

# Ternary Phase Equilibria of Polystyrene with a Second Polymer and a Solvent

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## SYNOPSIS

Phase diagrams including tie lines for nine ternary solvent-polymer-polymer systems have been obtained using size exclusion chromatography. The systems studied were toluene-polystyrene (PS)-isoprene rubber (IR), toluene-PS-butadiene rubber (BR), cyclohexane-PS-BR, tetrahydrofuran (THF)-PS-poly (methyl methacrylate) (PMMA), and THF-PS-poly (butyl methacrylate) (PBMA) at temperatures between 30 and 75°C. The results indicate PS-PMMA is less compatible than PS-PBMA in the presence of THF. Also, the combination of *trans*- and 3,4-IR-PS is less compatible than *cis*-IR-PS in the presence of toluene. The original Flory-Huggins model for ternary systems has been modified to account for the concentration dependence of the interaction parameters. The modified Flory-Huggins model consists of two interaction parameters per binary. Using this model, six parameters have been regressed for each of the experimental systems studied. Although the parameters are not physically meaningful, the model and the parameters obtained using it are useful for correlating the experimental phase diagrams. The results obtained using the modified six parameter model are shown to be superior to those obtained using the original three parameter model. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

For practical or academic reasons over the last four decades numerous studies on polymer-polymer incompatibility in the presence of a solvent have been conducted. Dobry and Boyer-Kawenoki<sup>1</sup> studied phase separation in 78 solvent-polymer-polymer solutions using the cloud-point isotherm method. They added solvent to a turbid mixture containing two incompatible polymers until the agitated mixture became clear. They also evaporated solvent from a clear mixture until the mixture became turbid and showed that the phenomena was reversible. A series of such experiments at various polymer-polymer weight ratios establishes the cloud-point isotherm. For six of the mixtures, the compositions of the resulting phases were determined using a variety of microanalytical methods depending upon the chemical nature of the polymers. Accuracy of  $\pm 5\%$

was deemed sufficient because the goal was to prove that each phase contained mainly one of the two polymers. Each of the phases was sampled, weighed, and dried to determine the solvent concentration. If the two polymers were sufficiently different chemically, microanalytical determination of carbon and hydrogen sufficed. In systems containing polystyrene (PS), the proportion of PS was determined by precipitating it with acetic acid and weighing the precipitate. Kern and Slocombe,<sup>2</sup> Kern,<sup>3</sup> Bristow,<sup>4</sup> Allen et al.,<sup>5</sup> Berek et al.,<sup>6</sup> and Djadoun et al.<sup>7</sup> used these and other microanalytical methods to determine phase compositions.

Allen et al.<sup>5</sup> also used ultraviolet (UV) spectrometry to determine phase compositions in a system containing PS and polyisobutylene (PIB). At a wavelength of 250–260 nm, PS has a strong adsorption band, which is linearly related to concentration, while PIB is transparent. Similarly, for a system containing polydimethylsiloxane and PIB, they used infrared spectrometry since polydimethylsiloxane absorbs at  $1261\text{ cm}^{-1}$  and PIB is transparent. van den Esker and Vrij<sup>8</sup> and Djadoun et al.<sup>7</sup> likewise

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used UV spectrometry for systems containing PS and a UV transparent polymer. The former also obtained spinodals using light scattering.

The advent of size exclusion chromatography (SEC) in the 1960s provided an alternative to drying ternary samples to determine their solvent concentration. SEC separates solvents from polymers and to a varying extent, polymers from polymers, based on the size of the molecules in solution. UV and refractive index (RI) detectors have been used to determine the concentrations of each of the polymers in each of the phases by Gaillard et al.,<sup>9</sup> Lloyd et al.,<sup>10</sup> Hashizume et al.,<sup>11</sup> Narasimhan and co-workers,<sup>12-14</sup> Lau et al.,<sup>15-17</sup> Robledo-Muniz et al.,<sup>18</sup> Tseng,<sup>19</sup> and Tseng and Lloyd.<sup>20</sup>

The purpose of this research was to obtain phase equilibria data using SEC for a number of systems containing PS with a second polymer and a solvent and to investigate the effect of stereo regularity, branching, and molecular weight on polymer-polymer compatibility. A further purpose was to modify the original Flory-Huggins model to account for one of its greatest weaknesses, the concentration dependency of the interaction parameters and to obtain an analytical expression that is capable of accurately describing the experimental data. The advantages of using a Flory-Huggins model are its simplicity, its wide acceptance and familiarity in industry and academia, and that only a knowledge of the components' molar volumes is required.

## THEORY

Scott<sup>21</sup> and Tompa<sup>22</sup> were the first to extend the Flory-Huggins theory of solvent-polymer solutions to ternary solutions. According to the theory, the reduced Gibbs free energy of mixing is given by

$$\frac{\Delta G_M}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + \chi_{12} m_1 n_1 \phi_2 + \chi_{13} m_1 n_1 \phi_3 + \chi_{23} m_2 n_2 \phi_3 \quad (1)$$

where  $n_i$  and  $\phi_i$  are the number of moles and the volume fractions of the ternary components, respectively,  $R$  is the gas constant,  $T$  is the temperature in kelvins, and the interaction parameters,  $\chi_{ij}$ , are defined on a per segment basis.  $m_i$  is the ratio of the molar volume of  $i$  to a reference component's volume, here taken to be that of the solvent, component 1; thus  $m_1 = 1$ .

The above equation assumes that the three interaction parameters are independent of concentra-

tion. However, in general, this is not the case. We have modified the Flory-Huggins model for ternary systems to account for concentration dependency of the parameters.<sup>23</sup> The reduced Gibbs free energy of mixing is given by

$$\frac{\Delta G_m}{RT} = n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + g_{12}(u_{12}) m_1 n_1 \phi_2 + g_{13}(u_{13}) m_1 n_1 \phi_3 + g_{23}(u_{23}) m_2 n_2 \phi_3 \quad (2)$$

where  $u_{ij}$  is defined, using notation similar to that of Zivný and Pouchlý,<sup>24</sup> as the ratio of the volume of the  $j$ th component to the combined volume of the  $i$ th and  $j$ th components, or

$$u_{ij} = \frac{\phi_j}{(\phi_i + \phi_j)} \quad (3)$$

Equation (2) is an equivalent, but modified form of eq. (6) presented in our earlier paper.<sup>23</sup>

The chemical potential of the  $i$ th component can be obtained by differentiating the Gibbs free energy of mixing with respect to  $n_i$ . The resulting equations are obtained.

