Phase Equilibrium of the Ternary System Consisting of Two Monodisperse Polystyrenes and Cyclohexane

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(Received November 18, 1983)

ABSTRACT: Cloud point curves, binodals, and separation factors were determined for ternary solutions consisting of two "monodisperse" polystyrenes ($M_1 = 4.53 \times 10^4$, $M_2 = 4.98 \times 10^5$) in cyclohexane. Very small fractions of a higher molecular weight component in the polymer mixture were found to have striking effects on the cloud point curve, critical point, and threshold point. The separation factor depended on polymer molecular weight, indicating that the Flory-Huggins χ parameter for the ternary system studied is a function of the concentrations of the individual polymer components, and not simply of their total concentration.

KEY WORDS Polystyrene / Phase Separation / Cloud Point Curve / Binodal / Critical Point / Threshold Point / Ternary Solution / Separation Factor / Flory-Huggins χ Parameter /

The complexity of equilibrium behavior of quasibinary polymer solutions may vary considerably, depending on the system and external conditions. When using the familiar Flory-Huggins-type expression to express the free energy of mixing, this behavior should be described and predicted quantitatively in terms of the Flory-Huggins interaction parameter χ .¹ This parameter involves all the thermodynamic deviations of actual quasibinary solutions from the classic Flory-Huggins solution taken as the reference state. Much effort²⁻⁵ over the past three decades has been directed to finding empirical expressions for χ consistent with observed phase relationships. However, no completely adequate expression has been found for treating even strictly binary polymer solutions, the simplest of polymer + solvent systems. The difficulty arises primarily from the fact^{6,7} that χ for such solutions depends on the polymer molecular weight as well as concentration and temperature. Thus χ for quasibinary polymer solutions should depend on the molecular weight distribution

of the polymer solute. It is also the problem as to whether χ of such solutions depends simply on the total polymer concentration or more generally on the concentrations of the individual polymer components.

To solve these problems, a series of phase separation experiments have been carried out on strictly ternary systems consisting of two monodisperse polystyrene samples and cyclohexane, which are the simplest of quasibinary polymer solutions. Hashizume *et al.*⁸ investigated a case in which the molecular weights of the polymer components 1 and 2 were 4.53×10^4 and 1.03×10^5 , respectively, to determine whether the separation (or partition) factor σ depends on molecular weight. They found σ to be approximately equal for the components 1 and 2, in contrast with the results from typical previous work⁹ dealing with polydisperse polymer samples. Hashizume *et al.*⁸ may have chosen polymer samples whose molecular weight ratio was too small (about 2.3) to detect the molecular

weight dependence of σ . Consequently, we carried out similar phase separation experiment using a pair of monodisperse polystyrene samples differing in molecular weight by a factor of about 10. The major experimental findings and conclusions from this experiment are described in the following.

EXPERIMENTAL

Polystyrene Samples

Two Toyo Soda's standard polystyrenes F4 and F40 were used, whose polymolecularity indices M_w/M_n were 1.01 and 1.05, respectively, according to the supplier. These samples were divided into several fractions by fractional precipitation or extraction with benzene + methanol mixtures to narrow their molecular weight distributions. The main fractions of F40 were further subjected to column elution fractionation. The central portions of the final fractions thus obtained from F4 and F40 were chosen as the test samples for the present experiment. These samples are referred to as f4 and f40 hereafter.

GPC measurements confirmed that the molecular weight distributions of the test samples were sufficiently narrow for our purposes. The weight-average molecular weight M_w , determined by light scattering with a Fica 50 light scattering photometer using benzene at 25°C as the solvent, was 45300 and 498000 for f4 and f40, respectively.

Preparation of Cyclohexane Solutions

Binary Solutions. Each test sample was dried at 50°C under reduced pressure for more than two days. A proper amount of the dry sample was weighed into a cylindrical cell of *ca.* 5 cm³ capacity containing a magnetic stirrer chip, and again thoroughly dried at 50°C for more than two days to remove traces of moisture. A desired amount of purified cyclohexane was then poured into the cell in a dry bag filled with nitrogen, and the cell was sealed with a ground glass stopper. After weighing, the cell

was further sealed with parafilm.

