Phase Equilibria of Quasi-Ternary Systems Consisting of Multicomponent Polymers in a Binary Solvent Mixture III. Effects of Average Molecular Weight and Molecular Weight Distribution of the Original Polymer

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ABSTRACT: The effects of average molecular weight and molecular weight distribution MWD of the original polymer on the phase equilibrium of quasi-ternary systems consisting of multicomponent polymers, solvent 1 and solvent 2 were studied by computer experiments. For this purpose, polymers having strict monodispersity, Poisson (the weight-average molar volume ratio of the polymer to the solvents, $X_w = 300$), Schulz-Zimm ($X_w = 150-6000$, the ratio of the X_w to number-average molar volume ratio of the polymer to the solvents, $X_w/X_n = 1.03-5.0$), and Wesslau ($X_w = 300$, $X_w/X_n = 2.0-8.0$) type molecular weight distributions were utilized. A small, but significant difference was observed for coexistence curves and other characteristic parameters between strictly monodisperse polymer and the Schulz-Zimm polymer ($X_w/X_n = 1.03$). As X_w of the original polymer, X_w° , decreases, the partition coefficient σ , phase volume ratio R , and the polymer volume fraction in a polymer-rich phase $v_{p(2)}$ increases, and the MWD of the polymers in both phases becomes sharp. As X_w/X_n of the original polymer (X_w°/X_n°) decreases, σ , R , and $v_{p(2)}$ increase for a small relative amount of polymer in a polymer-rich phase ρ_p , but in larger ρ_p region, σ , R , and $v_{p(2)}$ decrease with X_w°/X_n° .

KEY WORDS Quasi-Ternary Polymer Solution / Multicomponent Polymer-Solvent-Non-Solvent System / Phase Equilibrium / Average Molecular Weight / Molecular Weight Distribution / Computer Experiment /

In previous papers,^{1,2} a rigorous theory on the two phase separation phenomena of multicomponent polymers-binary solvent mixture system was established and computer experiments, based on the theory, were successfully carried out to clarify the criterion for a choice of two solvents to yield a phase separation under given conditions and the effects of the operating conditions, such as initial polymer volume fraction and relative amounts of polymers in the two phases, on the phase separation characteristics of the quasi-ternary systems were studied. In these studies, only a polymer having the Schulz-Zimm distribution (with a ratio of the weight- to number-average degree of polymerization, $X_w/X_n = 2.0$ and

$X_w = 300$) was used and hence the influence of the average molecular weight and distribution (MWD) of the original polymer was not clarified. For solutions consisting multicomponent polymers in a single solvent, important role of the molecular characteristics in the phase separation phenomena has already been shown by Kamide and his collaborators.³⁻⁶

In this paper, an attempt is made to elucidate these effects on the phase separation characteristics of the quasi-ternary systems.

The Molecular Characteristics of the Polymer and Computer Experiment

The simulation procedure, established in the previous paper,¹ was also used. Here, it was

assumed that all three thermodynamic interaction parameters, χ_{12} , χ_{13} , and χ_{23} , are independent of concentration.

Four typical MWD functions, $g(X)$, were adopted for the original polymer:

- (1) Single component (*i.e.*, monodisperse)
- (2) Poisson distribution

$$g(X) = (X_n^\circ)^{X-1} \exp(-X_n^\circ/(X-1)) \quad (1)$$

where X is the ratio of the molar volume of the polymer to the solvent and it is assumed that the molar volumes of the monomer unit, and that of the two solvents are the same. X may thus be regarded as the degree of polymerization.

- (3) Schulz-Zimm (SZ) distribution

$$g(X) = \frac{y^{h+1}}{\Gamma(h+1)} X^h \exp(-X) \quad (2)$$

where

$$y = h/X_n^\circ \quad (3)$$

and

$$h = ((X_w^\circ/X_n^\circ) - 1)^{-1} \quad (4)$$

- (4) Wesslau distribution

$$g(X) = \frac{1}{X\beta\sqrt{\pi}} \exp\left(-\frac{1}{2}(\ln X/X_0)^2\right) \quad (5)$$

where

$$\beta^2 = 2 \ln X_w^\circ/X_n^\circ \quad (6)$$

and

$$X^\circ = X_w^\circ/\exp(\beta^2/4) \quad (7)$$

the suffix o denotes the original polymer.