$$\frac{\Delta \mu_1}{RT} = \ln \phi_1 + \phi_2 + \phi_3 - \frac{\phi_2}{m_2} - \frac{\phi_3}{m_3} + [g_{12}(u_{12}) \phi_2 + g_{13}(u_{13}) \phi_3] (\phi_2 + \phi_3) - g_{23}(u_{23}) \phi_2 \phi_3 - \phi_1 u_{12}^2 \frac{\partial g_{12}(u_{12})}{\partial u_{12}} - \phi_1 u_{13}^2 \frac{\partial g_{13}(u_{13})}{\partial u_{13}}, \quad (4)$$

$$\frac{\Delta \mu_2}{RT} = \ln \phi_2 + \phi_1 + \phi_3 - m_2 \phi_1 - \frac{m_2 \phi_3}{m_3} + [g_{12}(u_{12}) m_2 \phi_1 + g_{23}(u_{23}) m_2 \phi_3] (\phi_1 + \phi_3) - g_{13}(u_{13}) m_2 \phi_1 \phi_3 + m_2 \phi_2 (1 - u_{12})^2 \frac{\partial g_{12}(u_{12})}{\partial u_{12}} - m_2 \phi_2 u_{23}^2 \frac{\partial g_{23}(u_{23})}{\partial u_{23}}, \quad (5)$$

$$\frac{\Delta \mu_3}{RT} = \ln \phi_3 + \phi_1 + \phi_2 - m_3 \phi_1 - \frac{m_3 \phi_2}{m_2} + [g_{13}(u_{13}) m_3 \phi_1 + g_{23}(u_{23}) m_3 \phi_2] (\phi_1 + \phi_2)$$

$$\begin{aligned}
 & -g_{12}(u_{12})m_3\phi_1\phi_2 + m_3\phi_3(1-u_{13})^2 \frac{\partial g_{13}(u_{13})}{\partial u_{13}} \\
 & + m_3\phi_3(1-u_{23})^2 \frac{\partial g_{23}(u_{23})}{\partial u_{23}}. \quad (6)
 \end{aligned}$$

The equations for the case where the parameters are considered independent of concentration are obtained by dropping out the terms containing partial derivatives.

In the model, we have assumed that the interaction parameters vary linearly with concentration,

$$g_{ij} = g_{ija} + g_{ijb}u_{ij}. \quad (7)$$

The resulting six parameters are  $g_{12a}$ ,  $g_{12b}$ ,  $g_{13a}$ ,  $g_{13b}$ ,  $g_{23a}$ , and  $g_{23b}$ . In general, the Flory-Huggins interaction parameters for binary systems continually increase, remains constant, or continually decrease with concentration and do not go through either a minimum or maximum. A linear relation is capable of describing all of these cases. Although the concentration dependence is probably more complex than this linear relation implies, it is necessary to attempt such a simplified form in order to keep the number of regression parameters reasonable. The ultimate test of the form is the ability of the model to satisfactorily correlate the data.

Finally, at equilibrium in a two-phase system the chemical potential of each separate component must be equal in each phase,

$$\Delta\mu_i^I = \Delta\mu_i^{II} \quad i = 1, 2, 3. \quad (8)$$

Using eqs. (3)–(8), the interaction parameters can be regressed from experimental tie line data.

### Parameter Estimation and Tie Line Calculation

The original Flory-Huggins model contains three adjustable interaction parameters. The modified Flory-Huggins model contains two parameters per binary for a total of six parameters. Their values are obtained by fitting the models to experimental data.

The model parameters were estimated by minimizing an objective function based on the equivalence of chemical potentials for each component in both phases. The IMSL minimization procedure DUNLSF was used. Expressed in terms of the least-squares principle, the objective function used was

$$\begin{aligned}
 F(p) &= \sum_k \sum_i W_i^2 [\Delta\mu_{ik}^I(\phi_{ik}^I, p) - \Delta\mu_{ik}^{II}(\phi_{ik}^{II}, p)]^2 \\
 & \quad i = 1, 2, 3 \text{ (components)} \\
 & \quad k = 1, 2, \dots, M \text{ (tie lines)}. \quad (9)
 \end{aligned}$$

$W_i$  is the weighing factor associated with component  $i$  and was set equal to the reciprocal of  $m_i$  to account for the large differences in molar volumes between the solvent and polymers.<sup>25</sup>  $\phi_{ik}^I$  is the experimental volume fraction of component  $i$  in phase I at tie line  $k$ . The calculated chemical potentials depend on the experimental volume fractions and the parameters.

To compare the results obtained using each of the models, a residual was calculated as follows

$$R = \left[ \frac{\sum_k \sum_i W_i^2 (\Delta\mu_{ik}^I - \Delta\mu_{ik}^{II})^2}{3M} \right]^{1/2}. \quad (10)$$

The regression program always converged quickly regardless of the values used for the initial guesses of the interaction parameters.

The tie lines corresponding to phase equilibrium were calculated using the equivalence of chemical potentials criteria given in eq. (8) along with the following material balances,

$$\sum_i \phi_i^I = \sum_i \phi_i^{II} = 1. \quad (11)$$

The IMSL minimization procedure DNEQNF was used. Values of  $\phi_3^{II}$  as well as guesses of  $\phi_1^I$ ,  $\phi_2^I$ ,  $\phi_3^I$ ,  $\phi_1^{II}$ , and  $\phi_2^{II}$  were supplied.

## EXPERIMENTAL

### Apparatus

Quantitative analysis of the ternary samples was done using a Varian LC5500 liquid chromatograph equipped with a Varian UV-200 variable wavelength UV detector operated at 254 nm and a Varian RI-4 refractive index detector. The detectors were positioned in series along the eluant path and their outputs were recorded by a Varian Data System DS-654. The data system included software to adjust baselines and compute areas. A Toya Soda TSKgel G4000HXL column containing styrene-divinylbenzene packing was used. The packing consisted of 5  $\mu$ L particles with an average pore diameter of 4000 Å. Samples were loaded into a Varian 8085 auto-

**Table I Characteristics of Polymer Samples: Manufacturers' Data**

Sample	$M_n$	$M_w/M_n$	Supplier
BR (22,600) <sup>a</sup>	22,600	1.06	Pressure Chemical Co. (Pittsburgh, PA)
IR (10,800) <sup>b</sup>	10,800	1.11	Goodyear Tire and Rubber Co. (Akron, OH)
PBMA (54,400)	54,350	1.18	DuPont Co. (Philadelphia, PA)
PMMA (32,800)	32,841	1.13	DuPont Co. (Philadelphia, PA)
PMMA (296,000)	296,300	1.10	Pressure Chemical Co. (Pittsburgh, PA)
PS (13,000)	12,987	1.05	Pressure Chemical Co. (Pittsburgh, PA)
PS (53,100)	53,100	1.05	Pressure Chemical Co. (Pittsburgh, PA)
PS (91,200)	91,200	1.04	Pressure Chemical Co. (Pittsburgh, PA)
PS (275,000)	274,600	1.05	Pressure Chemical Co. (Pittsburgh, PA)

<sup>a</sup> 3.2% volatile solvent; 0.45% styrenated diphenylamine antioxidant; 52% *trans* 1,4; 40% *cis* 1,4; and 8% 1,2.