Ternary Solutions. Dried samples f4 and f40 mixed at a desired weight ratio were freeze-dried from a benzene solution. Since traces of benzene were found to greatly affect phase-equilibrium behavior, the polymer mixture was again freeze-dried from a cyclohexane solution. Then, the same procedure as described above for binary solutions was used to make up a test solution.

The total polymer weight fraction w in the test solution and weight fraction ξ_4 of the sample f4 in the polymer mixture were determined gravimetrically. Here ξ_4 is expressed by

$$\xi_4 = w_4 / (w_4 + w_{40}) \quad (1)$$

with w_4 and w_{40} the weight fractions of the samples f4 and f40, respectively. The total polymer volume fraction ϕ was calculated from w using the relation

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

where v_0 and v_p are the specific volumes of the pure solvent and polymer, respectively. We used 1.2924 cm³ g⁻¹ for v_0 and 0.9343 cm³ g⁻¹ for v_p at any temperatures studied, though they refer to 25°C. It should be noted that ϕ is simply a converted weight fraction and is the basic composition variable in the framework of the Flory-Huggins theory.

Determination of Cloud Points

The cylindrical cell containing a given test solution was mounted on a metal rack suspended in the inner bath of a double water thermostat. The solution was warmed to 35–40°C and then allowed to cool naturally by switching-off the temperature regulation system for the inner water bath, while the outer water bath was maintained at about 0.1 or 0.2°C lower than the cloud point (estimated by a preliminary experiment). During this cooling process, the solution was continuously stirred to maintain its temperature and concentration uniformly. In this way, the rate of cooling

Figure 1. Cloud point determination for a polystyrene mixture f4 + f40 ($\xi_4 = 0.950$) in cyclohexane at $\phi = 0.1196$.

could be slowed to about $0.01^\circ\text{C min}^{-1}$ or less near the cloud point. A He-Ne laser beam was passed through the cooling solution, and the intensity of the transmitted light was monitored with a photodiode. Simultaneously, the temperature of the solution was measured at appropriate time intervals, using a Hewlett Packard Model 2802A or a Guildline Model 9535 digital thermometer. The intensity of the transmitted light decreased sharply when the temperature passed through the cloud point (see Figure 1). The cloud point was determined from the break point of the intensity vs. time curve, with an uncertainty of about $\pm 0.01^\circ\text{C}$. This point was independent of the cooling rate slower than 0.01°C/min . Sometimes, cloud points were determined by visual observation of the appearance of speckles in the light path in the solution, and differed no more than 0.02°C from those determined by the more refined method using a laser beam.

Determination of Conjugate Phases

Phase separation was allowed to take place for a variety of initially uniform solutions at four temperatures from 14 to 25°C . A solution of known ϕ was slowly cooled to each of these temperatures under continuous stirring and left standing at that temperature. In most cases, the solution separated into two liquid phases in equilibrium after one or two days. Attainment of equilibrium was reached 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 GPC method described by Hashizume *et al.*⁸ was used to determine the total polymer concentration and polymer composition in each separated phase. Figure 2 illustrates these results for an original solution of $\xi_4 = 0.500$ separated into two phases of $\xi_4 = 0.883$ (upper phase) and $\xi_4 = 0.375$ (lower phase). The GPC peaks for samples f4 and f40 were completely

Figure 2. GPC curves for binary polystyrene mixtures in the two phases separated at 22°C from a cyclohexane solution with $\xi_4=0.500$ and $\phi=0.1006$.

Figure 3a. Critical point determination for a polystyrene mixture f4+f40 with $\xi_4=0.500$ in cyclohexane.

