

## An Additional Test of Modern Theory of Molecular Weight Fractionation Based on Solubility Difference

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**ABSTRACT:** For the purpose of verifying the validity of modern fractionation theory by experimentation, atactic polystyrene in methylcyclohexane was fractionated by employing a successive solutional fractionation (SSF) method. SSF was duplicated under different operating conditions. The fractions thus prepared and those in a previous paper (*Makromol. Chem.*, **117**, 485 (1976)) were eluted through a GPC column, whose resolution factor  $h$  was very accurately determined in advance. The experimental relations of the ratio of the weight- to number-average molecular weight  $M_w/M_n$  vs.  $M_w$  obtained for three SSF runs fit in well with those predicted by the theory with  $p=0.7$ , which was already evaluated by the phase-separation experiment on the same polymer/solvent system, where  $p$  is a parameter representing concentration dependence of the thermodynamic polymer/solvent interaction parameter  $\chi$  given by  $\chi=\chi_0(1+pv_p)$  ( $\chi_0$ , constant and  $v_p$ , polymer volume fraction).

**KEY WORDS** Molecular Weight Fractionation / Computer Simulation / Successive Solutional Fractionation / Gel Permeation Chromatography / Atactic Polystyrene /

When phase separation from a solution of polydisperse polymer in a single solvent occurs, (1) the volume ratio,  $R$ , of a polymer-lean phase to a polymer-rich phase and (2) the polymer volume fraction,  $v_{p(2)}$ , in the polymer-rich phase are essentially influenced by the concentration coefficient  $p$  of the polymer—solvent thermodynamic interaction parameter  $\chi$ , given by

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

where  $\chi_0$  is a parameter independent of the concentration expressed by the polymer volume fraction  $v_p$ .<sup>1</sup> By using this result which is deduced from theoretical calculations, the magnitude of  $p$  can be precisely estimated in such a manner that the experimental point of  $R$  or  $v_{p(2)}$  agrees well with the theoretical value both at a given fraction size<sup>2</sup> and a given initial polymer volume fraction  $v_p^0$ .

In a previous paper,<sup>3</sup> this method was experimentally applied to the system of polystyrene (PS) in methylcyclohexane (MCH) and of PS in cyclohexane (CH),  $p$  was determined to be

$0.69\pm 0.10$  and  $0.66\pm 0.10$  from  $R$  and  $v_{p(2)}$ , respectively, for the former system, and  $0.58\pm 0.05$  and  $0.56\pm 0.05$  from  $R$  and  $v_{p(2)}$ , respectively, for the latter system. The experimental values of the partition coefficient  $\sigma$ , the number- and the weight-average molecular weight of the polymers in a polymer-lean phase and in a polymer-rich phase,  $M_{n(1)}$ ,  $M_{w(1)}$ ,  $M_{n(2)}$ , and  $M_{w(2)}$  for the the PS/MCH system and the PS/CH system agreed well with the theoretical curve assuming  $p=0.7$  and  $0.6$ , respectively.

For the PS/MCH system, the successive fractionation run can be easily performed by cooling the solution to at most  $-10^\circ\text{C}$  because of its high theta temperature ( $78^\circ\text{C}$ ). The experimental relationship between  $M_w/M_n$  and  $M_w$  for a series of fractions obtained by a successive precipitatorial fractionation (SPF) run on the PS/MCH system, reasonably fit the corresponding theoretical curve of  $p=0.6-0.7$  (see Figure 21a) in ref 3). The experimental points, however, obtained by a successive solutional fractionation (SSF) run (hereafter referred to as Run

1 (initial polymer volume fraction  $v_p^0=0.94\%$  and total number of fractions  $n_t=23$ ) on the same polymer/solvent system represent a significant departure from the theoretical curve of  $p=0.7$ , suggesting that a much larger and unreal value of  $p$  than 0.7 should be assumed for interpreting these experimental SSF data (Figure 21b) in ref 3). An attempt, namely, to explain the  $M_w/M_n$  vs.  $M_w$  relation in the case of SSF with  $p=0.7$  met undoubtedly with failure. This is an unresolved problem, toward which, in this paper, further additional experiment and discussion are undertaken as an extension of earlier work.