<sup>b</sup> 1.7% volatile solvent; 0.5% styrenated diphenylamine antioxidant; 18% *trans* 1,4; 76% *cis* 1,4; and 6% 3,4.

sampler and each was analyzed four times to improve accuracy.

## Materials

Characteristics and the manufacturers of the polymer samples are given in Table I. The polymers were placed in a vacuum to remove any solvents present. Narrow molecular weight distribution polymer samples were used to minimize polydispersity effects on phase behavior.

Fisher Scientific Certified A.C.S. cyclohexane, Baker Analyzed HPLC Reagent tetrahydrofuran (THF) and Fisher Optima toluene were used for ternary sample preparation. All solvents were used as received. The Baker Analyzed HPLC Reagent THF was also used as the mobile phase and was kept under nitrogen to prevent organic peroxides from forming that affect UV transparency at 254 nm. The densities of the polymers and solvents used are listed in Table II.

## Procedure

A series of ternary mixtures of various compositions were prepared in 10 cm<sup>3</sup> test tubes with PTFE lined screw caps. The tubes were filled approximately half way and were thoroughly agitated using a vortex mixer. The compositions of the mixtures were chosen based on a simple cloud-point isotherm. A mixture in the dilute single-phase region was prepared and, while stirring, evaporated until cloudiness appeared. The rest of the mixtures were then prepared using higher polymer concentrations.

The mixtures were allowed to equilibrate in a temperature-controlled water bath. Temperatures

were measured using a thermometer with an accuracy of  $\pm 0.5^\circ\text{C}$ . The mixtures were considered to be equilibrated when the level of the interface remained constant and each of the phases appeared clear. The time required to attain equilibrium varied from a day to several weeks depending on the polymers. Some of the mixtures were centrifuged at approximately 4000 rpm for 15 min intervals to reduce this time.

When the mixture had equilibrated, the top phase was carefully sampled using a syringe. The aliquot was weighed into a 10 cm<sup>3</sup> volumetric flask and diluted with the mobile phase THF. The mass of the aliquot, and therefore the dilution factor, was selected such that the estimated mass of the polymer in the 20  $\mu\text{L}$  injection to the liquid chromatograph was within the range of the calibration of the detectors. Using a clean syringe, the bottom phase was similarly sampled, weighed, and diluted. This procedure was repeated for each equilibrated mixture.

**Table II Densities of Solvents and Polymers**

Component	Temperature (°C)	Density (g/cm <sup>3</sup> )
BR <sup>26</sup>	30	0.893
BR <sup>26</sup>	75	0.867
Cyclohexane <sup>27</sup>	75	0.7263
IR <sup>28</sup>	30	0.913
PBMA <sup>29</sup>	30	1.05
PMMA <sup>29</sup>	30	1.18
PS <sup>30</sup>	30	1.05
PS <sup>30</sup>	75	1.03
THF <sup>27</sup>	30	0.8746
Toluene <sup>31</sup>	30	0.8577

To analyze quantitatively the dilute samples prepared above, calibration curves of response (counts) versus mass of the pure polymers for the UV and RI detectors were first determined. An identical procedure was followed for each polymer. The result was a set of extinction coefficients that were used to determine concentrations of the ternary mixtures.

The dilute ternary sample to be analyzed was injected and the UV and RI areas determined. If the molecular weights of the two polymers were sufficiently different to cause the RI peaks to split, the masses of polymers P2 and P3 in the injected sample were found directly using the following equations:

$$A_{RI_{P_2}} = (RI_{P_2})(M_{P_2}) \quad (12)$$

$$A_{RI_{P_3}} = (RI_{P_3})(M_{P_3}) \quad (13)$$

where  $A_{RI_{P_2}}$  and  $A_{RI_{P_3}}$  represent the RI areas,  $RI_{P_2}$  and  $RI_{P_3}$  represent the RI extinction coefficients and  $M_{P_2}$  and  $M_{P_3}$  represent the unknown masses of polymer P2 and polymer P3, respectively.

When the RI peaks for the polymers overlap the following equations were used:

$$A_{UV} = (UV_{P_2})(M_{P_2}) + (UV_{P_3})(M_{P_3}) \quad (14)$$

$$A_{RI} = (RI_{P_2})(M_{P_2}) + (RI_{P_3})(M_{P_3}) \quad (15)$$

where  $UV_{P_2}$  and  $UV_{P_3}$  represent the UV extinction coefficients,  $RI_{P_2}$  and  $RI_{P_3}$  represent the RI extinction coefficients, and  $M_{P_2}$  and  $M_{P_3}$  represent the unknown masses of polymer P2 and polymer P3, respectively, and  $A_{UV}$  and  $A_{RI}$  represent the UV and RI total areas. These equations were solved simultaneously to determine the masses of polymer P2 and polymer P3 in the injected sample.

The total masses of these polymers in the dilute sample were then calculated. Since the aliquot was weighed into the volumetric flask, the weight of the solvent was calculated by mass balance. Therefore, the exact composition of the phase was established. By repeating the procedure for the sample prepared from the coexisting phase, the tie line was determined. By repeating for a number of mixtures, the binodal curve was generated. The plait point was located by extrapolating a line through the midpoints of the tie lines to the binodal.

## RESULTS AND DISCUSSION

### Polystyrene–Isoprene Rubber

Tseng<sup>19</sup> studied the ternary system of toluene–PS–isoprene rubber (IR) at temperatures of 15, 30, and