Figure 3b. Critical point determination for a polystyrene mixture f4+f40 with $\xi_4=0.950$ in cyclohexane (see the text for details).

separated and the position and half-width of each of these peaks remained unchanged before and after the phase separation. The latter finding confirms that both f4 and f40 may be treated as monodispersed. The polymer concentrations in the two phases were checked for

adherence to the lever rule, using the phase-volume ratio data obtained.

Determination of Critical Points

For the temperature at which the binodal was experimentally determined, the critical

concentration ϕ_c was determined from the point on the composition triangle at which the locus of the midpoints of a series of tie lines intersected the binodal. For other temperatures, the familiar phase-volume ratio method¹⁰ was used in the following way to determine ϕ_c .

For a chosen ξ_4 a guess was made as to the critical temperature T_c and ϕ_c . Several solutions having the chosen ξ_4 but different ϕ near the guessed critical concentration were prepared. Each solution was allowed to phase separate at various temperatures near the guessed critical temperature, and the phase-volume ratios r at the respective phase separation temperatures were determined. The plots of r vs. ΔT so obtained for $\xi_4=0.500$ and four different ϕ are shown in Figure 3a, and the corresponding plots for $\xi_4=0.950$ are shown in Figure 3b. Here, ΔT denotes the difference between the phase separation temperature and the cloud point, both referring to the chosen ξ_4 and ϕ .

We know by theory that the ϕ value for a particular r vs. ΔT curve converging to $r=1$ at $\Delta T=0$ gives ϕ_c for the chosen ξ_4 and the cloud point associated with this curve is equal to T_c for the same ξ_4 . Thus, we find from Figure 3a that ϕ_c for $\xi_4=0.500$ lies between 0.0791 and 0.0843. In fact, we determined ϕ_c for this ξ_4 to be 0.082. The data shown in Figure 3b does not readily allow estimation of ϕ_c for $\xi_4=0.950$. Hence, the method of Kuwahara *et al.*¹¹ was used. A horizontal line was drawn at $r=1$ and the values of ΔT at its intersections with the r vs. ΔT curves for different ϕ were determined. The phase separation temperature was then calculated from each of these ΔT values and plotted against the corresponding ϕ . The result is shown by a cross in the insert of Figure 3b. The square defines the point at which the dotted line connecting the crosses intersects the cloud point curve for $\xi_4=0.950$, giving the desired values of T_c and ϕ_c for this value of ξ_4 .

RESULTS AND DISCUSSION

Cloud Point Curves

Figure 4 shows the cloud point data for the ternary and binary solutions studied. The data points for the binary solutions of the sample f4 include Hashizume *et al.*'s data⁸ on an essentially identical polystyrene sample in cyclohexane. The filled circles were derived from binodals (see below) by the method described previously,⁸ while the unfilled circles were obtained by direct cloud point measurement. The squares indicate the critical points. It can be seen that the critical temperature T_c falls monotonically but the critical concentration ϕ_c passes through a maximum as ξ_4 increases from zero to unity. This behavior of ϕ_c was also observed by Hashizume *et al.*,⁸ though less clearly, probably because the molecular weight ratio of our polymer components was about 5 times that of theirs.

The most significant aspect of Figure 4 is the systematic change in the curvature of the branch of each cloud point curve to the right of the threshold point (the top of the cloud point curve) with an increase in ξ_4 . This branch remains convex upward for ξ_4 smaller than about 0.40, but shows a convex-downward part, *i.e.*, a dent, for larger ξ_4 . As ξ_4 approaches unity, the dent becomes deeper, eventually making the branch appear sharply bent at a point near the critical point. Surprisingly, even at $\xi_4=0.990$, the dent is still quite distinct and the branch to the left of the break point appears far above the cloud point curve for $\xi_4=1$ (pure F4). It should be noted that, at this ξ_4 value, the branch to the right of the break is almost indistinguishable from the curve for $\xi_4=1$. Thus, we see that the phase-separation behavior of our ternary solution in the region of ϕ below ϕ_c is extremely sensitive to ξ_4 when it is close to unity, *i.e.*, when the polymer mixture contains a small amount of the higher molecular weight component. The cause of this high sensitivity is not yet clear, but its elucidation should substantially provide

Figure 4. Cloud point curves for cyclohexane solutions of polystyrene mixtures f4+f40 with indicated ξ_4 . Unfilled circles, by direct determination; filled circles, from binodals; squares, critical points.

a better understanding of polydispersity effects on the phase relationships of quasibinary polymer solutions.