X_w° of the original polymer (X_w°) was varied for the Schulz-Zimm type polymer, ranging from 150 to 10000 and the ratio X_w°/X_n° was varied for the Schulz-Zimm type polymer with $X_w^\circ = 300$ from 1 to 5 and for the Wesslau type polymer with $X_w^\circ = 300$ from 2 to 8, respectively. Note that for the monodisperse polymer and the polymer with Poisson distribution X_w° was 300 (and in consequence X_w°/X_n° is 1 for the former and 1.003 for the latter).

After the original polymer was dissolved in a suitable solvent (solvent 1), a second solvent (solvent 2) was added to the solutions to cause the two phase separation. In this case, the

Figure 1. Phase diagrams of solutions consisting of a polymer in binary solvents: $\chi_{12} = 2.0$, $\chi_{13} = 0.75$, $\chi_{23} = 0.75$; full line, monodisperse polymer-solvent 1-solvent 2 system ($X^\circ = 300$, $v_p^s = 0.01$); chain line, multicomponent polymer-solvent 1-solvent 2 system (Schulz-Zimm distribution, $X_w^\circ = 300$, $X_w^\circ/X_n^\circ = 2.0$, $v_p^s = 0.01$); broken line, monodisperse polymer-solvent 1-solvent 2 system (single solvent approximation, $X^\circ = \infty$) (Scott); dotted line, monodisperse polymer-solvent 1-solvent 2 system ($X^\circ = \infty$, correct phase diagram (Scott)).

initial polymer volume fraction v_p^o was defined as the volume of original polymer V_3^o (usually unit volume was taken) divided by the sum of the volume of solvent 1 (V_1^o), solvent 2 (V_2^o) and the polymer so that,

$$v_p^o = \frac{V_3^o}{V_1^o + V_2^o + V_3^o} \quad (8)$$

v_p^o was varied from 10^{-5} to 0.1 for the polymer with SZ distribution and 0.005 for the polymers with other two MWDs. The starting polymer volume fraction v_p^s is defined in a similar manner by

$$v_p^s = \frac{V_3^o}{V_1^o + V_3^o} \quad (9)$$

The relative weight of the polymer in the polymer-rich phase ρ_p was widely varied from 1/10 to 49/50.

RESULTS AND DISCUSSION

To demonstrate the poor reliability of the approximate methods by Scott,⁷ a computer experiment was carried out to calculate the coexistence curve and tie line using the same values of three χ -parameters as those employed in Scott's paper.⁷ Figure 1 illustrates the phase diagrams obtained for solutions of single or multicomponent polymers-solvent 1-solvent 2. Here v_1 , v_2 , and v_p are the volume

Figure 2. Effects of the weight-average molar volume ratio X_w^o of the original polymer on phase diagram of quasi-ternary polymer solutions. The original polymer, Schulz-Zimm distribution, $X_w^o/X_n^o = 2.0$; $v_p^s = 0.01$; $\rho_p = 1/15$ (a), $3/10$ (b), $5/10$ (c), $7/10$ (d), $8/10$ (e), $14/15$ (f); $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.20$; $X_w^o = 150$ (broken line), 300 (chain line), 600 (dotted line), 1000 (full line).

Figure 3. Effect of molecular weight distribution on the phase diagram of solutions of a polymer dissolved in the binary solvent mixture. The original polymer, $X_w^o = 300$, monodisperse (full line), Poisson distribution (dotted line), Schulz-Zimm distribution, $X_w^o/X_n^o = 1.03$ (broken line), Schulz-Zimm distribution, $X_w^o/X_n^o = 1.05$ (chain line); $v_p^s = 0.01$; $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$; $\rho_p = 1/15$ (a), $3/10$ (b), $1/2$ (c), $7/10$ (d), $14/15$ (e).

fractions of solvent 1, solvent 2 and the polymer respectively. In Figure 1, the multicomponent polymers are the polymer with SZ distribution ($X_w^o = 300$, $X_w^o/X_n^o = 2.0$). Figure 1 also shows the results of Scott, who used a single solvent approximation method and a "correct" method (*i.e.*, monodisperse polymer with infinite X). The two diagrams evaluated by Scott are far from the actual experimental results in literature with regard to shape and moreover, two symmetric diagrams appear in the Scott's calculations for a given condition. The coexistence curve of a "correct diagram" is too extended to the right-hand corner (solvent 2). For a solution of the polymer dissolved in a binary solvents, the phase diagram is markedly skewed toward a low concentration due to a large difference in the molar volume between the polymer and solvent.