**Table III** Equilibrium Compositions for Experimental Solvent (1)–Polymer (2)–Polymer (3) Systems (Weight Percentages)

$w_1$	$w_2$	$w_3$	$w_1'$	$w_2'$	$w_3'$
System 1: Toluene–PS (53,100)–IR (10,800) at 30°C					
64.29	0.01	35.70	57.61	41.03	1.36
64.50	0.01	35.49	58.89	38.49	2.62
70.98	0.10	28.92	64.75	33.90	1.35
73.26	0.21	26.53	67.12	31.24	1.64
77.96	1.45	20.59	73.18	24.54	2.28
78.05	1.19	20.76	73.30	24.21	2.50
System 2: Toluene–PS (91,200)–IR (10,800) at 30°C					
78.59	0.12	21.29	72.20	24.72	3.08
80.74	0.55	18.71	75.56	21.29	3.15
System 3: Toluene–PS (13,000)–BR (22,600) at 30°C					
74.65	5.01	20.34	69.08	30.07	0.85
76.56	7.30	16.14	71.89	26.32	1.79
76.66	5.55	17.78	71.60	26.94	1.46
77.81	7.75	14.44	74.72	23.48	1.80
System 4: Cyclohexane–PS (13,000)–BR (22,600) at 75°C					
74.35	4.18	21.47	59.06	40.79	0.15
76.42	5.35	18.23	61.67	38.11	0.21
77.38	7.49	15.13	63.92	35.53	0.55
78.06	10.61	11.33	68.94	29.78	1.28
System 5: THF–PS (13,000)–PMMA (32,800) at 30°C					
61.94	37.82	0.24	51.77	3.63	44.60
67.00	31.18	1.82	59.99	6.74	33.27
68.00	29.55	2.45	61.70	9.28	29.02
68.84	26.27	4.90	63.75	11.20	25.06
System 6: THF–PS (13,000)–PMMA (296,000) at 30°C					
66.54	33.35	0.11	63.12	3.66	33.22
71.17	28.81	0.02	64.92	5.21	29.87
75.61	24.21	0.19	69.74	8.87	21.39
76.73	22.56	0.71	74.79	11.20	14.01
System 7: THF–PS (275,000)–PMMA (32,800) at 30°C					
76.18	20.82	3.00	71.71	0.26	28.03
77.60	18.73	3.67	73.43	0.19	26.38
78.50	16.78	4.72	74.89	0.81	24.30
79.85	13.29	6.86	77.55	0.71	21.74
System 8: THF–PS (275,000)–PMMA (296,000) at 30°C					
80.82	19.01	0.17	78.92	0.09	20.98
84.50	14.76	0.74	82.79	0.14	17.07
88.97	10.11	0.92	87.87	0.54	11.59
90.07	8.99	0.94	88.47	0.99	10.54
91.05	7.16	1.79	90.13	1.83	8.04
System 9: THF–PS (275,000)–PBMA (54,400) at 30°C					
62.90	0.16	36.94	63.30	34.92	1.78
71.53	0.39	28.08	71.11	25.82	3.07
75.12	0.98	23.90	73.15	21.72	5.12
73.68	1.24	25.07	73.51	21.18	5.31

45°C using various monodisperse polymers with molecular weights ranging from 10,800 to 220,520. In our work the systems toluene-PS(53,100)-IR(10,800) and toluene-PS(91,200)-IR(10,800), both at 30°C, were studied. The results are presented in Table III. Data were collected at only one temperature because the effect of temperature on the location of the binodal curve is minimal compared to the that of molecular weight.<sup>1,9,19</sup>

The phase diagram for the system toluene-PS(53,100)-IR(10,800) is shown in Figure 1. The mix points, tie lines, binodal curve, and plait point are shown. The results indicate experimental errors of ~ 2% and good reproducibility. Our results are compared with the system toluene-PS(51,200)-IR(10,800) of Tseng<sup>19</sup> in Figure 2. The differences are attributed to the dissimilarity in the stereo regularity of the IR used. Tseng used pure *cis*-IR while this study used random IR. From this result we conclude that the combination of *trans*- and 3,4-IR-PS is less compatible than *cis*-IR-PS in the presence of toluene.

For each tie line, the end points and the mixture point are nearly linear; in fact, the material balances are within 2%. A propagation of errors analysis also indicated errors of less than 2%.<sup>32</sup> The reproduc-

ibility of the experimental procedure can be seen by comparing the three pairs of tie lines in Figure 1; the binodal would have been practically the same had only one tie line of each pair been used.

### Polystyrene-Butadiene Rubber

The toluene-PS(13,000)-butadiene rubber (BR)(22,600) system at 30°C, which was previously investigated by Narasimhan et al.<sup>13,14</sup> and Paxton,<sup>33</sup> was also studied. The results are presented in Table III. The binodal obtained in this study lies as expected between the binodals obtained by Paxton and those obtained by Narasimhan et al. based on the relative molecular weights of the polymers. The results are also in agreement with the observations of Roe and Zin<sup>34</sup> who reported that in this temperature and molecular weight range, PS and BR are completely immiscible in the absence of a solvent.

Attempts were made to study the system cyclohexane-PS(13,000)-BR(22,600) at 30°C. Unfortunately upon mixing, precipitates were formed. Although both PS and BR dissolve in cyclohexane at 30°C, the presence of another polymer negatively affects the solubility of one or both of the polymers that results in the formation of a precipitate. This

