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Separation Factor Study of Model Polystyrene Mixtures in Cyclohexane

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ABSTRACT: Four narrow-distribution polystyrene samples ($M_w \approx 1 \times 10^4$, 4×10^4, 20×10^4, 80×10^4) were mixed at different weight ratios to prepare three model polymer mixtures, and cyclohexane solutions of these mixtures were allowed to separate into two liquid phases at 15 and 18 °C. The composition of each phase was determined by gel permeation chromatography, and the results were used to evaluate the separation factor σ_i for each polymer species. It was found that σ_i decreases monotonically and slowly with increasing relative chain length P_i of polymer species i and depends on the phase separation temperature, the solution concentration before phase separation, and the P_i distribution in the polymer mixture. It was also found that the empirical equation proposed by Einaga et al. for the Gibbs free energy of quasi-binary polymer solutions can predict nearly quantitatively these experimental findings on σ_i.

When a polydisperse polymer dissolved in a pure solvent separates into two liquid phases at equilibrium, each polymer species is distributed in the two phases at different concentrations. To discuss this distribution use is made of a dimensionless parameter σ_i called the separation factor or partition coefficient.[1] It is defined by

$$\sigma_i = (1/P_i) \ln (\phi_i''/\phi_i') \qquad (1)$$

where ϕ_i' and ϕ_i'' are the volume fractions of polymer species i with relative chain length P_i (defined as the molar volume of the polymer relative to that of the solvent) in the separated dilute and concentrated phases, respectively. One of the important problems in polymer solution thermodynamics is concerned with the P_i dependence of σ_i.

A systematic study of this problem was carried out by Breitenbach and Wolf,[2] who, using a continuous-distribution polystyrene (PS) sample, showed that σ_i was virtually independent of P_i. Later, from a similar study also using a continuous-distribution PS sample, Kleintjens et al.[3] found σ_i to decrease monotonically with increasing P_i and attributed Breitenbach and Wolf's failure of finding such P_i dependence of σ_i to their use of a sample with narrower distribution.

Recently, Hashizume et al.[4] studied a ternary system consisting of two narrow-distribution (essentially monodisperse) PS samples in cyclohexane (CH) by high-resolution gel permeation chromatography (GPC) and obtained σ_i independent of P_i. However, it was shown by a subsequent study of Tsuyumoto et al.[5] that the molecular weights of the PS samples used by Hashizume et al. were too close (actually their ratio was 2.3) to find a discernible P_i dependence of σ_i. In fact, Tsuyumoto et al. found a distinct decrease of σ_i with increasing P_i in the same ternary system in which the molecular weight ratio of the polymers was as large as 11.

The study reported in this paper was motivated by these previous investigations, which stimulated an investigation into effect of molecular weight distribution on chain length dependence of the separation factor. Thus, three model polydisperse polymers were prepared by mixing four narrow-distribution PS samples at different weight ratios, and σ_i of the individual polymer species was measured under various conditions of phase separation with the aid of a high-resolution GPC apparatus.

Experimental Section

Polymer Samples. Four narrow-distribution PS samples designated below as F1, F4, F20, and F80 were supplied by Toyo Soda Co. through the courtesy of Dr. M. Fukuda. Sample F20 was separated into five parts by column fractionation and its central fraction was chosen. The other samples were used without further fractionation. Table I shows the weight-average molecular weights (M_w) of the four samples determined by light scattering along with the M_w/M_n values given by the supplier, where M_n denotes the number-average molecular weight.

Table I
Characteristics of Polystyrene Samples

sample	M_w[a]	M_w/M_n[b]
F1	11 000	1.02
F4	44 500	1.01
F20	195 000	1.07
F80	807 000	1.01

[a] Determined by light scattering in benzene at 25 °C. [b] Manufacturer's data supplied by Toyo Soda Co.

Table II
Composition of Polystyrene Mixtures

	M1	M2	M3
ξ_1 (F1)	0.400	0.250	0.100
ξ_2 (F4)	0.300	0.250	0.200
ξ_3 (F20)	0.200	0.250	0.300
ξ_4 (F80)	0.100	0.250	0.400
M_w	137 500	264 400	391 300
M_n	22 600	33 400	64 000
M_w/M_n	6.08	7.92	6.11

Solvents. Cyclohexane was used for phase separation work and benzene for light scattering measurements. These were carefully purified and dried by standard methods.

