Molecular Weight Fractionation of Binary Mixtures of Monodisperse Poly(α -methylstyrene) by the Solubility Difference: Comparison of Experiment with Theory

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ABSTRACT: Molecular weight fractionations of binary mixtures of poly(α -methylstyrene)s having narrow molecular weight distributions were carried out by the methods of successive precipitational fractionation and successive solutional fractionation (column fractionation). The amount of polymer, its average molecular weight and the weight ratio of two components in the fraction were determined and the molecular weight distribution curve was constructed. The molecular weight distribution curves as well as the fractionation results were compared with the computer simulation of Kamide *et al.* The simulation results agreed well with the experimental results provided the concentration dependence of the thermodynamic interaction parameter in the theory of Flory–Huggins was taken into consideration.

KEY WORDS Molecular Weight Fractionation / Successive Precipitational Fractionation / Successive Solutional Fractionation / Computer Simulation / Binary Mixture / Monodisperse Poly(α -methylstyrene)

The theoretical basis for molecular weight fractionation¹ is given in the lattice theory of Flory and Huggins, and has been developed by Koningsveld and Starverman^{2,3} and Kamide, Miyazaki *et al.*,^{4–7} taking into account the polymer concentration dependence of interaction parameter χ . The reliability of the theory has been examined in detail by comparing it with the experimental data of successive precipitational and solutional fractionations (SPF and SSF) as well as with the experimental phase separation data of polydisperse polymers in a single solvent. However, since the samples used in previous studies were polymers having broad molecular weight distributions, comparisons between the theory and experimental results were not so sharp and clear-cut. In this work, we carried out experiments on both SPF and SSF, using mixtures of two samples of poly(α -methylstyrene)s having narrow molecular weight distributions and compared the resulting data with the theory of Kamide *et al.* The molecular weight distributions of two

samples were sharp enough that the systems could be assumed to be binary mixtures in a single solvent. Consequently, we were able to compare directly and with clarity the experimental and true molecular weight distributions with the theory since the molecular weight distributions of the original binary polymer mixture and fractions are given if the mixed ratios are known. Comparison of various experimental methods for molecular weight distribution determination using the same samples has already been reported.⁸

EXPERIMENTAL

Samples

The samples used were poly(α -methylstyrene)s prepared by an anionic polymerization technique as reported previously.⁹ The molecular characteristics of the samples are listed in Table I. Details of the means by which determination of the molecular weight and the intrinsic viscosity are described in

Table I. Molecular characteristics of monodisperse poly(α -methylstyrene) and the binary mixture

Sample code	$M_n \times 10^{-4}$	$M_v \times 10^{-4}$	$M_w \times 10^{-4}$	X_v ^a	M_w/M_n
a) Monodisperse sample					
α -8	—	20.8		1817	
α -15	38.5	41.0		3582	
α -004	34.2	34.1	34.2	2981	1.00
α -103	50.0	48.7		4255	
b) Binary mixture					
M1: α -8/ α -15 (0.514/0.486, w/w)	(27.3)	—	(30.6)	(2633)	(1.12)
M2: α -8/ α -15 (0.500/0.500, w/w)	(27.6)	—	(30.9)	(2658)	(1.12)
M3: α -004/ α -103 (0.501/0.501, w/w)	(40.1)	—	(41.4)	(3602)	(1.03)

$$^a X_v = (M_v/d_p)/(d_s/M_s) = (M_v/1.06)/(0.778/84).$$

previous papers.^{8,10}

The binary mixtures used for fractionation experiments, M1, M2, and M3 in Table I, were prepared by mixing two out of four monodisperse polymers. The mixed ratios in weight and the average molecular weights of the mixtures as calculated from the ratio, are also shown in Table I. The samples M1 and M2 are almost identical.

The average polymer-to-solvent molecular volume ratio of poly(α -methylstyrene) in cyclohexane $\bar{X}$ is evaluated by

$$\bar{X} = (\bar{M}/d_p)/(M_s/d_s) \quad (1)$$

where $\bar{M}$ and M_s and also d_p and d_s are the molecular weights and the densities of the polymer and cyclohexane ($M_s=84$, $d_p=1.06$, and $d_s=0.778$), respectively.