Figure 2 shows the effects of X_w^o of the original polymer having SZ distribution ($X_w^o/X_n^o = 2$) on the phase diagram such as

coexistence curves and the tie lines. A full line is for $X_w^o = 1000$, and a broken line, for $X_w^o = 150$. With an increase in X_w^o , (1) the branch of the coexistence curve at the polymer-rich phase side shifts to a lower v_p region, and (2) the peak point (or plait point) of the coexistence curve ($\approx$ cloud point) changes its composition, *i.e.*, increasing v_1 and decreasing v_p and v_2 , and (3) the distance of the tie lines corresponding to a given ρ_p decreases drastically. (2) and (3) are consistent with the fact that the solution of the polymer with larger X_w tends to separate into two phases with smaller amounts of solvent 2. At a given ρ_p , the polymer volume fraction in a polymer-rich phase $v_{p(2)}$ decreases with increasing X_w^o .

Figures 3–5 show the effects of X_w^o/X_n^o on the phase diagrams calculated under the same conditions: $X_w^o = 300$, $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$, $v_p^s = 0.01$. Figure 3 shows the phase diagrams of the monodisperse polymer ($X_w^o/X_n^o = 1.0$), the polymer with Poisson distribution ($X_w^o/X_n^o = 1.003$), and the polymer hav-

Figure 4. Effect of molecular weight distribution on the phase diagram of solutions of the polymer with Schulz-Zimm distribution ($X_w^o=300$) in the binary solvent mixture. The original polymer, $X_w^o/X_n^o=1.03$ (full line), 2 (dotted line), 3 (broken line), and 5 (chain line); $v_p^s=0.01$; $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.00$; $\rho_p=1/15$ (a), $2/10$ (b), $4/10$ (c), $6/10$ (d), and $9/10$ (e).

ing SZ distribution (with $X_w^o/X_n^o=1.03$ and 1.05 and hereafter referred to as SZ1.03 and SZ1.05, respectively) were shown. All of these polymers belong to the category of the so-called “monodisperse” polymers. The coexistence curves for these polymers are not easily distinguishable from each other, particularly in a large ρ_p region. Accordingly, experiments with polymers having X_w/X_n of 1.03 – 1.05 as monodisperse polymers for studying phase separation phenomena may be theoretically acceptable except at small ρ_p , provided only the coexistence curve is being considered. But,

the effect of X_w^o/X_n^o on the tie-line must never be neglected even if X_w^o/X_n^o is less than 1.05 . There is a significant difference in the tie line between the strictly monodisperse polymer and the polymer with $X_w^o/X_n^o=1.03$ – 1.05 . Unfortunately, this point has been overlooked hitherto and “monodisperse” polymers have been employed in actual experiments to obtain phase diagrams of “truly monodisperse” polymers.

Figures 4 and 5 indicate that coexistence curves are really insensitive to X_w^o/X_n^o when X_w^o/X_n^o is larger than 2 . In addition, the coexis-

Figure 5. Effect of molecular weight distribution on the phase diagram of solutions of the polymer with Wesslau distribution ($X_w^o/X_n^o = 300$) in the binary solvent mixture. The original polymer, $X_w^o/X_n^o = 2$ (dotted line), 3 (broken line), 5 (chain line); $v_p^s = 0.01$; $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$; $\rho_p = 1/40$ (a), $2/10$ (b), $4/10$ (c), $6/10$ (d), $8/10$ (e), and $14/15$ (f).

tence curve at the polymer-rich phase side is significantly different even for SZ1.03 and SZ2 polymers (Figure 4). The change in the composition of the coexistence curves with an increase in X_w^o/X_n^o is more remarkable in the SZ polymer than in a Wesslau polymer and in the direction of an increase in v_1 . This is closely correlated with the fact that the cloud point curve moves to solvent 1 side with an increase of X_w^o/X_n^o . The effect of the polydispersity of the original polymer is obvious for the tie lines. Note that the effect of X_w^o/X_n^o on the tie line changes its sign at a specific value of ρ_p , depending on the molecular characteristics of

the polymer and operating conditions. As the MWD of the original polymer becomes broader, the tie line shifts in the direction of increasing v_2 at $\rho_p > 3/10$, and decreasing v_2 in $\rho_p < 1/15$ (see Figure 4a)). The distance between the two aparting tie lines corresponding to a given ρ_p difference becomes large as X_w^o/X_n^o gets large. The role of X_w^o (Figure 2) and X_w^o/X_n^o differs in this regard. It is a characteristic feature that with a decrease in X_w^o/X_n^o or a decrease in ρ_p , the $v_{p(2)}$ decreases, in spite of a decrease in v_2 , in a hypothetical solution.