$M_w/M_n$  in the fractions obtained by SSF is not so sensitive to the  $p$  value as compared with SPF. This exemplified when an original polymer having the Schulz—Zimm distribution ( $M_w=2.4\times 10^5$ ,  $M_w/M_n=2.8$ ) is hypothetically dissolved in a 0.94-% solution, from which 18 fractions of identical amounts were separated by SPF. The  $M_w/M_n$  values of the fraction with  $M_w=3\times 10^5$  in the  $p$  range from 0 to 0.7 are 1.57~1.22, and those values are interpolated from the  $M_w/M_n$ — $M_w$  relations for a given series of the fractions. By way of contrast, in the case of SSF the  $M_w/M_n$  value of the fraction with  $M_w=3\times 10^5$  varies from 1.07 to 1.05, depending on the variation of  $p$  in the range 0—0.7. Thus, if we want to verify the validity of the fractionation theory with actual SSF experiments, we should evaluate  $M_w/M_n$  of those fractions obtained with high accuracy. For this purpose, in this paper, the GPC measurements were carried out again (1) for the same series of fractions, just as those isolated by the SSF run (Run 1) in a previous paper<sup>3</sup> and (2) for the fractions which were prepared additionally by two SSF runs under different operating conditions, by using new columns with high resolution, and (3) subsequently the theoretical  $M_w/M_n$ — $M_n$  relations of the fractions, which were derived on the bases of the modern theory of molecular weight fractionation, were compared with the experiments.

## EXPERIMENTAL

### Polymer

The sample polymer, the same as in a previous

paper<sup>3</sup> was employed here. The atactic polystyrene, commercially known as Styron 666 (Asahi-Dow Ltd.) was previously purified as described elsewhere<sup>4</sup> and is characterized as follows:  $M_w=2.32\times 10^5$  (by light scattering) and  $2.39\times 10^5$  (by GPC),  $M_n=8.9\times 10^4$  (by membrane osmometry) and  $8.6\times 10^4$  (by GPC).

### Fractionations

The fractionation apparatus was greatly improved and sophisticated, capable of producing large amount of the polymer fractions. This means that the scale of the fractionation experiment was 8 times that noted in the previous paper. The definite amount (180 or 360 g) of PS sample was dissolved in a nitrogen atmosphere in 18 l of MCH at 70°C to give the starting solutions ( $v_p^0=0.94$  or 1.89%). The solutions prepared were cooled down at a rate of 4°C/h to the designated phase separation temperature  $T_p$ , between 58°C and 7°C with  $\pm 0.05^\circ\text{C}$  or less, fluctuation. A very large amount of polymer was precipitated from the solution and the fraction was recovered from the polymer-lean phase. After allowing the solution to stand for 15 hr at  $T_p$  to reach equilibrium, the polymer-lean phase was removed from the system and the solvent in the polymer-lean phase was completely evaporated to dryness under reduced pressure (10 mmHg) at 50°C in a rotary evaporator. The remaining polymer fraction was redissolved in benzene, filtered into methanol at 25°C washed and dried *in vacuo* at 50°C. The recovered MCH was purified and employed in the next step. The polymer-rich phase remaining in the separation vessel was diluted with MCH at 70°C so that the volume of mother solution at each step was kept identical with that at the first step. The separation step was repeated 20 or 30 times. In Tables I and II the operating conditions, as well as the phase separation temperature  $T_p$  and the fraction size  $\rho_s$ , *i.e.*, the weight fraction of the polymer, which is in the polymer-lean phase (in the case of SSF), are listed for two SSF runs (Run 2;  $v_p^0=0.94\%$  and  $n_t=20$ , Run 3;  $v_p^0=1.89\%$  and  $n_t=30$ ) in the system of polystyrene and methylcyclohexane. Note that Run 2 is greatly different from Run 1 with regard to the experimental scale. The polymer recovery was as high as