Concentration and Molecular Weight Determinations

Viscosity-average molecular weights, M_v of the samples in Table I and their fractions in Tables II, III, and IV were evaluated from their intrinsic viscosities using the following Mark-Houwink-Sakurada equation for poly(α -methylstyrene) having a narrow molecular weight distribution in toluene at 25°C.¹⁰

$$[\eta] = 1.01 \times 10^{-4} M_w^{0.72} \quad (2)$$

The viscosity-average molecular weight may be satisfactorily used in place of the weight-average molecular weight when the data are compared with the theory since the ratios of the weight-average molecular weight to number average molecular

weight, M_w/M_n of the fractions are close to unity as the tables show. The weight of polymer in each fraction was determined by freeze-drying. The weight ratio of two components was determined from the peak area of the schlieren pattern in sedimentation. Since the ratio of the peak area of two components is not equal to their weight ratio due to the Johnston-Ogston effect, the weight ratio was determined using the experimental linear relationship between the weight ratio and the peak area ratio obtained by ultracentrifugation of the same polymer mixtures of known composition under the same sedimentation conditions for measuring weight ratio. Since the peaks in the schlieren patterns are broadened as a result of various effects such as diffusion, the molecular weight distribution of each sample could not be calculated from a single schlieren pattern. However the value of M_w/M_n was calculated from the weight ratio of two components, neglecting the molecular weight distribution of each component, since the samples were assumed to be nearly monodisperse. The sedimentation experiment was carried out in cyclohexane at 35°C with a Beckman Spinco Model E ultracentrifuge at a speed of 59780 rpm.

Successive Precipitational Fractionation

Sample M1 was dissolved in cyclohexane at 39°C. The initial polymer volume fraction of the solution was 0.80%. The solution was cooled down to the designed phase separation temperature. After keeping the temperature constant for 16 to 24 hours the polymer-rich phase was isolated. The above pro-

Table II. Characteristics of the fractions obtained in a successive precipitational fractionation (SPF) run (run 1) on poly(α -methylstyrene) mixture
M1-cyclohexane system ($v_p^0 = 0.808\%$, $n_t = 12$)^a

Fraction number	Experiment					Theory			
	Precipitation temperature, $T_p/^\circ\text{C}$	Fraction size $\rho_p/\text{wt}\%$	$M_v \times 10^{-4}$	$W_{\alpha-15}/W_{\alpha-8}$	M_w/M_n				
1P1	21.4	10.4	37.2	4.74	1.07				
1P2	20.7	14.9	36.4	4.17	1.08				
1P3	20.2	10.5	36.4	2.87	1.09				
1P4	19.6	8.2	35.4	2.49	1.10				
1P5	18.6	10.3	33.7	1.72	1.11				
1P6	17.5	7.1	30.6	1.08	1.12				
1P7	16.0	8.5	26.2	0.34	1.09				
1P8	14.7	8.8	22.1	0	1.0				
1P9	13.2	7.8	20.7	0	1.0				
1P10	11.9	4.9	20.0	0	1.0				
1P11	10.4	2.9	20.2	0	1.0				
1P12	—	5.7	11.5	0	1.0				
$\rho_p/\text{wt}\%$	$p=0$			$p=0.6$			$p=1.2$		
	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$W_{\alpha-15}/W_{\alpha-8}$	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$W_{\alpha-15}/W_{\alpha-8}$	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$W_{\alpha-15}/W_{\alpha-8}$
8.33	31.8	34.9	2.37	34.6	37.1	4.23	37.2	38.9	8.52
8.33	31.8	34.9	2.34	34.4	37.0	4.05	36.9	38.7	7.77
8.33	31.7	34.9	2.30	34.1	36.8	3.81	36.6	38.5	7.00
8.33	31.6	34.9	2.24	33.7	36.5	3.50	36.0	38.1	6.04
8.33	31.3	34.6	2.14	33.2	36.1	3.11	35.2	37.5	4.88
8.33	30.9	34.2	1.98	32.2	35.3	2.58	33.6	36.4	3.38
8.33	30.2	33.6	1.72	30.5	33.8	1.80	29.1	32.5	1.38
8.33	28.9	32.2	1.30	26.4	29.4	0.75	22.3	23.5	0.16
8.33	25.7	28.6	0.63	21.8	22.7	0.11	20.9	21.0	0.005
8.33	21.9	22.8	0.11	20.9	20.9	0.005	20.8	20.8	0
8.33	20.9	20.9	0.005	20.8	20.8	0	20.8	20.8	0
8.33	20.8	20.8	0	20.7	20.7	0	20.7	20.7	0

