40 ℃ and then allowed to cool naturally. During this cooling process, the solution was continuously stirred. In the vicinity of the cloud point, the cooling rate was controlled to be about 0.1 ℃ $\min^{-1}$ or less. The cloud point was then determined from the break point of intensity variations of the transmitted light versus temperature curve.

Determination of Conjugated Phases. Phase separation was allowed to take place for a variety of initially uniform solutions at three temperatures from 18.9 ℃ to 26.7 ℃ for the system A and 10.9 ℃ to 18.9 ℃ for the system B. A solution of known ϕ was slowly cooled to the phase separation temperature and controlled to maintain the temperature within the accuracy of ± 0.05 ℃. The solution was left standing until it separated into two equilibrium phases. When the height of the phase boundary ceased to change with time, the volume ratio of the upper to lower phase was determined from the height of the stationary phase boundary. The total polymer concentrations of the separated phases were determined from the weights of phases and of the dried polymer mixtures recovered from the solution by solvent evaporation.

The GPC method described by Hashizume *et al.*[12] was used to determine the polymer composition in each separated phase. From the calibration data, it was possible to establish equations relating the molar mass and compositions. Thus, the measurement of molar mass for the component in each separated phase can yield the composition of the system.

Results and Discussion

Cloud Point and Binodals. Cloud point data obtained from the ternary systems of A, B, and C are illustrated in Figures 1 to 3. Each curve represents the temperature of incipient phase separation as a function of the concentration of the polymer mixture having different values of ξ_3. Dashed lines in the figures are the results drawn by the data obtained experimentally from the binary system of PS-cyclohexane.

As usual, the cloud point curves move upward with an increase in the molar mass of constituent polymers. The common feature revealed by those figures is that the curves follow the behavior of a system in which constituent polymers are immiscible and solvent acts as a good solvent for one polymer but poor one for the other. However, the

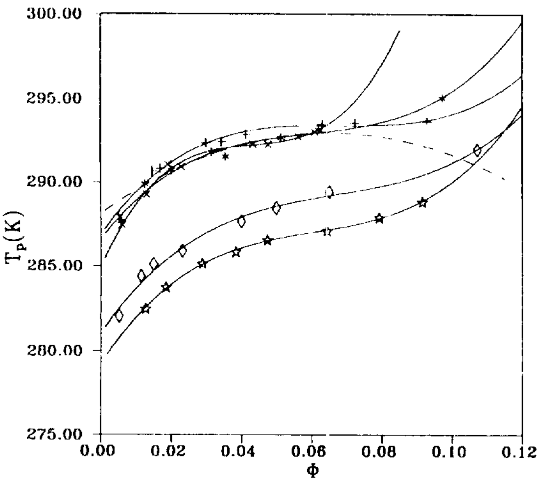

Figure 3. Cloud point curves of cyclohexane solutions of PS9(2) and raw(3) mixtures with different ξ_3 values ; ☆, 0.9399 ; ◇, 0.8952 ; $*$, 0.5093 ; ×, 0.2313 ; +, 0.0894 ; – – –, 0.

most significant aspect is the marked difference in shape between curves for low values of ξ_3, indicating an addition of small amount of PnBMA can change the phase separation behavior of PS-cyclohexane binary system markedly. This may be attributable to the immiscibility between PS and PnBMA.

It can also be seen that the T_p increased, on the whole, with polymer concentration to above the critical temperature of PS-cyclohexane system, but at low temperature close to or below the critical point of the binary system, the cloud point curves can be divided into two groups depending upon the composition of the polymer mixtures. The one is the case when the major constituent of the polymer mixture is PnBMA, which makes the curve moves to the demixing region of PS-cyclohexane system. On the other hand, when PnBMA is the minor constituent the cloud point curve tends to merge with that binary system as the T_p becomes lowered. The difference in the solvent affinity toward the constituent polymers may contribute to occur those phenomena just described.