## Additional Test of the Fractionation Theory

**Table I.** Characteristics of the fractions obtained in a successive solutional fractionation (SSF) run on polystyrene/methylcyclohexane system (Run 2: initial polymer volume fraction  $v_p^0=0.94\%$ ; total number of fractions,  $n_t=20$ )

Fractionation order $i$	Phase separation temp, $T_p$ in $^{\circ}\text{C}$	Fraction size, $\rho_s$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	Standard deviation, $\sigma' \times 10^{-3}$
1	7.0	0.043	12	20	11
2	16.3	0.021	33	41	16
3	26.5	0.028	52	58	19
4	33.7	0.056	68	75	24
5	37.0	0.072	85	95	33
6	39.2	0.062	105	114	33
7	40.5	0.052	129	136	32
8	41.5	0.040	141	151	41
9	42.5	0.035	153	162	38
10	44.1	0.031	168	179	47
11	45.7	0.049	185	197	49
12	46.6	0.048	201	212	50
13	47.8	0.046	239	252	57
14	48.8	0.050	239	252	59
15	49.9	0.046	254	266	56
16	51.3	0.053	290	305	71
17	52.4	0.049	316	332	74
18	53.7	0.050	363	379	78
19	55.0	0.049	401	424	100
20	—	0.060	489	529	150

96—98% throughout Run 1—Run 3.

*Molecular Weight Distribution of the Fractions and Resolution Factor*

$M_w$  and  $M_w/M_n$  of the fractions were calculated from GPC elution curves, which were obtained on a Shimadzu GPC, model 1A chromatograph. Cross-linked polystyrene (TSK gels manufactured by Toyo Soda Ltd., Japan) were employed as the gels for fractionation. Five columns were packed with gels of 2000s, 3000s, 4000s, 5000s and 6000s designated by the manufacturer and were combined in a serial order on the solution side. A theoretical plate count of the columns used was on the average 1000 plates/ft. for acetone at 1.0 ml/min flow rate. The instrument was operated with tetrahydrofuran (THF) as the solvent at  $25^{\circ}\text{C}$  under the following conditions: concentration of solution, 0.2 wt%; flow rate, 1.0 ml/min; and injection volume, 2 ml. Nine samples of well-defined, living polystyrenes supplied by Pressure Chemical Co. (USA) covering  $M_w$  range  $2 \times 10^3$  to  $2.1 \times 10^6$  were used as the references in order to transform the GPC curve to the molecular weight distri-

bution curve. The calibration curve (*i.e.*, the plot of  $\log M$  vs. elution volume  $V$  in ml) was able to be adequately approximated by a straight line over the entire experimentally accessible molecular weight range of the fractions obtained by SSF runs in the form:

$$V = 323.9 - 28.0 \log M \quad (2)$$

The resolution factor  $h$  ( $\text{count}^{-2}$ , 1 count = 5 ml) for the instrumental band broadening correction, defined by Tung, *et al.* (Equations 2—6 in ref 5) was determined by the reverse-flow technique on the above-mentioned living polystyrene. The values of the overall resolution factor  $h$  thus determined, slightly depend on  $M_w$  of the polymers and are written as:

$$h = 1.80 - 0.12 \log M \quad (3)$$

The values of  $h$  are of the order of 1.2 to 1.3 for all fractions encompassing a range reported below. In the previous paper,<sup>3</sup>  $h$  was evaluated as 0.9 by one point determination using a single sample with  $M_w = 2.1 \times 10^5$  and this value was utilized thereafter for band broadening correction.

**Table II.** Characteristics of the fractions obtained in a successive solution fractionation (SSF) run on polystyrene/methylcyclohexane system (Run 3: initial polymer volume fraction,  $v_p^0=1.89\%$ ; total number of fractions,  $n_t=30$ )