The effect of the type of MWD on the phase diagram can be seen by comparing SZ2 and

Figure 6. Relationships among total volume V , weight-average molar volume ratio X_w^o and relative amounts of a polymer in a polymer-rich phase ρ_p for a quasi-ternary polymer solution. The original polymer, Schulz-Zimm distribution, $X_w^o/X_n^o = 2.0$; $V_1^o = 100$ (arbitrary unit); $V_3^o = 1$ (arbitrary unit); $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$.

Figure 7. Relationships between total volume V , the ratio X_w^o/X_n^o of the original polymer and relative amounts of a polymer in a polymer-rich phase ρ_p for a quasi-ternary polymer solution. The original polymer, Schulz-Zimm distribution, $X_w^o = 300$, $v_p^o = 0.01$; $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$.

Figure 8. Effect of the weight-average molar volume ratio X_w^o and molecular weight distribution of the original polymer on the relation between the partition coefficient σ or phase volume ratio R and initial polymer volume fraction v_p^o . The original polymer, Schulz-Zimm distribution; (a) and (c), $X_w^o/X_n^o = 2.0$; (b) and (d), $X_w^o = 300$; $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.0$; $\rho_p = 1/15$.

Figure 9. Effect of the weight-average molar volume ratio on the dependence of the partition coefficient σ and phase volume ratio R on the relative fraction of the polymer in a polymer-rich phase. The original polymer, Schulz-Zimm distribution; Number on the curve denotes X_w^o ; $X_w^o/X_n^o = 2.0$; $v_p^o = 0.005$; $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.0$.

Wesslau2 polymers in Figures 4 and 5. The coexistence curve of a polymer-rich phase at a small ρ_p region differs slightly from polymer to polymer and the tie lines are notably different. Except for small ρ_p region the tie lines of Wesslau2 have smaller v_2 values than that of the SZ2 polymer.

Figures 6 and 7, respectively, show the effects of X_w^o and X_w^o/X_n^o on the total volume V ($\equiv V_1^o + V_2 + V_3$) of the solutions in equilibrium under the same conditions. As X_w^o decreases, a drastic increase can be observed in V , which is proportional to the volume of solvent 2 necessary to precipitate a given amount of the polymer-rich phase (in other words, a given amount of ρ_p). The effect of the polydispersity of the original polymer on V is rather complicated. For low ρ_p , V decreases near $X_w^o/X_n^o = 1$ and approaches an asymptotic value. V becomes constant at $\rho_p = 3/10$. For large ρ_p , V increases with an increase in X_w^o/X_n^o .

Figures 8a) and c) show the effects of X_w^o on the partition coefficient σ vs. v_p^o relations and on the phase volume ratio R vs. v_p^o relations,

Figure 10. Effect of the molecular weight distribution of the original polymer on the dependence of the partition coefficient σ and phase volume ratio R on the relative amounts of the polymer dissolved in a polymer-rich phase ρ_p . The original polymer, Schulz-Zimm distribution (a) and c) and Wesslau distribution (b) and d), $X_w^o = 300$; $v_p^o = 0.005$; $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$; number on curve denotes X_w^o/X_n^o .

respectively. Evidently, σ decreases gradually with increasing v_p^o throughout the entire range of v_p^o . At the same value of v_p^o , an increase in X_w^o by a factor of ten is substantially accompanied with a decrease in σ by a factor of ten. A single master curve is obtained by shifting concurrently the σ - v_p^o curves along the σ -axis and the v_p^o -axis. In R is approximately linear to

Figure 11. Effect of the relative amount of polymer dissolved in a polymer-rich phase ρ_p on the dependence of the partition coefficient σ and phase volume ratio R on the weight-average molar volume ratio X_w^o and X_w^o/X_n^o of the original polymer. The original polymer Schulz-Zimm distr., $X_w^o/X_n^o = 2.0$ (a) and b)), $X_w^o = 300$ (c) and d)), $v_p^o = 0.005$; $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$.