Polymer Mixtures. Three model polydisperse polymers M1, M2, and M3 were prepared by mixing the above four PS samples at the weight fractions ξ_i shown in Table II, where M_w, M_n, and M_w/M_n of the mixtures are also indicated; from now on, the subscripts 1, 2, 3, and 4 are used to designate samples F1, F4, F20, and F80, respectively. M1 and M3 are richer in lower and higher molecular weight samples, respectively, while M2 is even in all samples. Figure 1 shows the molecular weight distributions of the model mixtures.

Each model mixture was dissolved in benzene, stirred thoroughly, and freeze dried. A desired amount of the dried mixture was placed with a magnetic stirrer chip in a cell of about 5 cm^3 capacity and further dried under reduced pressure at 45 °C until no trace of benzene could be detected by GPC. A desired amount of purified cyclohexane (CH) was poured into the cell in a dry bag filled with nitrogen, and the cell was sealed with a ground-glass stopper. After it was weighed, the cell was further sealed with parafilm.

The volume fraction ϕ of the polymer in each CH solution of PS so prepared was calculated from

$$\phi = [1 + (v_0/v_p)(w^{-1} - 1)]^{-1} \qquad (2)$$

where w is the weight fraction of the polymer in the solution, and v_0 and v_p are the specific volumes of CH and PS, respectively; $v_0 = 1.2923$ cm^3/g and $v_p = 0.9343$ cm^3/g, both at 25 °C, were used for the calculation, regardless of the temperatures studied.

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Table III
Composition of Separated Solutions

	$\phi_1 \times 10^2$		$\phi_2 \times 10^2$		$\phi_3 \times 10^2$		$\phi_4 \times 10^2$		
$\phi \times 10^2$[a]	dil	conc	dil	conc	dil	conc	dil	conc	r (V'/V'')
Sample M1, T = 15 °C									
8.647	3.248	4.360	2.091	5.558	0.322	10.664		5.972	5.91
10.068	3.795	5.274	2.471	5.921	0.581	9.903		6.329	5.00
11.490	4.356	5.491	2.847	5.565	0.772	7.955		5.384	3.63
13.100	4.925	6.329	3.362	5.891	1.319	6.751		5.095	2.95
15.331	5.988	6.321	4.117	5.216	1.968	4.792	0.188	3.375	1.47
Sample M1, T = 18 °C									
7.774	2.938	3.335	2.079	3.859	0.800	7.890		6.730	8.38
9.449	3.593	4.106	2.548	4.159	1.154	6.690		6.070	5.42
10.636	4.148	4.475	2.922	4.282	1.390	5.689		5.488	4.71
Sample M2, T = 15 °C									
7.383	1.733	2.647	1.392	4.533	0.104	10.941		11.031	5.60
9.867	2.298	3.317	1.659	5.103	0.149	10.360		10.166	3.23
13.476	3.171	4.264	2.130	5.226	0.286	8.645		8.613	1.64
17.141	3.830	5.130	2.505	5.688	0.379	7.606		7.394	0.80
Sample M2, T = 18 °C									
9.048	2.201	2.548	1.851	3.526	0.668	7.327		8.931	3.34
11.391	2.726	3.152	2.245	3.897	0.906	6.509		7.960	1.99
12.609	2.926	3.372	2.476	4.004	1.027	6.300		7.267	1.45
15.629	3.574	4.098	3.005	4.347	1.487	5.135	0.312	5.732	0.56
Sample M3, T = 15 °C									
9.583	0.882	1.307	1.084	4.046	0.050	10.023		12.801	2.44
11.109	0.986	1.528	1.049	4.656	0.044	9.899		12.853	2.02
12.852	1.126	1.634	1.117	4.894	0.050	10.211		13.249	1.65
Sample M3, T = 18 °C									
6.076	0.616	0.775	0.920	2.451	0.204	9.161		12.703	4.46
8.021	0.778	0.961	1.159	2.827	0.236	8.621		11.984	3.01
11.893	1.115	1.358	1.524	3.613	0.281	8.328		11.045	1.38
14.911	1.355	1.653	1.648	4.039	0.315	7.702		10.225	0.76

[a] Solution concentrations before phase separation.