Observations of cloud point curve made so far lead to a conclusion that the behavior of phase separation for the ternary system given is influenced not only by the concentration, the temperature, and the mixing ratio of constituent polymer but also by the molar mass and the molar mass difference. Similar behaviors, it is reported, have also been observed for the ternary systems of polystyrene/cis-

Table IV. Phase Compositions and Interaction Parameters for PS9/PnBMA5/Cyclohexane System at 10.90, 14.70, and 18.90 ℃

Temp (℃)	Initial solutions		Volume fractions in conjugate phases				Interaction parameters		
	ϕ	ξ_3	ϕ'	ξ_3	ϕ''	ξ_3	x_{13}^{b}	x_{12}^{b}	x_{23}^{t}
10.90	0.0243	0.1317	0.0060	0.1167	0.0492	0.2907	0.4994	0.5235	0.0253
	0.0405	0.2173	0.0157	0.3248	0.0120	0.2833		0.5268	−0.0097
	0.0420	0.2524	0.0089	0.1685	0.1820	0.2313		0.5267	−0.0140
	0.0541	0.5083	0.0080	0.4875	0.1366	0.2621		0.5252	0.0257
	0.0563	0.4121	0.0215	0.5023	0.1203	0.2577		0.5273	0.0156
	0.0646	0.4118	0.0213	0.6291	0.0357	0.2605		0.5289	0.1107
14.70	0.0343	0.1312	0.0045	0.1333	0.0568	0.3169	0.4994	0.5243	0.0399
	0.0472	0.1314	0.0131	0.2672	0.1180	0.2949		0.5279	−0.0077
	0.0559	0.2165	0.0072	0.1389	0.1616	0.2834		0.5288	−0.0238
	0.0461	0.2513	0.0236	0.2034	0.2133	0.2986		0.5282	−0.0450
	0.0596	0.2517	0.0223	0.2735	0.0898	0.3229		0.5291	−0.0231
	0.0726	0.2521	0.0119	0.3361	0.1987	0.2637		0.5322	−0.0229
18.90	0.0821	0.1315	0.0361	0.1607	0.1570	0.2159	0.4994	0.5357	−0.0448
	0.1089	0.1322	0.0322	0.1087	0.1907	0.2360		0.5435	−0.0755
	0.0830	0.2169	0.0385	0.2675	0.0890	0.2798		0.5336	−0.0340
	0.0740	0.2162	0.0337	0.2730	0.2455	0.2692		0.5313	−0.0427
	0.1173	0.2515	0.0704	0.2585	0.1986	0.2226		0.5412	−0.0498
	0.1045	0.5081	0.0755	0.3007	0.1549	0.3028		0.5292	−0.0468
	0.1017	0.4120	0.0655	0.3355	0.2243	0.2648		0.5319	−0.0375

Table V. Phase Compositions and Interaction Parameters for PS5-1/PnBMA5/Cyclohexane System at 18.90, 25.30, and 26.70 ℃

Temp (℃)	Initial solutions		Volume fractions in conjugate phases				Interaction parameters		
	ϕ	ξ_3	ϕ'	ξ_3	ϕ''	ξ_3	x_{13}^{b}	x_{12}^{b}	x_{23}^{t}
18.90	0.0298	0.1501	0.0161	0.7764	0.1617	0.2715	0.4994	0.5174	0.0641
18.90	0.0580	0.0690	0.0222	0.7297	0.1531	0.3174		0.5300	0.0183
25.30	0.0537	0.7765	0.0267	0.9700	0.0349	0.2034		0.5136	0.1895
26.70	0.0717	0.7755	0.1401	0.4204	0.1099	0.2712		0.5142	0.0361
26.70	0.0609	0.5829	0.0431	0.6613	0.1123	0.1113		0.5172	0.0360

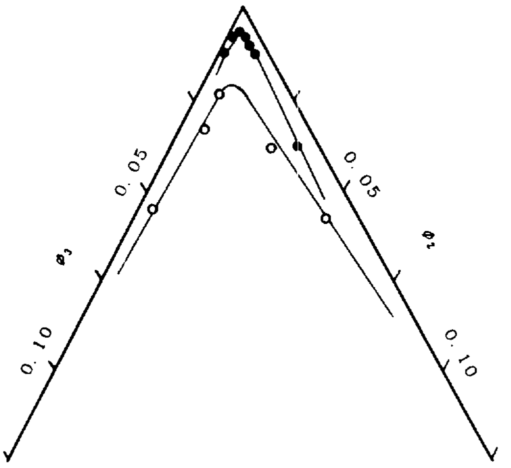

Figure 4. Phase diagrams for the PnBMA5(3)+PS5-1(2)+cyclohexane(1) ternary system at different temperatures ; ●, 18.9 ; ○, 25.3 ℃.