Fractionation order $i$	Phase separation temp, $T_p$ in $^{\circ}\text{C}$	Fraction size, $\rho_s$	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	Standard deviation, $\sigma' \times 10^{-3}$
1	9.8	0.042	9	17	12
2	16.5	0.019	21	33	18
3	20.6	0.012	31	39	18
4	24.1	0.011	38	47	21
5	27.7	0.014	50	57	20
6	33.3	0.031	61	69	25
7	35.7	0.034	69	78	28
8	37.3	0.037	82	97	42
9	38.6	0.035	88	111	57
10	39.6	0.029	104	121	48
11	40.7	0.030	118	131	43
12	41.7	0.030	126	144	55
13	42.8	0.032	147	165	58
14	43.8	0.032	149	166	56
15	44.7	0.032	173	189	56
16	45.7	0.033	183	199	57
17	46.6	0.034	195	212	63
18	47.4	0.037	210	232	73
19	48.4	0.035	221	239	67
20	49.2	0.039	249	272	81
21	50.2	0.043	273	293	79
22	51.5	0.053	295	320	93
23	52.5	0.047	312	333	86
24	53.0	0.038	360	388	108
25	53.5	0.031	390	416	107
26	54.7	0.038	447	480	130
27	56.4	0.044	486	512	138
28	57.5	0.038	555	596	161
29	58.0	0.016	671	729	214
30	—	0.008	857	934	278

Since the analysis of the GPC curve, taking into consideration the molecular weight dependence of  $h$  is extremely difficult, the value of  $h$  corresponding to  $M_w$  of the fractions was employed in a first approximation. For example,  $h$  was taken as 1.2 for the fraction with  $M_w=2.4 \times 10^5$ . The reliability of this value is much higher than that (0.9) used in a previous paper. The GPC chromatograms of the fractions obtained by SSF were highly symmetric and were able to be approximated with Gaussian distribution. Accordingly, the special solution described in Tung's paper<sup>6</sup> was used for band broadening correction.

#### Simulative Procedure

As described in a previous paper, the original polystyrene sample has a molecular weight distribution (MWD) very similar to the Schulz—Zimm distribution having  $M_w=2.4 \times 10^5$  and  $M_w/M_n=2.80$  (*i.e.*, the weight-average degree of polymerization  $X_{p,w}=2307$ , the weight-average ratio of the molar volume of polymer to solvent  $X_w=1810$  in MCH at  $20^{\circ}\text{C}$ ) (Figure 2 in ref 3).

The polymer solution theory of Flory, Huggins, and Fujishiro was employed as a basic principle, in which the concentration dependence of  $\chi$  is given by eq 1. The simulation was carried out over the range of the molar volume ratio of polymer to solvent  $X$  from 15 to 22500

at intervals of 15. In other words the original polymer was approximated so as to consist of 1500 species of components differing in  $X$ . The mathematical fractionation was performed by using an electronic computer (IBM system 370/158) according to the simulative procedure of Kamide and Sugamiya.<sup>1</sup> In this paper equal amounts of the fractions were hypothetically isolated (*i.e.*,  $\rho_s=1/n_t$ ).

### RESULTS AND DISCUSSION

The reliability of the  $p$  values estimated from the phase separation study can be further confirmed by relevant literature data<sup>7-10</sup> of  $p$  determined on the basis of other principles. The values of  $p$  evaluated for the PS/CH system are assembled in Table III. The  $p$  values determined by other methods average 0.57 at 10°C and 0.58 at 20°C, respectively, which are in rather close accord with those obtained in a previous paper.<sup>3</sup> Although, unfortunately, the validity of  $p$  values, obtained for the PS/MCH system, could not be confirmed because of lack of available literature data, the various above-mentioned, experimentally determined, characteristics of phase separation phenomena agree closely with the corresponding theoretical values, which are calculated on the assumption that  $p=0.7$ . In addition, the experimental relationship between  $M_w/M_n$  and  $M_w$  for a series of fractions obtained by a SPF run on the PS/MCH system showed reasonable agreement with the corresponding theoretical curve of  $p=0.6-0.7$  (see, Figure 21 in ref 3) as was described previously. But, the  $p=0.7$  apparently failed to explain the  $M_w/M_n$  vs.  $M_w$  relation in the case

of SSF.