Determination of Phase Composition. This was carried out by exactly following the method described and used by Hashizume et al.[4] and also by Tsuyumoto et al.[5] Phase separation for the measurement of σ_i was allowed to take place at 15 and 18 °C from uniform solutions of various concentrations. It took 1–2 weeks for a given solution to reach liquid–liquid phase equilibrium; the thermostat was maintained to within ±0.01 °C during this period of time.

Figure 2 illustrates typical GPC data before and after phase separation of a solution of the mixture M2. The peak positions of the curves for the upper (i.e., dilute) and lower (i.e., concentrated) phases exactly coincide with those for the original solution. This implies that the four narrow-distribution PS samples making up the model mixtures may be treated as monodisperse for our purposes. The GPC curve for each separated phase was resolved graphically into four curves in such a way that their centroids agree with the observed peaks, and the areas under the resolved curves were evaluated to determine the concentrations of the corresponding samples. Except for two cases, no measurable amount of sample F80 was obtained in dilute phases by our GPC apparatus, and hence its separation factor σ_4 was left indeterminate.

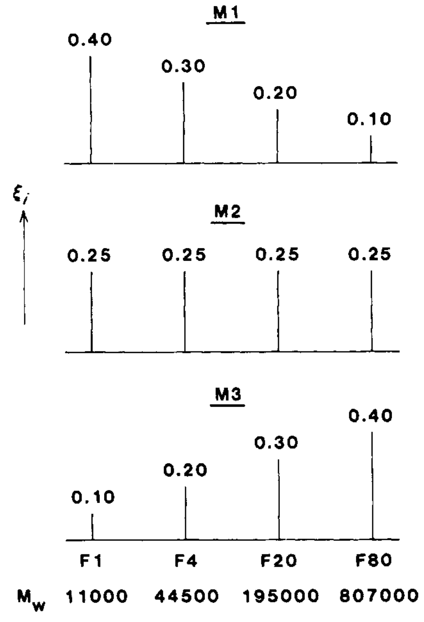

Figure 1. Composition of the model mixtures M1, M2, and M3, whose components F1, F4, F20, and F80 have the molecular weights indicated.

Results and Discussion

Cloud-Point Curves. Figure 3 shows the cloud-point data for the model mixtures in CH as a function of the polymer volume fraction ϕ. We do not discuss these data in comparison with those for the binary PS + CH system, since our primary interest here concerns the separation factor.

Composition of Separated Phases. Table III gives the complete set of data for the composition of separated phases. In the last column, r denotes the volume of the dilute phase relative to that of the concentrated phase at phase equilibrium. It can be seen that the concentration difference $\phi_i'' - \phi_i'$ between the two phases becomes smaller for a lower molecular weight polymer species, regardless of the phase-separation temperature, the total polymer concentration before phase separation, and the composition of the polymer mixture. This fact makes it difficult to determine the separation factor for such a polymer species.

Separation Factor. The columns with the heading exptl in Table IV list the values of σ_i computed from eq