Cloud point curves having such a dent have already been reported by several authors,^{2,8,12-14} since they were observed by Shultz and Flory¹² for polystyrene mixtures in cyclohexane. However, the dents in our cloud point curves are far more pronounced than those reported so far.

Our molecular weight ratio of 10 was comparable to Tompa's critical value¹⁵ for the onset of three-liquid-phase separation in the type of ternary solution studied here. How-

ever, we found no evidence for such multiphase separation in the ranges of ϕ and T investigated.

Binodals

Table I summarizes the composition data for conjugate phases separated from a variety of original solutions at four temperatures. Figures 5 and 6 illustrate these data at 22 and 14°C plotted on the composition triangle, where ϕ_4 and ϕ_{10} are the volume fractions of the samples f4 and f40, respectively, calculated by substituting w_4 and w_{40} for w in eq 2. The unfilled circles indicate the cloud points in-

Phase Equilibrium of Ternary Solutions

Table I. Phase-composition data for the system f4 + f40 in cyclohexane

ξ_4^a	ϕ^a	ϕ_4'	ϕ_{40}'	ϕ_4''	ϕ_{40}''	$\sigma_4 \times 10^3$	$\sigma_{40} \times 10^3$
14°C							
0.250	0.02043	0.004127	—	0.02500	0.3084	4.63	—
0.250	0.06985	0.009181	—	0.05735	0.2808	4.71	—
0.250	0.1543	0.01035	—	0.07791	0.2529	5.19	—
0.500	0.1261	0.02341	—	0.1312	0.1714	4.43	—
0.500	0.1886	0.02455	—	0.1458	0.1610	4.58	—
0.800	0.04945	0.03103	—	0.1639	0.1217	4.28	—
0.800	0.1281	0.04701	—	0.1909	0.06006	3.60	—
0.900	0.09531	0.05251	—	0.1858	0.03788	3.25	—
0.900	0.1438	0.06570	—	0.1865	0.02456	2.68	—
0.900	0.1793	0.06133	—	0.1947	0.02294	2.97	—
0.950	0.06547	0.05151	—	0.1894	0.04067	3.35	—
0.950	0.1196	0.06449	—	0.1956	0.01773	2.85	—
0.990	0.1379	0.0720	—	0.1863	0.002148	2.44	—
0.990	0.1451	0.0738	—	0.1778	0.001850	2.26	—
18°C							
0.250	0.04994	0.01019	—	0.02420	0.2464	2.22	—
0.500	0.04023	0.01745	—	0.05030	0.2090	2.72	—
0.500	0.1482	0.04387	0.000425	0.09793	0.1294	2.06	1.34
0.800	0.07603	0.05380	0.000445	0.1199	0.09244	2.06	1.25
0.800	0.09980	0.06945	0.001259	0.1356	0.08025	1.72	0.971
0.800	0.1446	0.1095	0.01208	0.1261	0.03607	0.363	0.256
22°C							
0.250	0.03497	0.007735	0.000516	0.01695	0.1834	2.02	1.37
0.250	0.09011	0.01612	0.001696	0.03166	0.1633	1.73	1.07
0.500	0.06042	0.02658	0.001894	0.04486	0.1407	1.34	1.01
0.500	0.08129	0.03400	0.003412	0.05575	0.1206	1.27	0.833
0.500	0.1006	0.04097	0.005413	0.06217	0.1038	1.07	0.690
0.500	0.1222	0.05034	0.008989	0.06663	0.08167	0.720	0.516
0.670	0.09009	0.05724	0.02170	0.06747	0.06585	0.423	0.259
25°C							
0.237	0.04458	0.09918	0.006524	0.01359	0.1104	0.809	0.661
0.237	0.09677	0.02003	0.01485	0.02529	0.08739	0.599	0.414
0.237	0.07146	0.01440	0.009165	0.02003	0.1008	0.848	0.560
0.485	0.04944	0.02300	0.02026	0.03154	0.06676	0.811	0.279