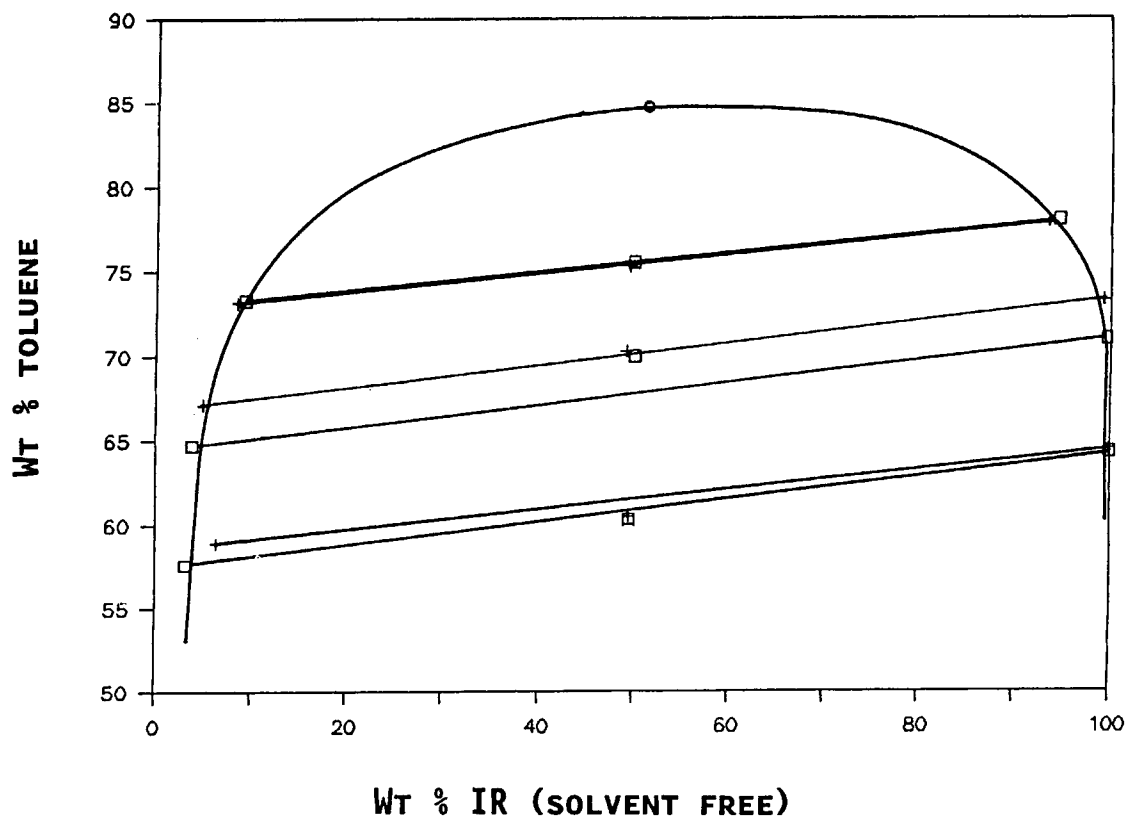
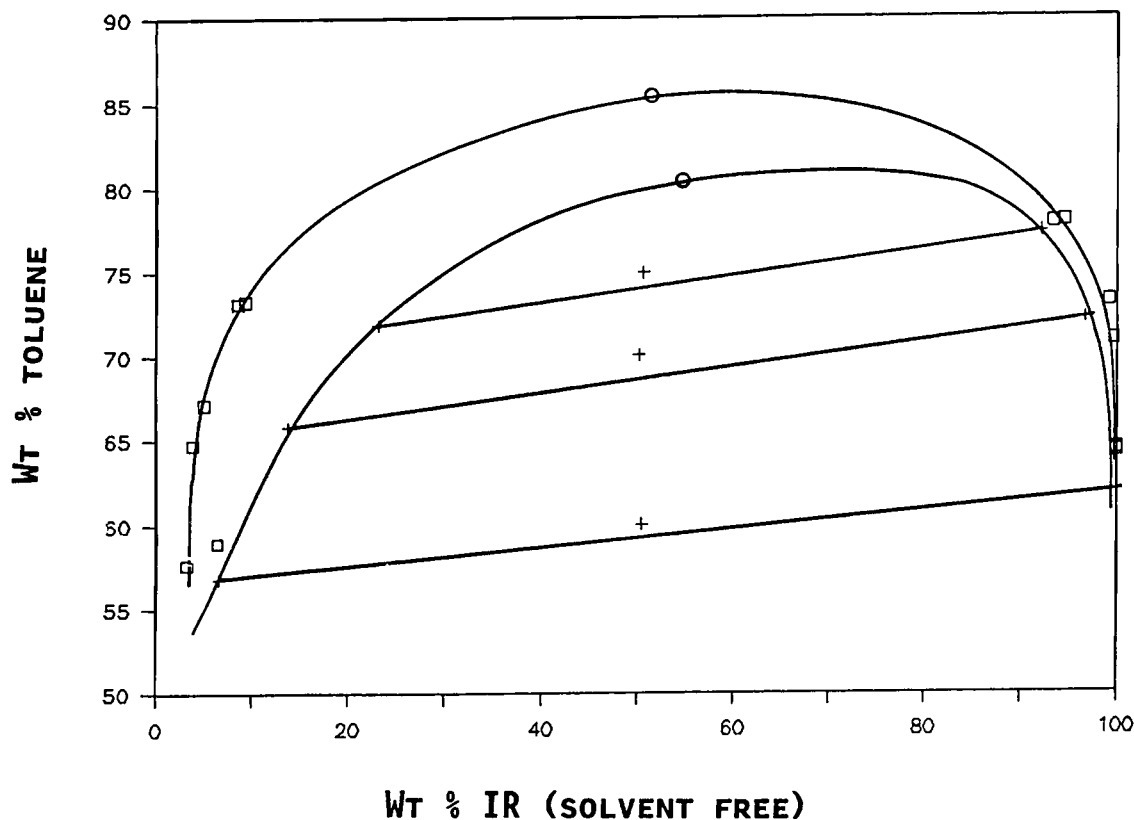


Figure 1 Liquid-liquid equilibria of the toluene-PS(53,100)-IR(10,800) system at 30°C.



**Figure 2** Comparison of phase diagrams for toluene-PS-IR at 30°C obtained (□) in this study and (+) by Tseng.<sup>19</sup>

study was repeated at 75°C because the solubilities of PS and BR in cyclohexane increase with increasing temperature. The results are presented in Table III.

#### Polystyrene-Poly(methyl methacrylate)

The effect of molecular weight on the compatibility of PS-poly(methyl methacrylate) (PMMA) in THF was investigated. The systems studied were THF-PS (13,000)-PMMA (32,800), THF-PS (13,000)-PMMA (296,000), THF-PS (275,000)-PMMA (32,800), and THF-PS (275,000)-PMMA (296,000) at 30°C. The results are presented in Table III and Figure 3.

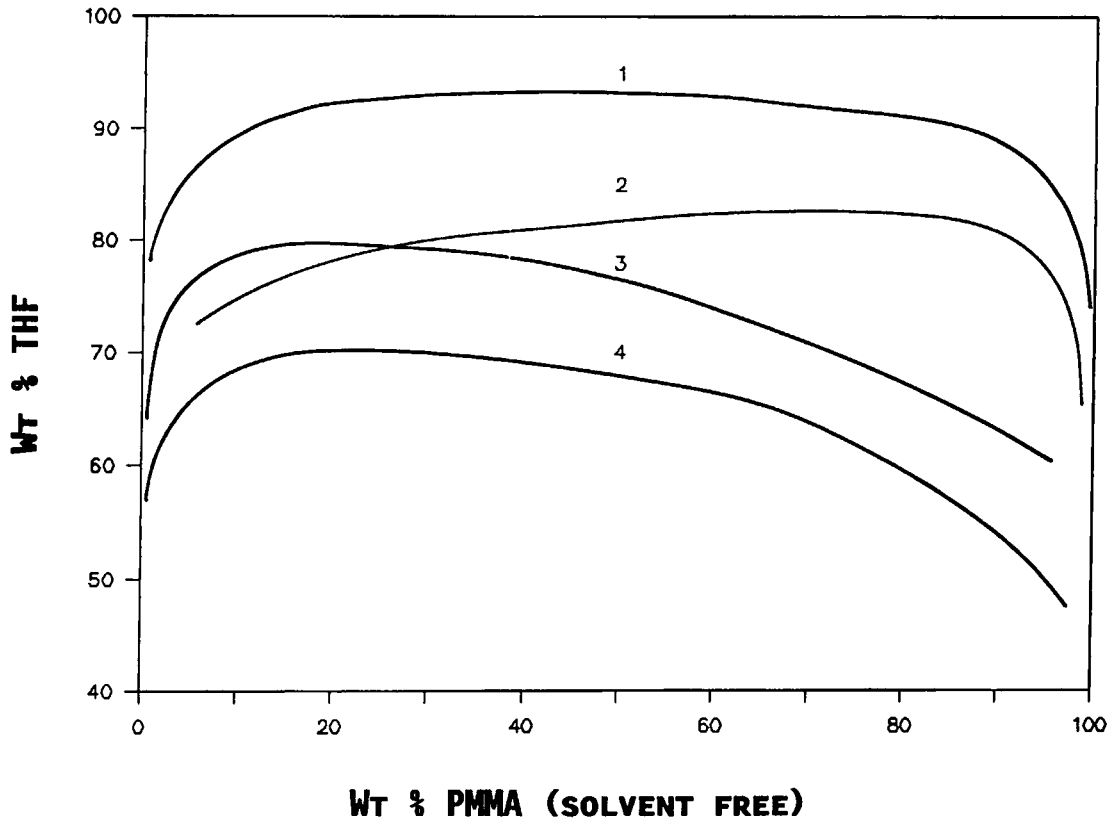
The positions of the binodals are as expected based on the relative molecular weights of the polymers. For the higher molecular weight polymers, the system is less compatible; hence, the binodal is moved upward. Also, the binodal is shifted toward the axis of the polymer with the lower molecular weight. These observations are in agreement with the experimental work of Narasimhan et al.,<sup>12</sup> Robledo-Muniz et al.,<sup>18</sup> Tseng,<sup>19</sup> and Tseng and Lloyd,<sup>20</sup> and the theoretical work of Hsu and Prausnitz.<sup>35</sup>