Table IV
Separation Factor

$\phi \times 10^2$ [a]	$\sigma_1 \times 10^3$ exptl	$\sigma_1 \times 10^3$ calcd	$\sigma_2 \times 10^3$ exptl	$\sigma_2 \times 10^3$ calcd	$\sigma_3 \times 10^3$ exptl	$\sigma_3 \times 10^3$ calcd	$\sigma_4 \times 10^3$ exptl	$\sigma_4 \times 10^3$ calcd	$-\Delta\mu_0/RT \times 10^4$ (calcd) dil	$-\Delta\mu_0/RT \times 10^4$ (calcd) conc
Sample M1, T = 15 °C										
8.647	3.12	3.55	2.56	2.33	2.09	1.77			3.13	3.55
10.068	3.48	2.90	2.29	1.76	1.69	1.24			3.51	4.83
11.490	2.45	2.65	1.75	1.62	1.39	1.16			3.90	4.15
13.100	2.66	2.06	1.47	1.18	0.97	0.79			4.21	4.97
15.331	0.57	1.17	0.62	0.63	0.53	0.38	0.42	0.28	4.84	4.55
Sample M1, T = 18 °C										
7.774	1.34	2.12	1.62	1.33	1.37	0.98			3.02	3.22
9.449	1.41	1.66	1.28	0.96	1.05	0.66			3.57	3.92
10.636	0.80	1.35	1.00	0.74	0.84	0.47			4.04	4.15
Sample M2, T = 15 °C										
7.383	4.48	4.66	3.09	3.26	2.78	2.63			1.88	2.32
9.867	3.88	4.14	2.94	2.80	2.53	2.19			2.37	3.10
13.476	3.13	3.61	2.35	2.36	2.04	1.79			3.07	3.30
17.141	3.09	3.11	2.15	1.97	1.79	1.44			3.57	4.05
Sample M2, T = 18 °C										
9.048	1.55	2.55	1.69	1.68	1.43	1.29			2.38	2.36
11.391	1.54	2.15	1.44	1.35	1.18	1.00			2.84	2.92
12.609	1.50	1.98	1.26	1.22	1.08	0.89			3.02	3.09
15.629	1.45	1.40	0.97	0.82	0.74	0.56	0.42	0.46	3.51	3.71
Sample M3, T = 15 °C										
9.583	4.17	5.65	3.44	4.17	3.16	3.50			1.08	0.24_9
11.109	4.63	5.47	3.90	4.01	3.23	3.35			1.17	0.95
12.852	3.95	5.14	3.86	3.70	3.17	3.06			1.31	1.64
Sample M3, T = 18 °C										
6.076	2.44	3.66	2.56	2.67	2.27	2.24			0.83	0.92
8.021	2.23	3.54	2.33	2.55	2.15	2.12			1.02	0.98
11.893	2.09	3.15	2.26	2.20	2.02	1.79			1.39	1.62
14.911	2.11	3.04	2.34	2.10	1.91	1.70			1.63	1.83

[a] Solution concentrations before phase separation.

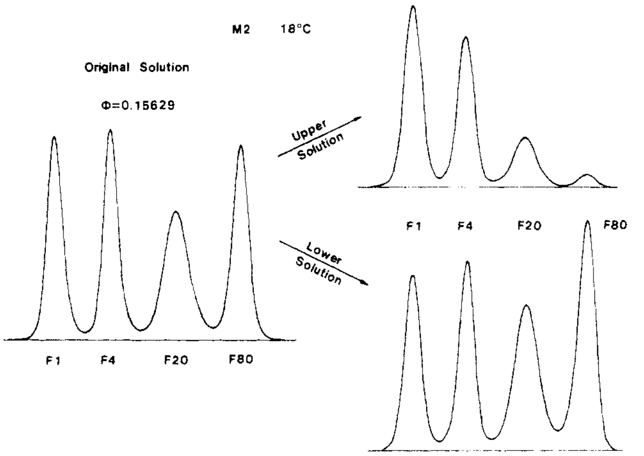

Figure 2. GPC (UV) curves for the mixture M2 before and after phase separation at 18 °C.

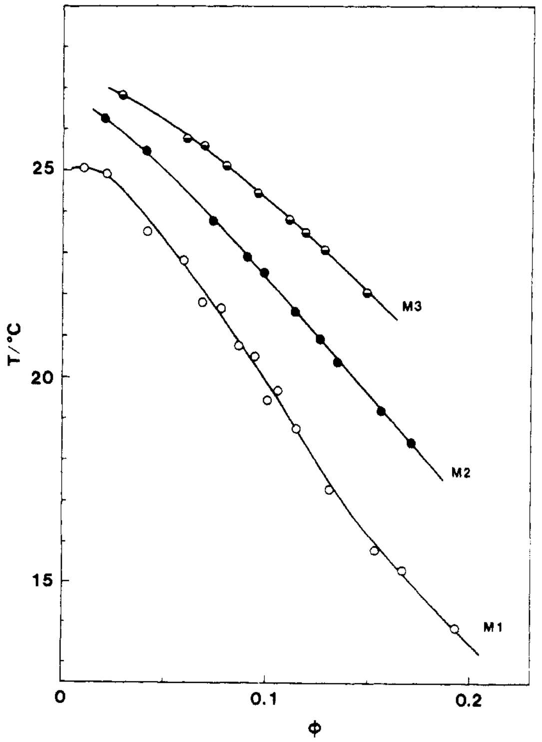

Figure 3. Cloud-point curves for the mixtures M1, M2, and M3 in cyclohexane.