^a Recovery, 96.5 wt%.

Table III. Characteristics of the fractions obtained in a successive solutional fractionation (SSF) run (run 2) on poly(α -methylstyrene) mixture M2-cyclohexane system
($v_p^0=0.4\%$, $n_i=12$)^a

Fraction no.	Experiment				Theory ($p=0.6$)				
	Separation temperature, $T_p/^\circ\text{C}$	Fraction size $\rho_s/\text{wt}\%$	Polymer volume fraction in a polymer-lean phase, $v_p(1) \times 10^{-4}$	$M_v \times 10^{-4}$	Fraction size, $\rho_s/\text{wt}\%$	Volume ratio, R	Polymer volume fraction in a polymer-lean phase, $v_p(1) \times 10^{-4}$	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$
1S1	10.6	7.8	2.2	15.1	8.33	55.7	3.4	20.80	20.87
1S2	12.5	10.7	2.9	20.3	8.33	61.0	3.4	20.84	20.92
1S3	13.5	13.9	3.8	21.6	8.33	67.1	3.4	20.90	21.03
1S4	13.6	13.5	3.7	22.9	8.33	74.2	3.4	21.03	21.26
1S5	14.3	7.4	2.0	26.0	8.33	81.6	3.4	21.48	22.08
1S6	15.2	5.8	1.6	35.4	8.33	88.3	3.4	24.08	26.33
1S7	16.4	7.1	1.9	36.9	8.33	99.5	3.4	31.83	34.95
1S8	17.4	10.5	2.9	39.9	8.33	121.9	3.4	38.32	39.50
1S9	18.4	17.2	4.7	39.4	8.33	162.1	3.4	40.44	40.6
1S10	19.0	2.8	0.8	39.9	8.33	243.5	3.3	40.88	40.92
1S11	19.6	1.1	0.3	—	} 8.33	487.7	3.3	41.97	41.98
1S12	20.6	0.82	0.2	—					
1S13	22.0	1.4	0.4	—	8.33	—	—	41.05	41.06

^a Recovery, 93.4 wt%.

Table IV. Characteristics of the fractions obtained in a successive solutional fractionation (SSF) run (run 3) on poly(α -methylstyrene) mixture M3-cyclohexane system
($v_p^0 = 0.4\%$, $n_t = 15$)^a