$-\ln v_p^o$ in the range of $R > 20$. The slope of the plot is estimated to be 1.15, irrespective of X_w^o . These findings are the same as observed for the quasi-binary solutions by Kamide *et al.*^{3,5} The volume fraction v_p^o , above which the linearity of the plot ceases to hold, is roughly in agreement with the critical volume fraction.

The effect of X_w^o/X_n^o on the correlation of σ and R with v_p^o is displayed graphically in Figures 8b) and d). Inversion of the effect of X_w^o/X_n^o is observed at $v_p^o \cong 0.05$ for σ and $\cong 0.02$ for R , above which σ as well as R are larger for the polymer with smaller X_w^o/X_n^o , suggesting the fractionation to become much effective for a polymer with a sharp MWD, at least, in a low v_p^o range.

Figures 9 and 10 show the effects of X_w^o and X_w^o/X_n^o on the σ - ρ_p and R - ρ_p relations, respectively. σ increases monotonously with ρ_p , but R decreases and then increases after passing through a minimum, both irrespective of X_w^o . The polydispersity dependence of the σ - ρ_p relations changes its sign at $\rho_p = 3/10$ for SZ polymers, but σ for Wesslau polymers increases with increasing X_w^o/X_n^o over the entire

range of ρ_p . For both SZ and Wesslau polymers, the large difference in R is observed with polymers having different X_w^o/X_n^o values in the large ρ_p region. The ρ_p value at minimum R ($R_{\min}$), $\rho_{p,\min}$ is constantly independent of X_w^o , but decreases with increasing X_w^o/X_n^o .

Figure 11 shows plots of σ and R as a function of X_w^o and X_w^o/X_n^o for constant ρ_p . Both σ and R decrease rapidly, first with an increase in X_w^o , approaching asymptotic values depending in ρ_p . This feature is much more pronounced with σ . The sign of $(\partial\sigma/\partial(X_w^o/X_n^o))_{\rho_p}$ changes at $\rho_p = 4/10$. R - X_w^o/X_n^o curves for various ρ_p values form an envelope line representing minimum R , $R_{\min}$ at a given X_w^o/X_n^o and the ρ_p value corresponding $R_{\min}$ depends markedly on X_w^o/X_n^o .

Figures 12a) and b) illustrate the effect of X_w^o and X_w^o/X_n^o on the normalized molecular weight distribution, $g_{(2)}(X)$ of the polymer ($\rho_p = 1/15$) in the polymer-rich phase from a quasi-ternary solution of $v_p^o = 0.005$. $g_{(2)}(X)$ becomes broader (*i.e.*, the content of the larger X component increases) with increasing X_w^o

Figure 12. The molecular weight distribution curves, $g_{(2)}(X)$, of the polymer in a polymer-rich phase separated from a quasi-ternary polymer solution. The original polymer, Schulz-Zimm distr. (a) and b)) and Wesslau distr. (c) and d)); $v_p^o = 0.005$; $\chi_{12} = 0.48$, $\chi_{13} = 0.20$ and $\chi_{23} = 1.00$ (a) and b)) or 1.30 (c) and d)); $\rho_p = 1/15$ (a), b) and d)) or $1/2 - 1/40$ (c)); a) $X_w^o/X_n^o = 2.0$, X_w^o is denoted on the curve; b) $X_w^o = 300$, X_w^o/X_n^o is denoted on the curve; c) $X_w^o = 300$, $X_w^o/X_n^o = 5.0$, ρ_p is denoted on the curve; d) $X_w^o = 300$, X_w^o/X_n^o is denoted on the curve.

Figure 13. Effect of the weight-average molar volume ratio X_w^o of the original polymer on the relation between X_w/X_n or σ'/σ'_0 and the relative amount of the polymer in a polymer-rich phase. The original polymer, Schulz-Zimm distr., $X_w^o/X_n^o=2.0$, X_w^o is denoted on the curve; $v_p^o=0.005$; $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.00$; PLP, polymer-lean phase; PRP, polymer-rich phase.

and X_w^o/X_n^o , and its peak becomes lower, but the ratio (X_w/X_n) of the polymers in polymer-rich phase becomes smaller.