1 with the known values of P_i and the data of Table III. We find that for any polymer mixture and under any phase separation conditions, σ_2 is larger than σ_3 and that for the cases in which σ_4 could be determined, σ_3 is larger than σ_4. Although $\sigma_1 > \sigma_2$ for two-thirds of the 24 cases examined, $\sigma_1 < \sigma_2$ for the rest. In the latter, the differences between σ_1 and σ_2 mostly remain less than 10% of σ_2, and 50% of $\sigma_1 < \sigma_2$ cases are associated with the phase separation of M3 at 18 °C. As can be seen from Table III, the values of $\phi_1'' - \phi_1'$ for this phase separation are smallest among all those obtained in the present experiment. Hence, for the reason mentioned above, the values of σ_1 for M3 at 18 °C are probably least reliable. Thus, we attribute the finding of $\sigma_1 < \sigma_2$ to errors in the GPC determination of ϕ_1'' and ϕ_1' and conclude that the separation factor is a monotonically and slowly decreasing function of chain length for any of the three model mixtures studied. This is consistent with the conclusion drawn by Kleintjens

et al.[3] from a similar study on a continuous-distribution PS sample in CH.

Breitenbach–Wolf Plots. Equation 1 can be rewritten

$$\ln (W_i'/W_i'') = \ln r - \sigma_i P_i \qquad (3)$$

where W_i' and W_i'' are the masses of polymer species i contained in the dilute and concentrated phases, respectively. Figure 4 shows the plots of $\ln (W_i'/W_i'')$ against M_i (usually referred to as Breitenbach–Wolf plots) constructed from the 18 °C data for M1, M2, and M3; here, M_i denotes the molecular weight of polymer species i. The points on the ordinate axes indicate the measured values of $\ln r$. Each solid curve has been drawn to emphasize the trend of the plotted points; it should be noted that the portions between plotted points have no physical meaning.

The indicated curves all have negative slopes and are slightly convex downward. According to eq 3, this implies that the separation factor is positive and decreases slowly with increasing chain length, regardless of the solution concentration ϕ before phase separation and the composition of the polymer mixture. The ϕ dependence of the Breitenbach–Wolf plot is different for different mixtures. When compared at comparable ϕ values, the average slope of this plot is larger for a mixture richer in high molecular weight polymer species; i.e., roughly, the magnitude of the separation factor is in the order M1 < M2 < M3.

The Breitenbach–Wolf plots from the 15 °C data for M1, M2, and M3 exhibited features very similar to those described above.

Theoretical Analysis. When applied to the system containing four polymers, our recently derived expression[6] for the Gibbs free energy of a quasi-binary solution yields

$$(\mu_i - \mu_i^\infty)/RT = \ln (\xi_i\phi) - \frac{P_i}{P_\mathrm{n}}\phi + P_i\phi(1-\phi)\Gamma + P_i\int_0^\phi \Gamma\, \mathrm{d}u + P_i\int_0^\phi \left[(1-\xi_i)\frac{\partial\Gamma}{\partial\xi_i} - \sum_{j\neq i}^{3}\xi_j\frac{\partial\Gamma}{\partial\xi_j} \right] \mathrm{d}u \qquad i = 1, 2, 3 \quad (4)$$

$$(\mu_4 - \mu_4^\infty)/RT = \ln \left(1 - \sum_{i=1}^{3}\xi_i\right)\phi - \frac{P_4}{P_\mathrm{n}}\phi + P_4\phi(1-\phi)\Gamma + P_4\int_0^\phi \Gamma\, \mathrm{d}u - P_4\int_0^\phi \sum_{j=1}^{3}\xi_j\frac{\partial\Gamma}{\partial\xi_j}\, \mathrm{d}u \qquad (5)$$

where μ_i and μ_i^∞ are the chemical potential and reference chemical potential of polymer species i, R is the gas constant, T is the absolute temperature, P_n is the number-average relative chain length of the polymer mixture defined by

$$P_\mathrm{n} = \left(\sum_{i=1}^{4}\xi_i P_i^{-1}\right)^{-1} \qquad (6)$$

where ξ_i is the weight fraction of polymer species i in the polymer mixture, and Γ a characteristic function of the system to be determined by experiment. Actually, this function is defined by the relation

$$(\mu_0 - \mu_0^\circ)/RT = -\phi/P_\mathrm{n} - \Gamma\phi^2 \qquad (7)$$

where μ_0 and μ_0° are the chemical potential of the solvent in the solution and that in the pure state, respectively.