Fraction no.	Experiment				Theory				
	Separation temperature, $T_p/^\circ\text{C}$	Fraction size $\rho_s/\text{wt}\%$	Polymer volume fraction in a polymer-lean phase, $v_p(1) \times 10^{-4}$	$M_v \times 10^{-4}$	Fraction size, $\rho_s/\text{wt}\%$	Volume ratio, R	Polymer volume fraction in a polymer-lean phase, $v_p(1) \times 10^{-4}$	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$
2S1	10.3	1.0	0.3	14.6	6.67	45.3	2.7	34.93	35.29
2S2	14.5	5.5	1.5	33.3	6.67	48.8	2.7	35.08	35.49
2S3	15.0	6.8	1.9	33.9	6.67	52.6	2.7	35.28	35.76
2S4	15.5	7.6	2.1	34.4	6.67	57.2	2.7	35.56	36.12
2S5	16.0	8.6	2.4	36.1	6.67	62.4	2.7	35.97	36.64
2S6	16.5	7.9	2.2	38.3	6.67	68.9	2.7	36.54	37.36
2S7	17.0	8.0	2.3	41.7	6.67	76.7	2.7	37.43	38.44
2S8	17.5	8.5	2.4	42.9	6.67	86.5	2.7	38.78	39.97
2S9	18.0	8.6	2.4	45.2	6.67	99.5	2.7	40.71	42.01
2S10	18.5	7.0	2.0	47.5	6.67	117.8	2.7	43.12	44.28
2S11	19.0	12.2	3.5	51.2	6.67	146.0	2.7	45.44	46.25
2S12	20.0	7.3	2.1	48.8	6.67	193.7	2.7	47.18	47.61
2S13	21.0	1.5	0.4	48.1	6.67	289.9	2.7	48.17	48.35
2S14	22.5	2.8	0.8	44.0	6.67	580.2	2.7	48.62	48.68
2S15	—	6.9	2.0	49.3	6.67	—	—	48.83	48.84

^a Recovery, 96.4 wt%.

Fractionation of Poly(α -methylstyrene)

cedure was carried out successively and 12 fractions were obtained.

Successive Solutional Fractionation

Successive solutional fractionations were carried out using a column, 4 cm in inner diameter and 60 cm in length, in which about 850 g glass beads of 100–150 mesh were packed. The temperature was kept constant by circulating, at constant temperature, water in a water jacket. Sample M2 or M3 was dissolved in cyclohexane whose temperature was about 45°C. The solution, whose polymer volume fraction was 0.40%, was poured into the column and cooled down to enable the polymer to deposit on the glass beads. Then the column was heated to the designed phase separation temperature. After keeping the temperature constant for about 2 hours, 300 ml of the polymer-lean solution were then allowed to flow out by pouring the same amount of cyclohexane into the column. The above procedure was repeated successively.

Computer Simulation

The fractionation experiments described above were simulated according to the method of Kamide-Sugamiya^{1,11,12} with a computer IBM system 370-158. The details of this computer simulation are described in previous paper(s).^{11,12} In this simulation, the differential weight distribution of the molecular weight in each component $g(X)$, (a component of the binary mixture), was assumed to follow the Poisson distribution,

$$g(X) = \bar{X}_n^{X-1} \exp(-\bar{X}_n) / (X-1)! \quad (3)$$

where X is the polymer-to-solvent volume ratio and $\bar{X}_n$ is the number average of X . The number of components in the simulation were 4000 for M_1 and M_2 , and 5000 for M_3 . The concentration dependence of the thermodynamic interaction parameter χ in the Flory-Huggins theory was assumed to be,

$$\chi = \chi_0(1 + pv_p) \quad (4)$$

where χ_0 is the interaction parameter, independent of the concentration; v_p is the polymer volume fraction, and p is the parameter characteristic of the concentration dependence of χ . At a θ -temperature χ may be given approximately by

$$\chi = \frac{1}{2} \left(1 + \frac{2}{3} v_p \right) \quad (5)$$

Since the phase separation temperatures are not far from the θ -temperature (34.5°C) for the poly(α -methylstyrene)-cyclohexane system,¹³ the p value in eq 4 may be assumed to be equal to 2/3. Actually, Kamide *et al.*⁶ found that p are 0.6 and 0.7 for the polystyrene-cyclohexane and -methylcyclohexane systems, respectively, and that the former value is in good agreement with the values obtained by other methods.⁷ Therefore, in this paper, the computer simulation was carried out for $p=0$, $p=0.6$, and $p=1.2$ in SPF so as to clarify the effect of the concentration dependence of χ on the fractionation, but only for $p=0.6$ in SSF, since the p value does not much affect the simulation result of SSF. To clarify the effect of the initial polymer concentration on SSF, simulations were carried out not only for the experimental initial volume fraction ($v_p^0=0.40\%$) but also for $v_p^0=0.1$ and 1.0% . Moreover, it should be noted that the fraction size ρ , that is, the weight ratio of each fraction to the original sample, is assumed to be constant in the present simulation program because the improvement of the present program for a variable fraction size exceeds the capacity of the computer. Though not impossible, it is very difficult to keep the fraction size constant in the experiments. Thus, the fraction size in the simulation is selected so as to be close to the experimental values in the majority of fractions. The number of fractions for M2 in the simulation of SSF was 12, while the experimental number was 13.