Recently, Kato, *et al.*,<sup>11</sup> determined  $h$  according to the reverse-flow method on the same type of GPC instrument combined with the columns of the same polystyrene gels and the same solvent (THF) as those in a previous paper and they estimated the experimental error of  $h$  to be  $\pm 10\%$ , if  $h$  is obtained for a single sample. The value of  $h$  used in a previous paper is then expected to be subject to an experimental error of the same order ( $\pm 10\%$ ). The value of  $M_w/M_n$  for the fractions obtained by correcting the GPC trace with band broadening, designated by  $(M_w/M_n)_c$  is related to the true  $M_w/M_n$  value,  $(M_w/M_n)_t$ , and an error  $\Delta(M_w/M_n)$  through the equation:

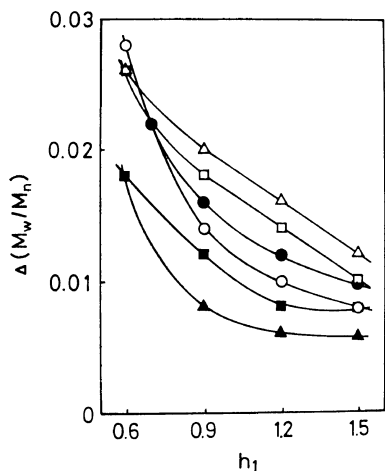
$$(M_w/M_n)_c = (M_w/M_n)_t \pm \Delta(M_w/M_n) \quad (4)$$

In this equation, the sign + indicates the case when  $h$  is overestimated, and the sign - the case when  $h$  is underestimated. The relationships between a relative error of  $h$  (*i.e.*,  $\pm \Delta h$ ) and  $\Delta(M_w/M_n)$  can be obtained as follows. Initially, three polymers with log-Gaussian distribution for  $M_w/M_n=1.05$  ( $\equiv (M_w/M_n)_t$ ) and various values of  $M_w$  should be considered. The MWD curve of the polymer is transferred reversely to the GPC curve by using the calibration curve experimentally determined and by Tung's method. In this case, a given value of  $h(h_1)$  is assumed. Subsequent to this step, the GPC curve thus obtained is converted again to the MWD curve by using the same calibration curve, Tung's method and the different value of  $h$  (*i.e.*,  $h_1 \pm h_1/10$ ).  $(M_w/M_n)_c$  is evaluated from the MWD curve. In this manner,  $\Delta(M_w/M_n) = |(M_w/M_n)_c - (M_w/M_n)_t|$  was evaluated as a function of  $h_1$ , as

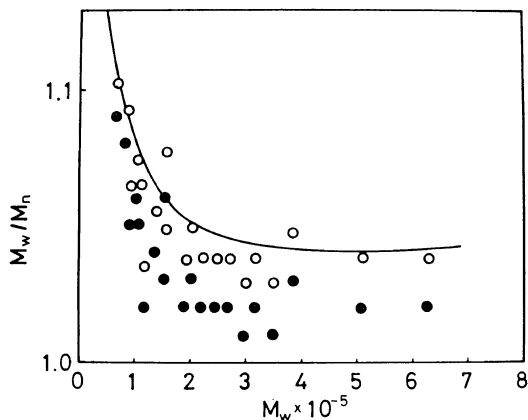
Table III. Values of  $p$  evaluated for the system of polystyrene in cyclohexane

Author(s)	Year	Method	$p$	
			at 10°C	at 20°C
Krigbaum—Geymer <sup>8</sup>	1959	Osmotic pressure	0.57	0.58
		Isothermal distillation		
		Vapor pressure		
Koningsvelt, <i>et al.</i> <sup>9</sup>	1970	Critical miscibility	0.59	0.60
Scholte <sup>10</sup>	1970	Ultracentrifuge	0.52	0.53
Kuwahara, <i>et al.</i> <sup>7</sup>	1973	Critical miscibility	0.59	0.60
Kamide, <i>et al.</i> <sup>3</sup>	1976	Phase separation	0.56	0.58
			(10.7	—

shown in Figure 1. As  $h_1$  decreases, in other words, as the columns with lower resolution power are employed, the error of  $M_w/M_n$ ,