^a Solution composition before phase separation.

terpolated from the smooth curves in Figure 4, while the filled circles represent the directly measured compositions of conjugate phases. Both filled and unfilled points can be fitted well by a single curve (Figure 5), justifying our basic assumption that samples f4 and f40 may be regarded as monodispersed.

In Figure 5, the four crosses on the dot-dash line indicate the original solutions having the same ξ_4 but different ϕ , each eventually separating into conjugate phases connected by a

tie line. The dash line joins the midpoints of a series of tie lines and defines the critical point at its intersection with the binodal.

The tie lines at 22°C for different ξ_4 and ϕ (each cross indicates these two quantities) remain almost parallel to the ϕ_{40} axis (Figure 5), whereas those at 14°C change their direction from the ϕ_{40} axis to the ϕ_4 axis as ξ_4 increases from zero to unity (Figure 6). The binodal at 14°C intersects the ϕ_4 axis at a pair of points, though only one for the higher ϕ_4 can be

Figure 5. Binodal for the ternary system f4 + f40 + cyclohexane at 22°C. Unfilled circles, from cloud point curves; filled circles, from composition analysis; crosses, solutions before phase separation; square, critical point. Solid curve, binodal; thin straight lines, tie lines; dashed curve, locus of the midpoints of tie lines; dot-dash line, composition line for $\xi_4 = 0.500$.

Figure 6. Binodal for the ternary system f4 + f40 + cyclohexane at 14°C. The symbols and lines have the same meaning as in Figure 5.

identified clearly in this figure. Thus, the binary solution of f4 is phase separated at 14°C.

The four binodals obtained, along with the critical points, are shown in Figure 7 to illustrate how the binodal changes with temperature. In the open region to the right of the dash line connecting the critical points, the binodal expands almost uniformly with lowering temperature, giving a larger demixing area at a lower temperature. From this feature, it follows that, in the region of ϕ above ϕ_c , the

cloud point curves for different ξ_4 (except those at ξ_4 close to unity) are nearly parallel to that for $\xi_4 = 0$, as evident from Figure 4.

In the corner region to the left of the dash line in Figure 7, the binodal extends toward the ϕ_4 axis. In particular, those at 18 and 22°C appear to touch the ϕ_4 axis tangentially, but, in fact, there is some finite clearance from the ϕ_4 axis. It thus follows that even a composition line almost coinciding with the ξ_4 axis, *i.e.*, one for $\xi_4 \sim 1$, intersects these binodals. This ex-

Figure 7. Solid lines, binodals for the ternary system f4 + f40 + cyclohexane at the indicated temperatures. Dashed line, locus of critical points.

plains why, in the region of ϕ below ϕ_c , the cloud point curves for ξ_4 close to unity go far above T_c , as seen in Figure 4. The binodals in Figure 7 are similar in overall shape to those obtained by Hashizume *et al.*,⁸ but differ from the latter in that they extend to the more dilute region.

Critical Points and Threshold Points

Our data for critical points (T_c , ϕ_c) and threshold points (T_{th} , ϕ_{th}) are summarized in Table II, and, along with those of Hashizume *et al.*, plotted against ξ_4 in Figures 8 and 9. These figures show to what extent the ξ_4 dependence of critical and threshold behavior for the ternary system treated here varies as the molecular weight ratio M_2/M_1 of the polymer components increases from 2.3 (Hashizume *et al.*'s case⁸) to 10 (our case).

The following features should be noted.