Analytical Procedure of Fractionation Data

According to the method of Schulz^{14,15} the cumulative weight fraction, $I(M_{w,j})$ of the j th fraction for SPF and SSF is given by,

$$\begin{aligned} I(M_{w,j}) &= \sum_{k=j+1}^{n_t} \sum_{M=0}^{\infty} g_k(M) + \frac{1}{2} \sum_{M=0}^{\infty} g_j(M) \\ &= \sum_{k=j+1}^{n_t} \rho_{p,k} + \frac{1}{2} \rho_{p,j} \quad \text{for SPF} \end{aligned} \quad (6)$$

$$\begin{aligned} I(M_{w,j}) &= \sum_{k=1}^{j-1} \sum_{M=0}^{\infty} g_k(M) + \frac{1}{2} \sum_{M=0}^{\infty} g_j(M) \\ &= \sum_{k=1}^{j-1} \rho_{s,k} + \frac{1}{2} \rho_{s,j} \quad \text{for SSF} \end{aligned} \quad (7)$$

where n_t is the total fraction size, and the subscripts

for p , p and s , denote SPF and SSF, respectively. On the basis of detailed data of experiment and simulation, Miyazaki and Kamide¹⁵ showed that the method of Schulz is not accurate enough to predict the true cumulative weight fraction when the average molecular weight of an original sample is high and its distribution is narrow. However, the method of Schulz may be safely employed for comparison between the experimental and simulation results of fractionation provided it is used for the analyses of both experimental and simulation data.

RESULTS

The results of experimental fractionation and simulation are listed in Tables II, III, and IV. The experimental data can be used for quantitative analyses since the sample recovery after the fractionation is at least higher than 93% for every run. The cumulative weight fraction–molecular weight relationship, *i.e.*, the molecular weight distributions of the binary mixtures calculated according to the method of Schulz from the data in these tables are shown in Figures 1 and 2 where the solid curves denote the “true” cumulative weight fraction–molecular weight relationship calculated on the assumption that the molecular weight distribution of the each component is the Poisson distribution. Moreover, examples of the schlieren patterns of the fractions of M1 by SPF are shown in Figure 3, while the corresponding profiles obtained by the simulation are shown for both SPF and SSF in Figure 4. The weight ratio of two components,

Figure 1. Cumulative weight fraction $I(M_{w,j})$ –molecular weight relationship of the mixture M1 obtained by SPF: ●, experimental results; full line, “true” cumulative weight fraction $I(M)$; dotted line, theory ($p=0$); chain line, theory ($p=0.6$); broken line, theory ($p=1.2$).

Figure 2. Cumulative weight fraction $I(M_{w,j})$ –molecular weight relationships of the mixtures M2 and M3 obtained by SSF: ●, experimental result for M2; ○, experimental results for M3; full line, “true” cumulative weight fraction $I(M)$; dotted line, theory ($p=0.6$, $v_p^0=0.1\%$); chain line, theory ($p=0.6$, $v_p^0=0.4\%$); broken line, theory ($p=0.6$, $v_p^0=1.0\%$).

Figure 3. Examples of schlieren patterns of fractions from M1 obtained by SPF. The patterns are shown for 1P1, 1P5, and 1P8 from top to bottom.

$W_{\alpha-15}/W_{\alpha-8}$, of fraction in SPF was obtained from the schlieren peak area in Figure 3 and the value of M_w/M_n of the fraction was calculated from the ratio assuming that both components were monodisperse. The values of the weight ratio and M_w/M_n are shown in Table II.