#### Polystyrene-Poly(*n*-butyl methacrylate)

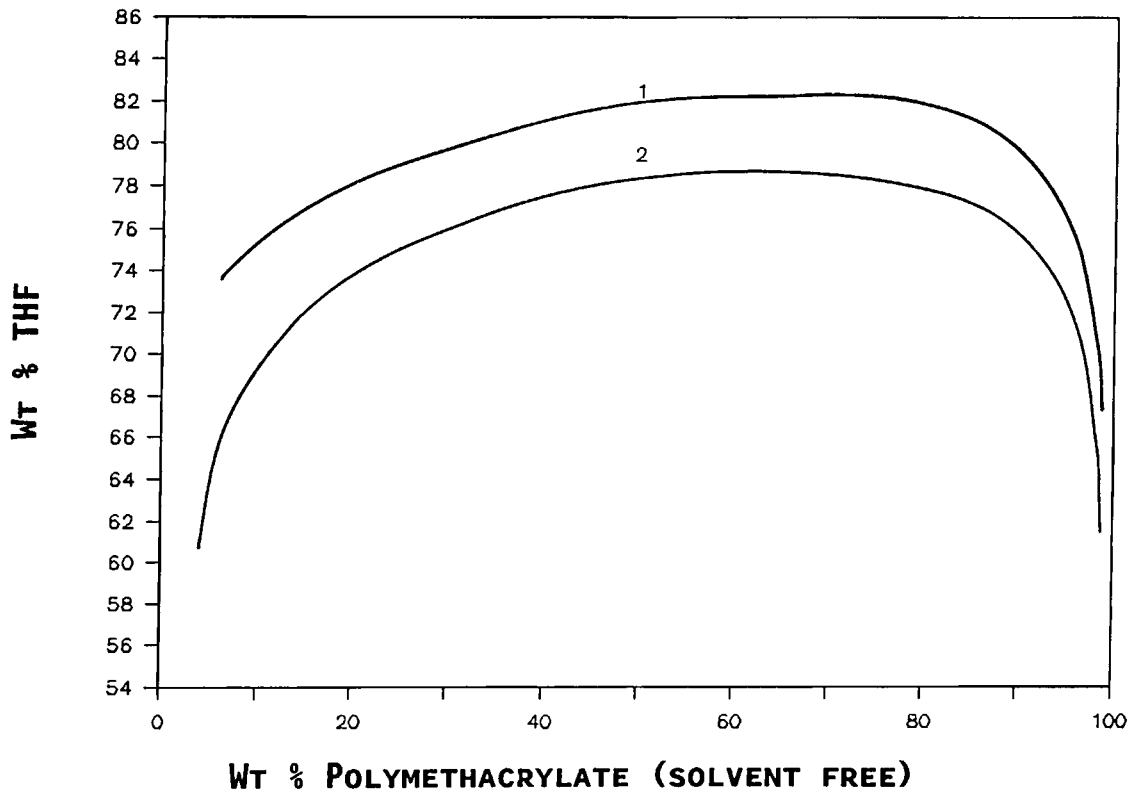
Phase equilibria data and the phase diagram for the THF-PS (275,000)-poly(butyl methacrylate) (PBMA) (54,400) system at 30°C are presented in Table III and Figure 4. Comparing Figures 3 and 4, it is concluded that the combination PS-PMMA is less compatible than PS-PBMA in the presence of THF.

#### Correlations

The experimental data were regressed using both the original Flory-Huggins model with three parameters (FH3) and the modified model with six parameters (FH6) to obtain interaction parameters. No boundaries were placed on the parameters. The parameters obtained using the FH6 model are presented in Table IV, along with the residuals that were calculated using eq. (10). In general, the parameters are realistic; their values are between zero and one. Because the model is semiempirical, however, the values of the individual parameters should not be interpreted quantitatively. Although the parameters for the systems of THF with various mo-



**Figure 3** Effects of molecular weight on the location of the phase diagram for THF-PS-PMMA at 30°C: [1] PS(275,000)-PMMA(296,000); [2] PS(275,000)-PMMA(32,800); [3] PS(13,000)-PMMA(296,000); and [4] PS(13,000)-PMMA(32,800).



**Figure 4** Comparison of phase diagrams for THF with PS(275,000) and two polymethacrylates at 30°C: [1] PMMA(32,800) and [2] PBMA(54,400).



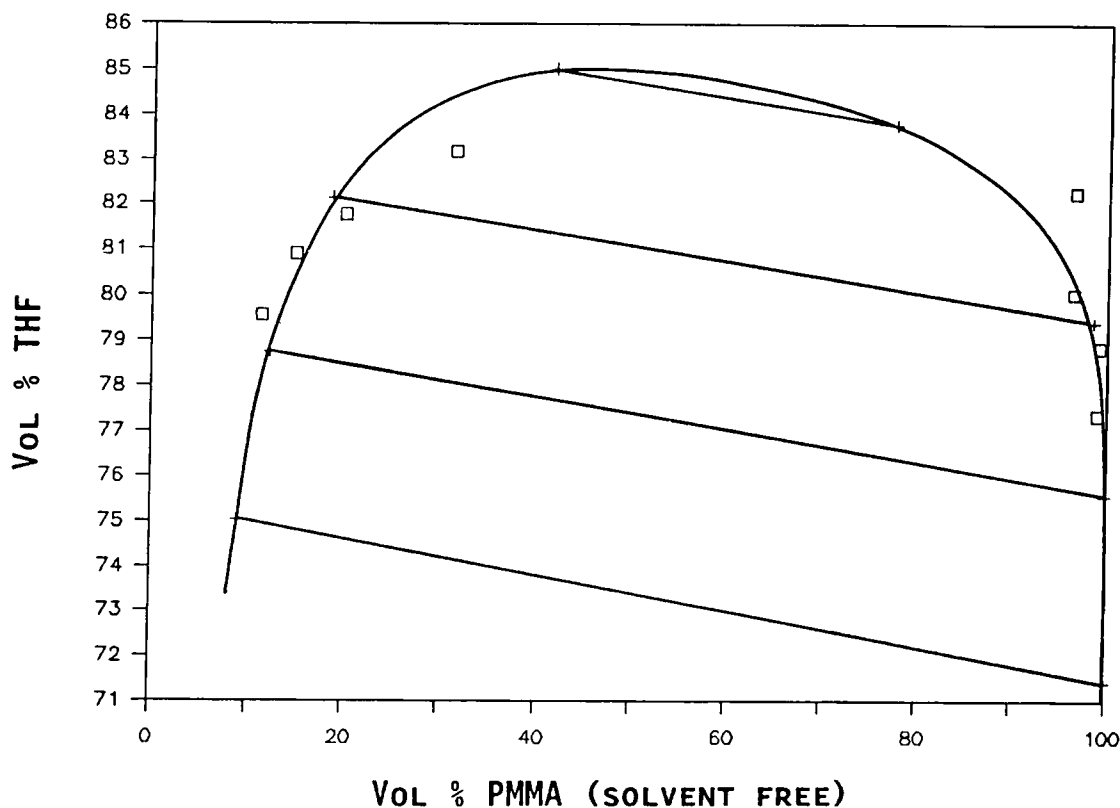
**Table IV Regressed Interaction Parameters and Residuals for Experimental Systems Using the FH6 Model**