(1) The T_c curve for Hashizume *et al.*'s case is convex upward over the entire range of ξ_4 , while that for our case has an inflection at a ξ_4 value near 0.90. In either case, the changes in

Table II. Critical and threshold points for the ternary system consisting of two "mono-dispersed" polystyrenes and cyclohexane

ξ_4	T_c °C	ϕ_c	ξ_4	T_{th} °C	ϕ_{th}
f4 + f40 (Present data)					
0	27.55	0.047	0	27.55	0.047
0.436	25.00	0.073	0.25	26.5	0.026
0.500	24.08	0.082	0.50	25.6	0.022
0.64	22.00	0.100	0.80	24.1	0.020
0.86	18.00	0.131	0.90	23.0	0.019
0.950	15.01	0.152	0.95	21.9	0.020
0.990	14.43	0.126	0.98	19.9	0.023
1	14.14	0.108	0.99	19.0	0.025
			1	14.14	0.108
f4 + f10 (Hashizume <i>et al.</i> ⁸)					
0	20.64	0.086	0	20.64	0.086
0.350	19.00	0.096	0.150	20.12	0.067
0.532	18.00	0.101	0.300	19.34	0.057
0.685	17.00	0.105	0.501	18.36	0.050
0.78	16.00	0.110	0.651	17.50	0.052
0.867	15.71	0.114	0.850	16.00	0.055
0.885	15.39	0.113	1	14.14	0.112
1	14.14	0.112

Figure 8. Critical temperature T_c and threshold temperature T_{th} as functions of ξ_4 for binary polystyrene mixtures in cyclohexane. Circles, for mixtures f4+f40 (present data); squares, for mixtures f4+f10 (Hashizume *et al.*⁸). Unfilled symbols, T_c ; filled symbols, T_{th} .

Figure 9. Critical concentrations ϕ_c and threshold concentrations ϕ_{th} for binary polystyrene mixtures in cyclohexane. Circles, for mixtures f4+f40 (present data); squares, for mixtures f4+f10 (Hashizume *et al.*⁸). Unfilled symbols, ϕ_c ; filled symbols, ϕ_{th} .

Figure 10. Ratio ϕ_c/ϕ_{th} for binary polystyrene mixtures in cyclohexane plotted against M_w/M_n (filled symbols) and M_z/M_w (unfilled symbols). Circles, for mixtures f4+f40 (present data); squares, for mixtures f4+f10 (Hashizume *et al.*⁸).

T_c with ξ_4 are monotonic and gradual.

(2) In Hashizume *et al.*'s case, T_{th} almost agrees with T_c throughout the entire range of ξ_4 , while, in our case, T_{th} appears far above T_c over a substantial range of ξ_4 . The fall of T_{th} for the latter in the region near $\xi_4=1$ is too sharp to be determined accurately.

(3) In either case, ϕ_c shows a maximum at a

ξ_4 near unity. The maximum is very pronounced in our case.

(4) In either case, ϕ_{th} passes through a broad minimum. It is interesting that, with increasing ξ_4 , the threshold point first moves toward a lower concentration. Also of interest is the finding that ϕ_{th} for our case remains far below the value at $\xi_4=1$ until ξ_4 comes very close to

unity. Thus, in the vicinity of $\xi_4 = 1$, our ϕ_{th} vs. ξ_4 curve has an almost infinite slope (see the dash line in Figure 9).

From these data, we find that when M_2/M_1 is as large as 10, a very small fraction of the higher molecular weight component has a striking effect on ϕ_c , T_{th} , and ϕ_{th} for the ternary system under consideration. In this connection, we note that our experimental curves for T_c and ϕ_c are comparable to those derived theoretically by Vink¹⁶ for $M_2/M_1 = 10$ under variously assigned M_1 and M_2 values. Unfortunately he did not treat the threshold point.