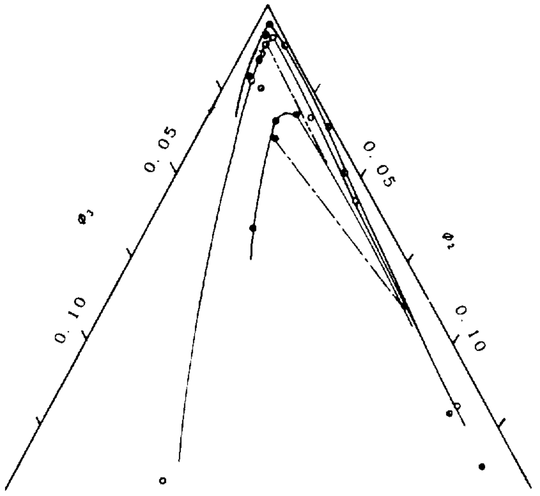

Figure 5. Phase diagrams for the PnBMA5(3)+PS9(2)+cyclohexane(1) ternary system at different temperatures ; ◐, 10.9 ; ○, 14.7 ; ●, 18.9 ℃.

polyisoprene/cyclohexane[13] and polystyrene/polyisobutylene/benzene.[14]

Tables IV and V summerize the composition data for conjugated phases separated from original solutions of the systems A and B at given temperatures. Figures 4 and 5 show the evolution of phase diagrams for the systems A and B at different temperatures in the phase triangles. For the system C where unfractionated PnBMA is used, however, it was unable to measure molar mass of polymer constituents in concentrated phase and hence no binodal curves for this system could be constructed.

Both diagrams revealed that the binodal curves move away from the solvent apex as the temperature increases but the extent is not so significant. This suggests the size of the binodal curve is influenced slightly by the phase separation temperature. However, a comparison of Figures 4 and 5 makes it clear that the difference of the molar mass affects significantly the overall shape of binodal curve. When the difference is prominent as shown in Figure 5, the curves exhibit asymmetry and incline toward PS-cyclohexane axis. In addition, tie lines are sloped down toward the axis representing PS-cyclohexane and become almostly parallel with this axis as the phase separation temperature is lowered. This can be ascribed to the difference in the solvent affinity to the polymer constituents having different molar masses.

Composition Determination of Phases Separated. A typical example of GPC chromatogram and calibration curve for the original solution of system B with different values of ξ_3 are illustrated in Figures 6 and 7, respectively. The relationship between the molar mass and the polymer composition for the respective system can be formulated

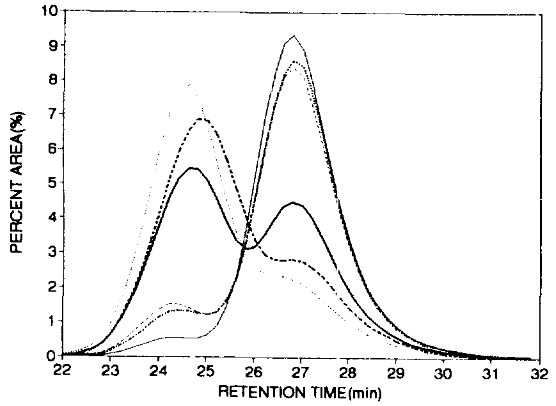

Figure 6. GPC curves for PS9(2) and PnBMA5(3) mixtures of an original solution with different ξ_3 values ; ——, 0.1320 ; – – – – – –, 0.2516 ; · · · · ·, 0.4120 ; ——, 0.5081 ; –·–, 0.5715 ; -----, 0.8028.

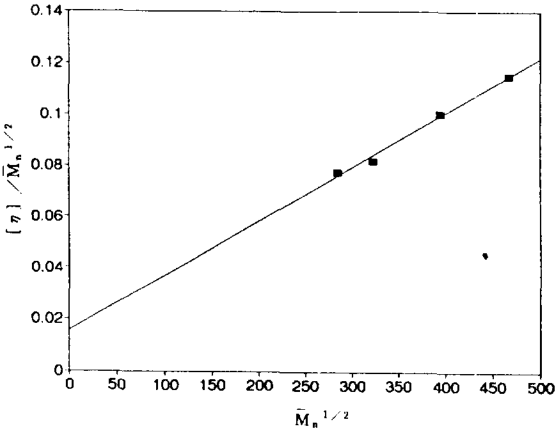

Figure 8. The Stockmayer-Fixman-Burchard plot for the poly(n-butyl methacrylate)+cyclohexane binary solution at 34.1 ℃.