DISCUSSION

As shown in Figure 1, the experimental molecular weight distribution obtained from SPF according to

Figure 4. Molecular weight distribution $g(M)$ of some typical fractions from M1 and M2 obtained by SPF(a) and SSF(b), respectively.

the method of Schulz is in good agreement with the theoretical curve for $p=0.6$ except for a low-molecular-weight tail part, but deviates from the "true" distribution. The disagreement found in the tail part is understandable and not serious enough to prevent comparison between the experiment results and theory since the low-molecular-weight tail part was not included in the Poisson distribution used in the present simulation. Thus, it may be concluded that the simulation result can satisfactorily reproduce the experimental molecular weight distribution if $p=0.6$ is selected. Moreover, it is clear that the cumulative weight fraction–molecular weight relationship constructed from SPF data by the method of Schulz does not sufficiently give the molecular weight of the fractions in the region of high molecular weight as reported previously.¹⁵ This is also clear from the fact that both the schlieren patterns and corresponding simulation results contain the low-molecular component even in the first fraction, as shown in Figures 3 and 4a. The data in Figure 3 are replotted in the form of the weight ratio of the two components vs. cumulative weight fraction in Figure 5 in comparison with the simulation results. Moreover, the weight content (%) of α -8, $W_{\alpha-8}$, is plotted against the molecular

Figure 5. Relationship between weight ratio of components in fractions, $W_{\alpha-14}/W_{\alpha-8}$, and cumulative weight fraction $I(M_{w,j})$ of M1 obtained by SPF: ●, experimental result, dotted line: theory ($p=0$); chain line, theory ($p=0.6$); broken line, theory ($p=1.2$).

Figure 6. Relationship between molecular weight and weight content of α -8 in fractions of M1 obtained by SPF: ●, experimental result ($M_{v,j}$); full line, theory ($p=0$ —1.2, $M_{w,j}$).

weight of the fraction in Figure 6. The linear relationship between $W_{\alpha-8}$, and M_w of the fraction extends to the region of high molecular weight with increasing p and $p=0.6$, covering the entire range of the experimental results as shown in the figure. From these figures, it is clear that the experimental data for the fraction in SPF are also in good agreement with the simulation for $p=0.6$ and it is noted that the larger the value of p is the higher the resolving power of the fractionation becomes.¹¹

The cumulative weight fraction–molecular weight relationships of M2 and M3 in Figure 2, constructed

from SSF data also clearly show that agreement between the experimental and simulation results is excellent, except for the low-molecular-weight tail part, though it is less satisfactory for M3 than for M2. The latter problem arises from the fact that M3 has a higher molecular weight and a narrower distribution than M2 does. Moreover, it is noted that the molecular weight distribution curve obtained by SSF does not markedly depend on the initial polymer volume fraction v_p^0 .

The cumulative weight fraction-molecular weight relationship from SSF reproduces the "true" distribution not perfectly but much better than that from SPF does, as shown in Figures 1 and 2. This is also confirmed by the simulation results in Figure 4, that the last fraction, *i.e.*, the fraction having the highest molecular weight in SSF consists of only the component with the high molecular weight, in contrast to SPF. The resolving power in SSF was recently studied in detail by Kamide and Miyazaki.¹⁶

Moreover, the values of M_w/M_n of the fractions in SPF and SSF are plotted against M_w of the fractions in Figure 7, together with the experimental data of SPF. An agreement between the experiment and simulation of SPF is satisfactory. Symmetrical concaved curves are found for the binary mixture,

Figure 7. Plot of M_w/M_n against M_w of fractions of M1 obtained by SPF ($\triangle$, experimental result and $\bullet$, theory; $p=0.6$, $v_p^0=0.80\%$ and $n_i=12$) and of M2 obtained by SSF ($\circ$, theory, $v_p^0=0.40\%$ and $n_i=12$).

though the curve is generally complex in the case of ordinary samples having the Schulz-Zimm or Wesslau distribution. This figure clearly indicates that the fractions having high molecular weight can be obtained more easily by SSF than by SPF.

Thus, the present results of the molecular weight fractionation of the binary polymer mixtures represent a further demonstration of the validity of the theory.

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