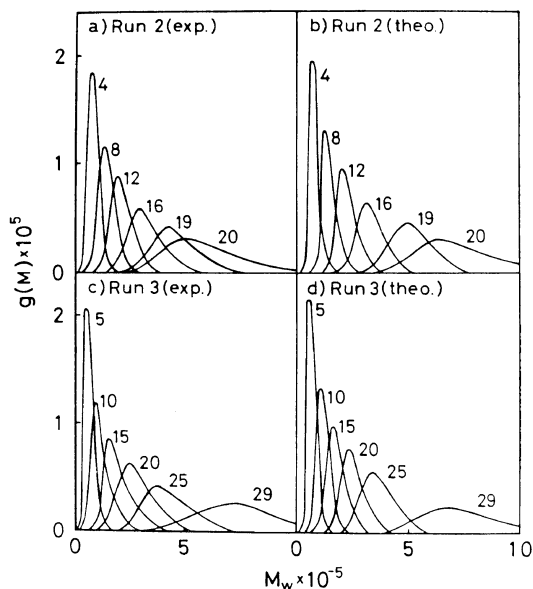


**Figure 1.**  $\Delta(M_w/M_n)$  defined by eq 4 in the case where the observed resolution factor  $h$  is 10% larger or 10% smaller than the true value  $h_1$ ; the polymer, the log-Gaussian distribution ( $M_w/M_n=1.05$ ): Closed mark,  $h=h_1+h_1/10$ ; open mark,  $h=h_1-h_1/10$ ; triangle,  $M_w=6.3 \times 10^5$ ; rectangle,  $M_w=2.1 \times 10^5$ ; circle,  $M_w=5.25 \times 10^4$ .



**Figure 2.** Plot of  $M_w/M_n$  vs.  $M_w$  of a series of the fractions obtained by SSF Run 1 on the system of polystyrene and methylcyclohexane: ●, experimental data estimated by GPC in a previous paper;<sup>3</sup> ○, data points corrected for  $\Delta(M_w/M_n)$  by assuming that the observed  $h$  value (0.9) in a previous paper was underestimated by 10% as compared with the true value (0.99); full line, theoretical curve ( $p=0.7$ , cf. eq 1);  $v_p^0=0.94\%$  and  $n_t=23$ .

$\Delta(M_w/M_n)$ , caused by using an  $h$  value 10% smaller than the true value, increases markedly. With the help of Figure 1, the value of  $M_w/M_n$  of fractions separated by Run 1, reported in a previous paper,<sup>8</sup> was recalculated to give  $(M_w/M_n)_t$  by postulating that the observed value of (0.9) was about 10% smaller than the true one (0.99). In Figure 2 the  $M_w/M_n$  values corrected and uncorrected are plotted as a function of  $M_w$ . Figure 2 includes also the theoretical curve with  $p$  assumed constant (0.7) for comparison sake. From Figure 2, the agreement between the experimental and calculated  $M_w/M_n$  of the fractions by Run 1 is well within the reproducibility of the experiments, although the uncertainty of  $h$  is somewhat great due to a noticeable broadening effect. In other words, it is particularly noteworthy about this figure, that the previous paper<sup>3</sup> is not sufficiently precise for comparison with the theoretical predictions. From the foregoing discussion it can



**Figure 3.** Normalized molecular weight distribution curves of the fractions separated by successive solution fractionation (SSF) runs (Run 2:  $v_p^0=0.94\%$   $n_t=20$  and Run 3:  $v_p^0=1.89\%$   $n_t=30$ ): a) and c), experiments for polystyrene in methylcyclohexane; b) and d), theoretical calculations  $p=0.7$  (cf. eq 1); numbers at curves denote fraction number.

be expected that the reliability of  $h$  value plays a predominantly important role, especially in the case when  $M_w/M_n$  of the fractions with very narrow MWD, obtained by SSF is to be determined by GPC. In this paper, therefore, the columns having high resolution were carefully selected and the  $h$  value for these columns was determined on nine polymer samples in order to minimize the error due to the broadening effect.