Šolc¹⁷ has investigated theoretically the dependence of ϕ_c/ϕ_{th} for quasibinary polymer solutions on the polydispersity indices M_w/M_n , M_z/M_w , and so forth, confining himself to the special case in which Flory-Huggins interaction parameter χ is independent of concentration. In Figure 10, the values of ϕ_c/ϕ_{th} computed from Hashizume *et al.*'s data and ours are plotted against both M_w/M_n and M_z/M_w . Clearly, the data points have no correlation with M_w/M_n , in agreement with Šolc's conclusion that critical and threshold behavior has nothing to do with M_n . On the other hand, it appears that ϕ_c/ϕ_{th} depends approximately on M_z/M_w only.

Separation Factors

Table I also shows the values of the separation factors σ_4 and σ_{40} for the samples f4 and f40; these were computed by substituting the tabulated values of ϕ_i' and ϕ_i'' ($i=4, 40$) into the defining equation

$$\sigma_i = (1/P_i) \ln (\phi_i''/\phi_i') \quad (3)$$

where P_i is the relative chain length of the sample i . It can be seen that, except for a few cases, the difference $\sigma_4 - \sigma_{40}$ amounts to values as large as 35% of σ_4 , in contrast to the case (f4+f10 in cyclohexane) studied by Hashizume *et al.*,⁸ in which the difference $\sigma_4 - \sigma_{10}$ was less than 10% of σ_4 or essentially negligible within experimental accuracy. Thus,

we may conclude that the separation factor is molecular-weight dependent, as has been argued by previous authors⁹ and that, as noted in the Introduction, Hashizume *et al.*⁸ chose the polymer samples whose molecular weights were too close to observe this dependence clearly.

The molecular weight dependence of the separation factor introduces greater complexity into the theoretical treatment of quasibinary polymer solutions, since it implies that the parameter χ depends not on the total concentration of the solute but on the concentrations of the individual polymer components.¹⁸

Acknowledgment. The authors wish to thank Dr. M. Fukuda of Toyo Soda Co., for kindly providing the polystyrene samples used in this study.

REFERENCES

1. M. Kurata, "Thermodynamics of Polymer Solutions," translated from the Japanese by H. Fujita, Harwood Academic, N. Y., 1982.
2. R. Koningsveld, Thesis, Leiden University, 1967.
3. R. Koningsveld and L. A. Kleintjens, *Macromolecules*, **4**, 637 (1971).
4. R. Koningsveld, W. H. Stockmayer, J. W. Kennedy, and L. A. Kleintjens, *Macromolecules*, **7**, 73 (1974).
5. H. Fujita and A. Teramoto, Proceedings of MMI Symposium on Polymer Compatibility and Incompatibility, Harwood Academic, N. Y., 1982, p 125.
6. TH. G. Scholte, *Eur. Polym. J.*, **6**, 1063 (1970).
7. Y. Einaga, S. Ohashi, Z. Tong, and H. Fujita, *Macromolecules*, to be published.
8. J. Hashizume, A. Teramoto, and H. Fujita, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1405 (1981).
9. L. A. Kleintjens, R. Koningsveld, and W. H. Stockmayer, *Br. Polym. J.*, **8**, 144 (1976).
10. R. Koningsveld, L. A. Kleintjens, and A. R. Shultz, *J. Polym. Sci., A-2*, **8**, 1261 (1970).
11. N. Kuwahara, M. Nakata, and M. Kaneko, *Polymer*, **14**, 415 (1973).
12. A. R. Shultz and P. J. Flory, *J. Am. Chem. Soc.*, **74**, 4760 (1952).
13. G. Rehage, D. Moller, and O. Ernst, *Makromol. Chem.*, **88**, 232 (1965).
14. G. Rehage and R. Koningsveld, *J. Polym. Sci., Polym. Lett. Ed.*, **6**, 421 (1968).

15. H. Tompa, *Trans. Faraday Soc.*, **45**, 1142 (1949).
16. H. Vink, *Eur. Polym. J.*, **12**, 77 (1976).
17. K. Šolc, *J. Polym. Sci.*, **12**, 1865 (1974).
18. H. Fujita and A. Teramoto, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 893 (1982).