System	$\xi_{12a}$	$\xi_{12b}$	$\xi_{13a}$	$\xi_{13b}$	$\xi_{23a}$	$\xi_{23b}$	Residual
1	0.609	0.0658	0.532	-0.106	0.0252	0.0368	$6.98 \times 10^{-4}$
2 <sup>a</sup>	1.62	-0.301	2.68	0.526	0.343	-0.131	0
3	0.719	0.0315	0.672	-0.0609	0.0414	0.0228	$2.48 \times 10^{-4}$
4	0.768	0.157	0.464	-0.429	-0.143	0.102	$2.29 \times 10^{-4}$
5	0.870	-0.0118	0.880	0.151	0.150	-0.0691	$2.96 \times 10^{-4}$
6	0.691	-0.0225	0.694	0.0265	0.0362	-0.00182	$4.76 \times 10^{-4}$
7	0.572	-0.0714	0.653	0.0408	0.0130	-0.0262	$7.68 \times 10^{-5}$
8	0.556	-0.00594	0.560	0.000656	0.00586	0.0000168	$3.90 \times 10^{-5}$
9	0.639	-0.0107	0.652	0.00788	0.0128	-0.00733	$8.40 \times 10^{-5}$

<sup>a</sup> Data consist of two tie lines; parameters were calculated directly.

molecular weights of PS and PMMA (systems 5 through 8) appear to indicate a trend with molecular weight, such an inference is not justified. In general, the effect of molecular weight on the Flory-Huggins interaction parameter is small. In fact, Fukuda and Inagaki studied the system bromobenzene-PS-PMMA by light scattering and concluded that the PS-PMMA interaction parameter is independent of molecular weight.<sup>36</sup>

Nonetheless, the utility of the model, and the parameters obtained using it, is that an analytical expression can be found that is capable of accurately describing the system. As an example, the correlated phase diagram including tie lines for the system THF-PS (275,000)-PMMA (32,800) is shown in Figure 5. By introducing three concentration dependent parameters, in effect, the model allows each phase to have its own unique set of three Flory-



**Figure 5** Correlation using FH6 model (+) for the THF-PS (275,000)-PMMA (32,800) system. (□) Experimental data.

**Table V Comparison of Interaction Parameters in Coexisting Phases for the THF-PS (275,000)-PMMA (32,800) System in Figure 5**

Phase	Bottom Tie Line			Top Tie Line		
	$g_{12}$	$g_{13}$	$g_{23}$	$g_{12}$	$g_{13}$	$g_{23}$
PS rich	0.555	0.654	0.0107	0.565	0.656	0.00208
PMMA rich	0.572	0.665	-0.0131	0.569	0.658	-0.00726

Huggins interaction parameters. This is further illustrated in Table V where the three interaction parameters;  $g_{12}$ ,  $g_{13}$ , and  $g_{23}$ , are calculated, using eq. (7), for each phase for two of the correlated tie lines shown in Figure 5. For the bottom tie line, the PMMA rich phase (which also is more dilute in solvent) has a greater  $g_{12}$  and  $g_{13}$  and lesser  $g_{23}$  than the PS rich phase. For the top tie line, as the plait point is approached, the difference between the phase's compositions becomes less as does their interaction parameters.

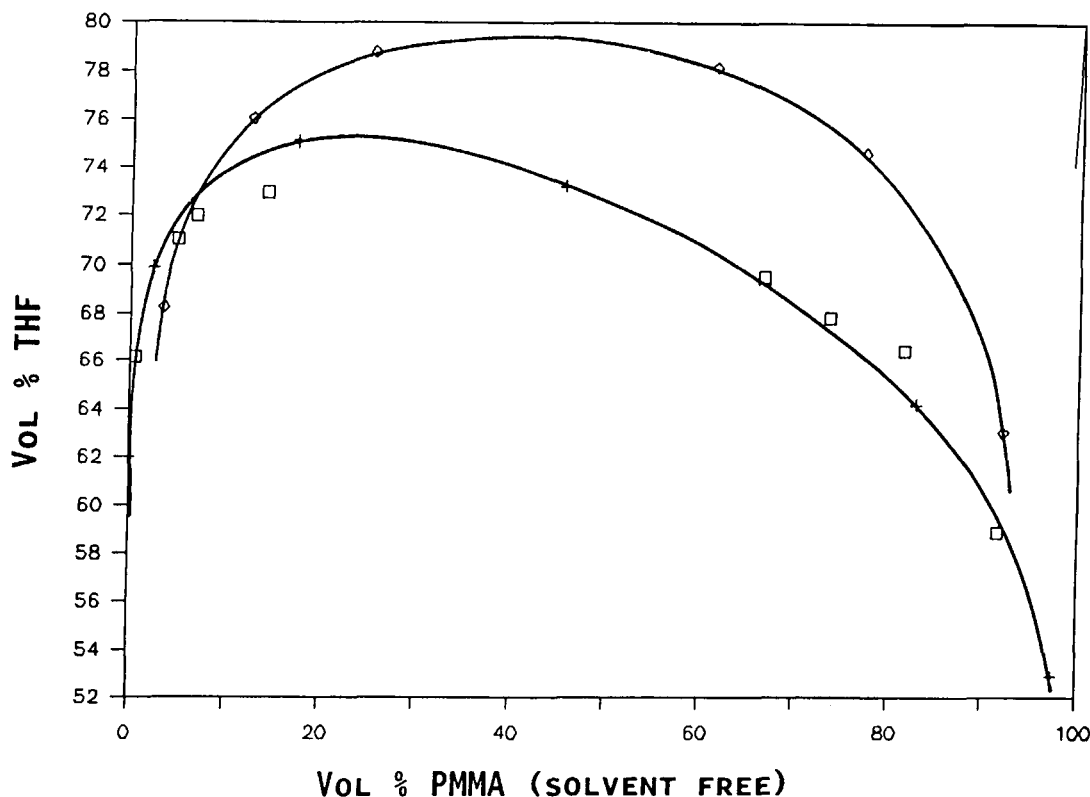
Using the FH3 model, the parameters shown in Table VI were obtained. The residuals were calculated using eq. (10). They are roughly an order of magnitude greater than those obtained using the FH6 model. This is further illustrated in Figure 6.