Einaga et al.[6] determined an empirical expression of Γ for the binary system consisting of PS and CH from light scattering data and modified it by certain ad hoc assumptions to a system containing an arbitrary number of PS components with different chain lengths. They showed that the modified expression can almost quantitatively describe observed phase behavior in the system containing two PS fractions. We now try to check present separation factor data to determine whether it works for the system containing four PS fractions.

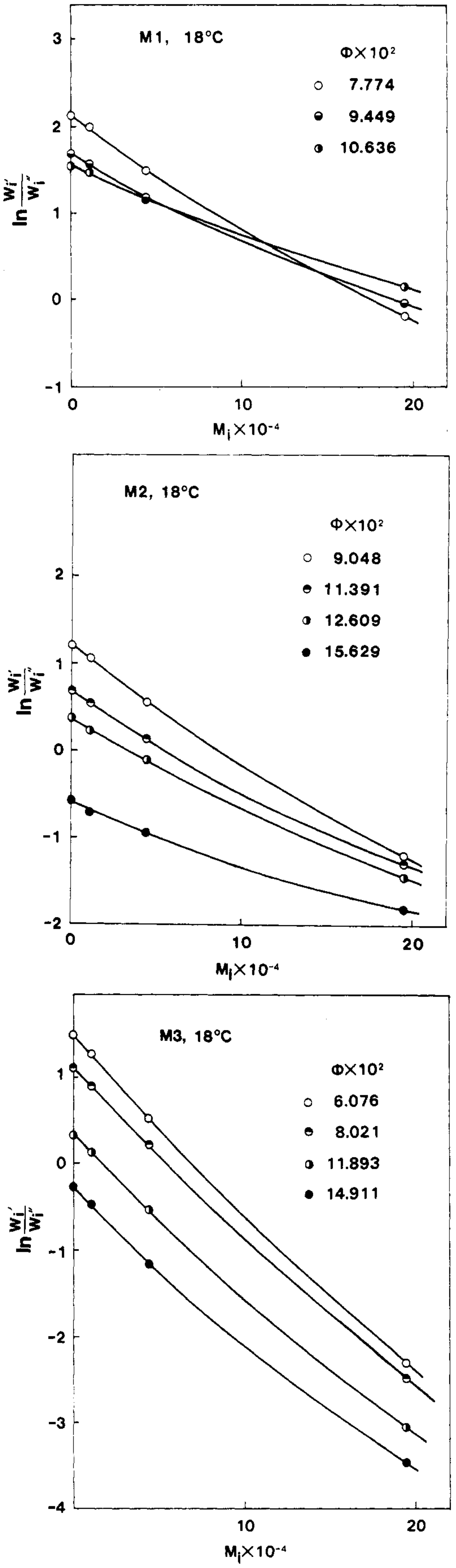

Figure 4. Breitenbach–Wolf plots for cyclohexane solutions of the mixtures M1, M2, and M3 with the concentrations indicated.

For this system the modified Γ is given by[6]

$$\Gamma = \Gamma_{c0} + \frac{1}{2}\Gamma_{c1}\phi^2 + \frac{2}{\phi^2 P^{**}}(\Gamma_{\text{dil}}{}^{\circ} - \Gamma_{c0})[1 - (1 + \phi P^{**1/2})e^{-\phi P^{**1/2}}] \quad (8)$$

where

$$\Gamma_{\text{dil}}{}^{\circ} = -0.26(\Theta/T - 1) - 4.6(\Theta/T - 1)^2 \quad (9)$$

$$\Gamma_{c0} = 0.036P^{*-1/3} - 0.23(\Theta/T - 1) \quad (10)$$

$$\Gamma_{c1} = 0.47 - 3.5(\Theta/T - 1) \quad (11)$$

$$P^* = (\sum_{i=1}^{4}\xi_i P_i^{-1/3})^{-3} \quad (12)$$

$$P^{**} = (\sum_{i=1}^{4}\xi_i P_i^{-1/2})^{-2} \quad (13)$$

and Θ is the theta temperature of the system. We note that eq 8 contains no adjustable parameter and that Γ depends on the concentrations of the individual polymer species through the terms P^* and P^{**}.