Figures 12c) and d) show that when the polymer-rich phase is separated at small ρ_p from the solution of the original polymer having a broad molecular weight distribution, another peak appears near $X=0$ and with decreasing ρ_p and increasing X_w^o/X_n^o , its height increases. The possibility of the appearance of double peaks for polymers in a polymer-rich phase has already been noted for quasi-binary solutions.⁶ The discussions described apply to all quasi-ternary systems.

Figure 13 shows the effects of X_w^o on the relationships between X_w/X_n of polymers in the polymer-rich phase and polymer-lean phase or on the ratio of the standard deviation of $g_{(1)}(X)$ and $g_{(2)}(X)$ to that of $g_0(X)$, σ'/σ'_0 , and ρ_p . This figure was obtained for the polymers with $X_w^o=150-1.5 \times 10^3$ having the SZ distribution, $X_w^o/X_n^o=2.0$, assuming $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.00$, and $v_p^o=0.005$. As X_w^o

increases, X_w/X_n of the polymer in the polymer-rich phase increases significantly and the minimum value of X_w/X_n , $(X_w/X_n)_{\min}$, increases, shifting $\rho_{p,\min}$ towards a higher ρ_p region. An increase in X_w^o exerts an influence, entirely analogous to that of increasing v_p^o ,² on the relations between X_w/X_n or σ'/σ'_0 and ρ_p . σ'/σ'_0 for PRP exhibits a minimum in a comparatively higher ρ_p region ($\rho_p > 0.5$) and $\sigma'_{\min}$ appears independently of X_w^o . X_w/X_n of the polymer-rich phase is smaller than that of the polymer-lean phase, except for the large ρ_p region. This does not indicate that the polydispersity of the polymer in a polymer-rich phase is lower than that in the polymer-lean phase. σ' , the most reasonable parameter representing the polydispersity, is much smaller in the polymer-lean phase than in the polymer-rich phase over the entire range of ρ_p .

Figure 14 shows the effect of the type and breadth in MWD of the original polymer on the ρ_p dependence of X_w^o/X_n^o of polymers in both phases. The polymers have SZ and

Figure 14. Effect of the polydispersity of the original polymer on the relations between X_w/X_n or σ'/σ'_0 and relative amount of the polymer in a polymer-rich phase. The original polymer, Schulz-Zimm distr. (a) and c)), Wesslau distr. (b) and d)), $X_w^\circ = 300$, X_w°/X_n° is denoted on the curve; $v_p^\circ = 0.005$; $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$; PLP, polymer-lean phase; PRP, polymer-rich phase.

Wesslau distributions with $X_w^\circ = 300$ and $X_w^\circ/X_n^\circ = 1.03-8$ and $v_p^\circ = 0.005$, $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, and $\chi_{23} = 1.00$ are used. The characteristic features of the X_w/X_n or σ'/σ'_0 vs. ρ_p relations observed for the SZ ($X_w^\circ/X_n^\circ = 2$) polymers hold for polymers with different

MWD types and breadths (X_w/X_n). $\rho_{p,\min}$ is 0.50 ± 0.02 for the SZ polymers and 0.4 ± 0.01 for the Wesslau polymer, independent of the breadth in MWD of the original polymer.

Figure 15 shows the effects of X_w° on relations between $X_{w(2)}/X_{n(2)}$ or $\sigma'_{(2)}/\sigma'_{(2)0}$ and v_p° . In

Figure 15. Effect of the initial polymer volume fraction v_p^0 on the ratio X_w/X_n and $\sigma'_{(2)}/\sigma'_0$ of the polymer in a polymer-rich phase. The original polymer, Schulz-Zimm distr., $X_w^0/X_n^0=2.0$, X_w^0 , number on the curve; $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.00$; the relative amount of polymer in a polymer-rich phase $\rho_p=1/15$.

this case, solutions of the SZ polymer with $X_w^0/X_n^0=2$ are phase-separated under the conditions of $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.00$, and $\rho_p=1/15$. As X_w^0 increases, the curves shift toward the lower concentration range. Interestingly, the polydispersity expressed by σ' of the polymers in the polymer-rich phase is occasionally larger than that of the original polymer. That is, a conventional fractionation by solubility difference does not always yield polymers with MWD narrower than that of the original polymer, except for an extremely low concentration region.