The high concentration dependence of the interaction parameters for the system THF-PS (13,000)-PMMA (32,800) is additionally shown by noting the large values of  $g_{13b}$  and  $g_{23b}$  in Table IV.

## CONCLUSIONS

Phase diagrams including tie lines for nine solvent-polymer-polymer ternary systems have been successfully obtained using SEC. These systems represent a significant increase in the available well-documented ternary LLE database. Errors of  $\leq 2\%$  and good reproducibility were observed.

It is concluded that PS-PMMA is less compatible than PS-PBMA in the presence of THF. Also, the



**Figure 6** Comparison of correlations obtained using FH3 ( $\diamond$ ) and FH6 (+) models for the THF-PS (13,000)-PMMA (32,800) system. Experimental data ( $\square$ ).

**Table VI Regressed Interaction Parameters and Residuals for Experimental Systems Using the FH3 Model**

System	$\chi_{12}$	$\chi_{13}$	$\chi_{23}$	Residual
1	0.264	0.178	0.0632	$2.47 \times 10^{-3}$
4	0.601	0.445	0.0493	$1.40 \times 10^{-3}$
5	0.903	0.857	0.0464	$4.94 \times 10^{-3}$

combination of *trans*- and 3,4-IR-PS is less compatible than *cis*-IR-PS in the presence of toluene.

The Flory-Huggins model has been modified to account for one of its greatest weaknesses, the concentration dependence of the interaction parameters. The modified Flory-Huggins model consists of two interaction parameters per binary. Using this model, six parameters have been regressed for each of the experimental systems studied.

The advantages of using a Flory-Huggins model are its simplicity, acceptance, and familiarity. Its disadvantage is that it is a semiempirical model; it is difficult to extract information on solvent-polymer and polymer-polymer compatibility from the interaction parameters obtained. The model, and the parameters obtained using it, however, are valuable in that they enable an analytical expression to be found that is capable of accurately describing the experimental data. Finally, the results obtained using the modified six parameter model are shown to be superior to those obtained using the original three parameter model.

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## REFERENCES

1. A. Dobry and F. Boyer-Kawenoki, *J. Polym. Sci.*, **2**, 90 (1947).
2. R. J. Kern and R. J. Slocombe, *J. Polym. Sci.*, **15**, 183 (1955).
3. R. J. Kern, *J. Polym. Sci.*, **21**, 19 (1956).
4. G. M. Bristow, *J. Appl. Polym. Sci.*, **2**, 120 (1959).
5. G. Allen, G. Gee, and J. P. Nicholson, *Polymer*, **1**, 56 (1960).
6. D. Berek, D. Lath, and V. Durdovic, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 659 (1967).
7. S. Djadoun, R. N. Goldberg, and H. Morawetz, *Macromolecules*, **10**, 1015 (1977).
8. M. J. W. van den Esker and A. Vrij, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 1943 (1976).
9. P. Gaillard, M. Ossenbach-Sauter, and G. Reiss, in *Polymer Compatibility and Incompatibility*, K. Solc, ed., Harwood Academic, Chur, Switzerland, 1980.
10. D. R. Lloyd, V. Narasimhan, and C. M. Burns, *J. Liquid Chromatogr.*, **3**, 1111 (1980).
11. J. Hashizume, A. Teramoto, and H. Fujita, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1405 (1981).
12. V. Narasimhan, D. R. Lloyd, and C. M. Burns, *J. Appl. Polym. Sci.*, **23**, 749 (1979).
13. V. Narasimhan, R. Y. M. Huang, and C. M. Burns, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 1993 (1983).
14. V. Narasimhan, R. Y. M. Huang, and C. M. Burns, *J. Polym. Sci., Polym. Symp.*, **74**, 265 (1986).
15. W. W. Y. Lau, C. M. Burns, and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **29**, 1531 (1984).
16. W. W. Y. Lau, C. M. Burns, and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **30**, 1187 (1985).
17. W. W. Y. Lau, C. M. Burns, and R. Y. M. Huang, *Eur. Polym. J.*, **23**, 37 (1987).
18. J. G. Robledo-Muniz, H. S. Tseng, and D. R. Lloyd, *Polym. Eng. Sci.*, **25**, 934 (1985).
19. H. S. Tseng, Ph.D. thesis, University of Texas at Austin, Austin, TX, May 1985.
20. H. S. Tseng and D. R. Lloyd, *J. Polym. Sci., Polym. Phys. Ed.*, **25**, 325 (1987).
21. R. L. Scott, *J. Chem. Phys.*, **17**, 279 (1949).
22. H. Tompa, *Polymer Solutions*, Butterworths, London, 1956.
23. D. J. Geveke and R. P. Danner, *Polym. Eng. Sci.*, **31**, 1527 (1991).
24. A. Zivný and J. Pouchlý, *J. Polym. Sci., Part A-2*, **10**, 1467 (1972).
25. F. W. Altena and C. A. Smolders, *Macromolecules*, **15**, 1491 (1982).
26. J. W. Barlow, *Polym. Eng. Sci.*, **18**, 238 (1978).
27. T. E. Daubert and R. P. Danner, *Physical and Thermal Properties of Pure Compounds: Data Compilation*, Hemisphere, New York, 1989.
28. L. A. Wood, *Rubber Chem. Tech.*, **12**, 130 (1939).
29. O. Olabisi and R. Simha, *Macromolecules*, **8**, 206 (1975).
30. A. Quach and R. Simha, *J. Appl. Phys.*, **42**, 4592 (1971).
31. J. Timmerman, *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier Publishing, New York, 1950.
32. D. A. Scoog and D. M. West, *Analytical Chemistry*, Rinehart and Winston, New York, 1974.
33. T. R. Paxton, *J. Appl. Polym. Sci.*, **7**, 1499 (1963).
34. R. J. Roe and W. C. Zin, *Macromolecules*, **13**, 1221 (1980).
35. C. C. Hsu and J. M. Prausnitz, *Macromolecules*, **7**, 320 (1974).
36. T. Fukuda and H. Inagaki, *Pure Appl. Chem.*, **55**, 1541 (1983).

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