Introducing eq 4, 5, and 7 into the phase equilibrium relations $\mu_i' = \mu_i''$ (i = 0, 1, 2, 3, and 4), solving for ϕ_i' and ϕ_i'' (i = 1, 2, 3, and 4), and inserting the resulting expressions into eq 1, we obtain

$$\sigma_i = -\Delta\left\{\Gamma\phi + \int_0^{\phi}\Gamma\, du + \int_0^{\phi}\left[(1 - \xi_i)\frac{\partial\Gamma}{\partial\xi_i} - \sum_{j\neq i}^{3}\xi_j\frac{\partial\Gamma}{\partial\xi_j}\right] du\right\} \qquad i = 1, 2, 3 \quad (14)$$

$$\sigma_4 = -\Delta\left\{\Gamma\phi + \int_0^{\phi}\Gamma\, du - \int_0^{\phi}\sum_{j=1}^{3}\xi_j\frac{\partial\Gamma}{\partial\xi_j}\, du\right\} \quad (15)$$

where ΔX stands for $X'' - X'$. It follows that if Γ depends on ϕ only, σ_i beocmes independent of P_i. Any P_i dependence of σ_i is thus a manifestation of the fact that Γ depends on the concentrations of the individual polymer species. With eq 8 substituted into eq 14 and 15, analytical expressions for σ_i (i = 1, 2, 3, 4) can be derived, but they are too lengthy to display here.

The values of σ_i computed from these expressions and the phase composition data given in Table III are presented in the columns with the heading calcd in Table IV. The following features may be pointed out:

(1) Regardless of T, ϕ, and the composition of the polymer mixture, the calculated σ_i values decrease monotonically and gradually with increasing P_i, in conformity with the conclusion from experimental data.

(2) As a whole, there is good agreement between calculated and measured σ_i not only in order of magnitude but also in absolute value. This is especially true of σ_2 and σ_3.

(3) For M3 at 18 °C the calculated σ_i values are systematically too large in comparison with the measured ones. This may in part be due to the fact that, as mentioned above, σ_1, especially that for M3, was not always accurately measurable. However, the following point is worth noting.

After completion of this work, we found that light scattering data obtained for sample F1 in CH lead to Γ that, in the region of high concentration, cannot be described accurately by the empirical equation of Einaga et al.; note that this equation was established in terms of light scattering data on higher molecular weight samples. Therefore, it is quite probable that the use of eq 8 for Γ, which is its extension to quasi-binary systems, fails to predict correct σ_i for a polymer species whose molecular weight is as low as 1×10^4. An improvement of eq 8 is underway.

Finally, the values of $\Delta\mu_0/RT$ ($\Delta\mu_0 = \mu_0 - \mu_0{}^{\circ}$) for dilute and concentrated phases calculated from eq 7 and the phase composition data of Table III are given in the last two columns in Table IV. Theoretically, the values in the two columns must agree. Except for 7 out of the 24 cases examined, their differences are less than 15% of the values for the concentrated phases.

From the above comparisons between measured and calculated results we find that eq 8 for Γ can predict nearly quantitatively the phase separation behavior of the three model polydisperse polymers in cyclohexane. This finding lends additional support to the ad hoc assumptions invoked in our previous paper[6] for inferring the function Γ of quasi-binary polymer systems. However, it should be noted that the evidence shown here is indirect, since we have not evaluated the composition of each separated phase by solving the phase equilibrium relations (this is computationally very difficult for a system containing as many components as five) to compare directly with experimentally determined phase composition.

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Registry No. PS (homopolymer), 9003-53-6; cyclohexane, 110-82-7.

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