Figure 16 shows the effects of X_w^0 on relative breadths in MWD such as $(X_{w(1)}/X_{n(1)})/(X_w^0/X_n^0)$, $(X_{w(2)}/X_{n(2)})/(X_w^0/X_n^0)$, $\sigma'_{(1)}/\sigma'_0$ and $\sigma'_{(2)}/\sigma'_0$, of polymers in the two phases, under the same conditions (*i.e.*, $X_w^0/X_n^0=2.0$, $\sigma'_0=212$, $v_p^0=0.005$, $\chi_{12}=0.48$, $\chi_{13}=0.20$, $\chi_{23}=1.00$). Both $(X_{w(1)}/X_{n(1)})/(X_w^0/X_n^0)$ and $\sigma'_{(1)}/\sigma'_0$ increase slightly with X_w^0 , but are primarily controlled

by ρ_p . For smaller ρ_p , the X_w^0 dependence becomes remarkable. As shown in Figure 16b), $(X_{w(2)}/X_{n(2)})/(X_w^0/X_n^0)-X_w^0$ curves for various ρ_p values form an envelope line, which gives the minimum $X_{w(2)}/X_{n(2)}$ attainable for a given X_w^0 . The polymers in the polymer rich phase have occasionally larger polydispersity than the original polymer in a small ρ_p region (in this case, $\rho_p < 7/10$). $\sigma'_{(2)}/\sigma'_0$ increases gradually with X_w^0 , particularly at smaller ρ_p in the low X_w^0 ($X_w^0 < 10^3$) region.

Figure 17 shows the effects of X_w^0/X_n^0 on the relative breadths in MWD, expressed as

$$(X_{w(1)}/X_{n(1)})/(X_w^0/X_n^0), (X_{w(2)}/X_{n(2)})/(X_w^0/X_n^0),$$

$\sigma'_{(1)}/\sigma'_0$, and $\sigma'_{(2)}/\sigma'_0$ of polymers in the two phases.

$$(X_{w(1)}/X_{n(1)})/(X_w^0/X_n^0), (X_{w(2)}/X_{n(2)})/(X_w^0/X_n^0),$$

and $\sigma'_{(1)}/\sigma'_0$ of polymers separated under the same conditions decreases monotonously

Figure 16. Effect of the weight-average molar volume ratio X_w^o/X_n^o of the original polymer on relative breadths in the molecular weight distribution of polymers in two phases. The original polymer, Schulz-Zimm distr., $X_w^o/X_n^o = 2.0$; $v_p^o = 0.005$; $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$; ρ_p is denoted on the curve.

with an increase in X_w^o/X_n^o over whole range of ρ_p , but the dependence of $\sigma'_{(2)}/\sigma'_0$ on X_w^o/X_n^o changes its sign at a specific ρ_p . It should be noted however that a polymer having sharp MWD yields small X_w/X_n and σ' for a polymer in a polymer-rich phase. The effect of X_w^o on the breadth in MWD of polymers in two phases, separated from quasi-ternary polymer solutions, is just the reverse, except for $\sigma'_{(2)}/\sigma'_0$ to that of X_w^o/X_n^o (Figure 16). The conclusions deduced from Figures 16 and 17 should hold for various combinations of three χ parameters and are consistent with those obtained for quasi-

Figure 17. Effect of the polydispersity of the original polymer on relative breadths in the molecular weight distribution of polymers in two phases. The original polymer, Schulz-Zimm distr., $X_w^o = 300$; $v_p^o = 0.005$; $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$; ρ_p is denoted on curve.

Figure 18. Correlations between ρ_p and the v_p^o yielding constants $\sigma'_{(1)}$ and $\sigma'_{(2)}$. The original polymer, Schulz-Zimm distr., $X_w^o = 300$, $X_w^o/X_n^o = 2.0$, $\sigma'_0 = 212$; $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$.

binary systems.³⁻⁶

Figure 18 shows the correlation between ρ_p and v_p^o at constant values of $\sigma'_{(1)}$ and $\sigma'_{(2)}$. In the figure, the broken line corresponds to a case in which the polymer in a phase has the same σ' as that of the original polymer ($\sigma' = 212$). The

Figure 19. Change in the polymer volume fraction of a polymer-rich phase $v_{p(2)}$ with relative amount of the polymer ρ_p . The original polymer, Schulz-Zimm distr.; a) X_w° is denoted on the curve; $X_w^\circ/X_n^\circ = 2.0$; b) $X_w^\circ = 300$, X_w°/X_n° is denoted on the curve; the polymer volume fraction of the initial solution $v_p^\circ = 0.005$; $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.30$ a) or 1.00 b).