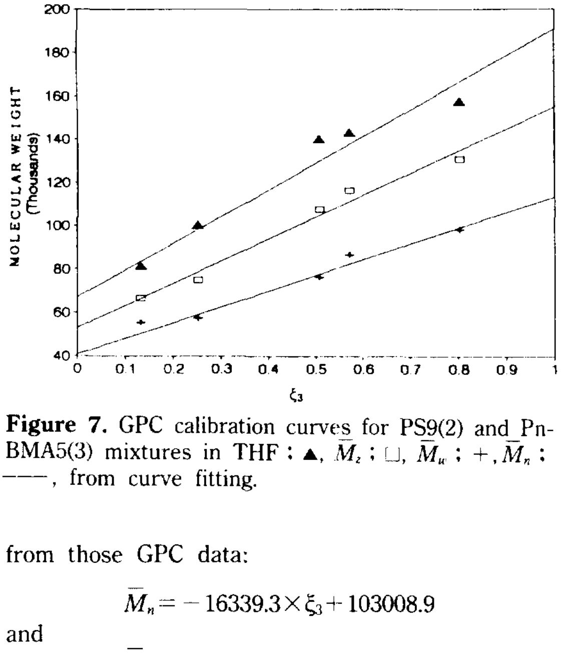

Figure 7. GPC calibration curves for PS9(2) and PnBMA5(3) mixtures in THF : ▲, $\bar{M}_z$; □, $\bar{M}_w$; +, $\bar{M}_n$: ——, from curve fitting.

from those GPC data:

$$\bar{M}_n = -16339.3\times\xi_3 + 103008.9$$

and

$$\bar{M}_w = -22022.0\times\xi_3 + 124786.0 \qquad (3)$$

for the system A and

$$\bar{M}_n = -72534.1\times\xi_3 + 40783.5$$

and

$$\bar{M}_w = -101865.0\times\xi_3 + 48879.8 \qquad (4)$$

for the system B

By employing these relations the phase composition data listed in Tables IV and V were determined. The data listed in both tables show trends that each unstable mixture separates into a concentrated PS rich bottom phase and a dilute PnBMA rich top phase when compared with the values at given initial concentration and temperature. This is the reason why the tie lines are shaped down toward the axis representing the binary system with the larger interaction parameter.

The Interaction Parameters. One of the main interests of thermodynamics on the phase behavior of multicomponent polymer system is to find out the extent of miscibility among various polymer pairs. Obviously, one of the goals of this study is to quantify the interaction parameter of the system of PS-PnBMA mixture.

The interaction parameter χ_{12}^b for the binary system PS-cyclohexane was evaluated by employing the equation established by Hashizume *et al.*[12]

$$\chi_{12}^b = 0.2035 + 90.50\cdot T_c^{-1} + 2600\cdot P^{-0.38}\cdot(T^{-1} - T_c^{-1}) + 0.3092\cdot\phi + 0.1554\cdot\phi^2 \qquad (5)$$

where T_c is the maximum points of the measured cloud-point curves, and P is the relative chain length of the polymer defined by $P = \upsilon_p M/\upsilon_o M_o$. On the other hand, the interaction parameter χ_{13}^b for PnBMA-cyclohexane system was determined by measuring the solution viscosity. It is well known that a transport property such as the intrinsic viscosity, $[\eta]$,[15] is related with parameter χ, and hence χ can be determined if one uses the plot like the Stockmayer-Fixman(SF) equation.[3,16] Figure 8 shows the result of the SF plot and straight line yields χ_{13}^b as 0.4994 at 34.1 ℃.

According to an expression for the polymer-polymer interaction $\chi_{23}{}^{t}$ of a three-component system proposed by Tseng *et al.*,[17] which is formulated by the simple modification of Flory-Huggins theory,[18] the $\chi_{23}{}^{t}$ has the following form :

$$\chi_{23}^{t}=\Big[\frac{1}{m_3}\ln\Big(\frac{\phi_3''}{\phi_3'}\Big)-\frac{1}{m_2}\ln\Big(\frac{\phi_2''}{\phi_2'}\Big)-(\chi_{13}^{b}-\chi_{12}^{b})(\phi_1'-\phi_1'')\Big]\Big/[\phi_3''-\phi_3'+\phi_2'-\phi_2''] \qquad (6)$$

where ϕ_i' and ϕ_i'' are the volume fractions of the i-the component in dilute and concentrated phases, respectively, χ_{ij} is the Flory-Huggins interaction parameter between components i and j, and m_i is the ratio of the molar volume of component i to the molar volume of the solvent. By employing equation (6) and χ parameters evaluated from those binary systems, the χ_{23}^{t} for the present systems A and B can be calculated and are summarized in Tables IV and V, respectively.