Figure 20. Relationships among polymer volume fractions in polymer-lean and -rich phases, $v_{p(1)}$ and $v_{p(2)}$, the relative amount of a polymer in a polymer-rich phase ρ_p , and X_w° and X_w°/X_n° of the original polymer. The original polymer, Schulz-Zimm distr., $X_w^\circ/X_n^\circ = 2.0$ (a) and b)), $X_w^\circ = 300$ (c) and d)); $v_p^\circ = 0.005$; $\chi_{12} = 0.48$, $\chi_{13} = 0.20$, $\chi_{23} = 1.00$.

polydispersity of a polymer in a polymer-lean phase is always smaller than that of the original polymer and predominantly ρ_p -depen-

dent. In contrast, the polydispersity of the polymer in the polymer-rich phase is v_p° -dependent in the lower v_p° region and ρ_p -de-

Table I. I. Effects of X_w° and X_w°/X_n° on phase separation parameters for quasi-ternary solutions

Parameters	Effect	
	X_w°	X_w°/X_n°
Coexistence curve	Shifts to lower v_2^a	Shifts to lower v_2
Tie line	Shifts to lower v_2	Shifts to lower v_2 at small ρ_p Shifts to higher v_2 at large ρ_p
Total volume V	— ^b	— at small ρ_p + at large ρ_p
Composition V_1/V_2	+ ^c	+ at small ρ_p — at large ρ_p
Partition coefficient σ	—	— at small v_p° + at large v_p° — at small ρ_p + at large ρ_p
Phase volume ratio R	—	— at small v_p° + at large v_p° — at small ρ_p + at large ρ_p
Breadth in mol. wt. distr. of polymer in PRP	+	+
Double peaked MWD of polymer in PRP		+, Wesslau at small ρ_p
ρ_p giving minimum X_w/X_n of polymer in PRP	+	$\sim 0^d$
$(X_w/X_n)_{\min}$ in PRP	+	+
Polymer volume fraction $v_{p(2)}$ in PRP	—	+(Except for small region) p

^a Parameter shifts to lower or higher v_2 with an increase in X_w° or X_w°/X_n° ; ^b —, decrease; ^c +, increase; ^d ~ 0 , almost insensitive; PRP, polymer-rich phase.

pendent in the higher v_p° region. In the latter region, the polymer in the polymer-rich phase has a broader MWD than the original polymer. The transition from v_p° -dependence to ρ_p -dependence occurs about the broken line in the figure.

Figure 19 shows the effects of X_w and X_w/X_n of the original polymer on the $v_{p(2)}-\rho_p$ relations. In this case, the solutions ($v_p^\circ=0.005$) of the SZ polymer with $X_w^\circ/X_n^\circ=2$ a) and $X_w^\circ=300$ b) were phase-separated at $\chi_{12}=0.48$, $\chi_{13}=0.20$, and $\chi_{23}=1.30$. The polymer volume fraction in the polymer-rich phase $v_{p(2)}$ increases with ρ_p and decreases with X_w° . The effect of X_w°/X_n° on $v_{p(2)}$ changes its sign at $\rho_p=0.24$, above which $v_{p(2)}$ increases with X_w°/X_n° .

Figure 20 shows the effect of ρ_p on the polymer volume fraction in the polymer-lean phase $v_{p(1)}$ (or $v_{p(2)}$) vs. X_w° (or X_w°/X_n°) relations. As expected, $v_{p(1)}$ is nearly independent

of X_w° irrespective of ρ_p . In contrast, $v_{p(2)}$ decreases remarkably with an increase in X_w° and is independent of X_w°/X_n° at $\rho_p=0.24$. For $\rho_p>0.24$, $v_{p(2)}$ increases with X_w°/X_n° , but at $\rho_p<0.24$, $v_{p(2)}$ gradually decreases with X_w°/X_n° . Effects of X_w° and X_w°/X_n° of the original polymer on the phase separation parameters for quasi-ternary solutions are summarized in Table I.

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