As Table V shows, no distinctive variation of χ_{23}^{t} values obtained for the system A can be found in the ranges of both the temperature and the concentration given. This suggests that when the system is composed of large and similar order of molar masses, polymer-polymer interaction parameter is less influenced by the temperature or the concentration. However, for the system B, the χ_{23}^{t} shows a tendency of diminution with the increment of the phase temperature, though it reveals no significant concentration dependence as in the case of system A. One more thing to note is the sign of χ_{23}^{t} of this system changes from positive to negative as a function of the temperature. This result implies that the interaction behavior between components existing in multicomponent system can strongly be affected by the difference of molar mass of constituent polymers. From the structural point of view, a specific interaction between PS and PnBMA can hardly be anticipated. Thus, the enhancement of miscibility for this system is considered to be due to an increased favorable entropy of mixing of the low molar mass PS component.

Conclusion

Turbidimetry and GPC were used to determine the phase equilibrium behavior of ternary system composed of polystyrene-poly(n-butyl methacrylate)-cyclohexane at temperature range of 10.9–26.7 ℃. Well fractionated polymer samples with molar mass of PS in the range of $0.54\times10^5-1.66\times10^5$ g mol^{-1} and PnBMA (1.49×10^5 g mol^{-1}) and unfractionated sample($\bar{M}_w=1.44\times10^5$ g mol^{-1}) were used. Cloud point curves revealed an increasing trend of immiscibility with the increment of molar masses of constituent polymers. When the system contains polymers of different molar masses, the binodal curves moved much away from the solvent apex compared with the system having the same molar mass, and showed asymmetry distorted toward the axis of binary system that have higher value of interaction parameter. The influence of temperature on the size and the location of binodal curves is relatively small, particulary in the case where the same molar mass is concerned. The value of χ_{23}^{t} found for the systems studied varies from 0.19 to −0.076. All the experimental results lead to a conclusion that PS and PnBMA are basically immiscible but the system can be made partly miscible by controlling the polymer molar mass to be mixed.

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References

(1) M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941).
(2) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).
(3) H. Tompa, *Polymer Solutions*, Butterworths, London (1956).
(4) R. L. Scott, *J. Chem. Phys.*, **17**, 27 (1949).
(5) G. Allen, G. Gee, and P. Nicholson, *Polymer*, **1**, 56 (1960).
(6) V. Narasimhan, R. Y. M. Huang, and C. M. Burns, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 1993 (1983).
(7) J. Kumaki, *Macromolecules*, **19**, 763 (1986).
(8) H. S. Tseng, D. R. Lloyd, and T. C. Ward, *J. Polym. Sci., Polym. Phys. Ed.*, **25**, 325 (1987).
(9) D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed., Pergamon Press, London (1988).
(10) M. L. Huggins, *J. Am. Chem. Soc.*, **64**, 2716 (1942).
(11) K. D. Lee and D. C. Lee, *Polymer*(Korea), **15**, 274 (1991).
(12) J. Hashizume, A. Teramoto, and H. Fujita, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1405 (1981).
(13) Z. Tong, Y. Einaga, H. Miyashita, and H. Fujita, *Macromolecules*, **20**, 1888 (1987).
(14) Z. Tong, Y. Einaga, T. Kitagawa, and H. Fujita, *Macromolecules*, **22**, 450 (1989).
(15) A. Camps, B. Celda, J. Mora, and J. E. Figueruelo, *Polymer*, **25**, 1479 (1984).
(16) W. H. Stockmayer and M. J. Fixman, *J. Polym. Sci.*, **C1**, 137 (1963).
(17) H. S. Tseng, D. R. Lloyd, and T. C. Ward, *J. Polym. Sci., Polym. Phys. Ed.*, **29**, 161 (1991).
(18) R. L. Scott, *J. Chem. Phys.*, **17**, 279 (1949).