As an illustration, Figures 3 a) and c) represent the MWD curves of some typical fractions obtained by Runs 2 and 3 for 0.94 and 1.98-% solutions of polystyrene in methylcyclohexane. Figures 3b) and d) exemplify those curves obtained by computer simulation SSF assuming  $p=0.7$  ( $v_p^0=0.94\%$  and  $n_t=20$  for Run 2 and  $v_p^0=1.98\%$  and  $n_t=30$  for Run 3). The results indicate that the characteristic features, obtained by the computer simulations, are also maintained qualitatively in the practical experiment. These results are essentially identical with those of the previous paper.<sup>3</sup> In 4th—6th columns of Tables I and II, the values of  $M_n$ ,  $M_w$  and the standard deviation  $\sigma'$  of the form:

$$\sigma'^2 = \int_0^\infty (M - \mu_1)^2 g(M) dM = M_w^2 \{ (M_z/M_w) - 1 \} \quad (5)$$

estimated from the GPC curve are summarized. Here,  $\mu_1$  is the first moment of the differential weight MWD function  $g(M)$  and  $M_z$  is the Z-average molecular weight. The plots of  $M_w/M_n$  against  $M_w$ , thus estimated for three series of fractions by SSF runs, are shown as open marks in Figures 4—6, where the corresponding theoretical curves ( $p=0.7$ ) together with experimental data obtained in a previous paper (closed marks) are also included. The data points obtained by improved GPC measurements coincide closely as expected, with the theoretical curve assuming  $p=0.7$ , when the unavoidable variation of the fraction size is considered (*i.e.*, the standard deviation of the fraction size was 0.012 and 0.011 for Runs 2 and 3, respectively) during a given experimental run together with the assumption of constant  $h$  being independent of the molecular weight.

As a further check, in Figure 7, the ratio of the standard deviations  $\sigma'$  of the fractions, ob-

tained by SSF runs to that of the original polymer  $\sigma_0'$  is employed instead of  $M_w/M_n$  as a measure for representing the breadth of the fraction in MWD. For comparison, the figure also gives a family of theoretical curves relating  $\sigma'/\sigma_0'$  to  $M_w$  of the fractions for various  $p$  values. Despite the variation of  $v_p^0$  and  $n_t$  in Runs 1—3, theoretical  $\sigma'/\sigma_0'$  vs.  $M_w$  curve was common for a given value of  $p$ .  $\sigma'/\sigma_0'$  increases nearly linearly with increasing  $M_w$ . The effect of  $p$  on the  $\sigma'/\sigma_0' - M_w$  relation is significant and the

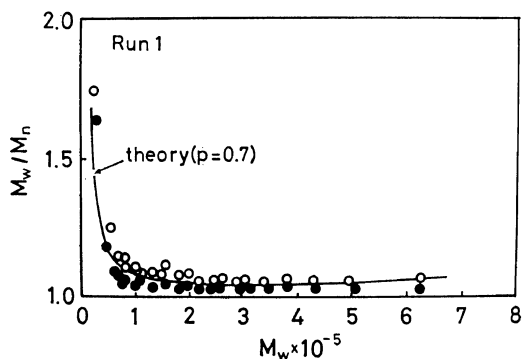


Figure 4. Plot of  $M_w/M_n$  vs.  $M_w$  of a series of the fractions obtained by SSF Run 1 ( $v_p^0=0.94\%$ ,  $n_t=23$ ) on the system of polystyrene and methylcyclohexane:  $\circ$ , experimental data estimated by GPC with a high resolution column combination;  $\bullet$ , experimental data estimated by GPC with a low resolution column combination and less accurate  $h$  value; full line, theoretical curve ( $p=0.7$ , cf. eq 1).

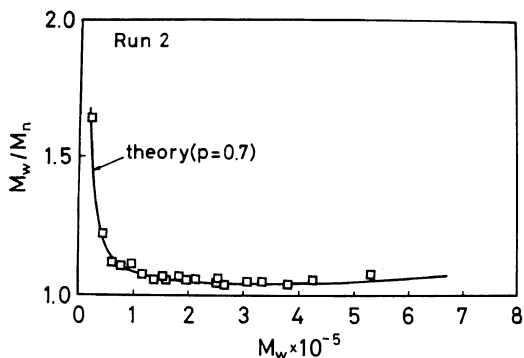
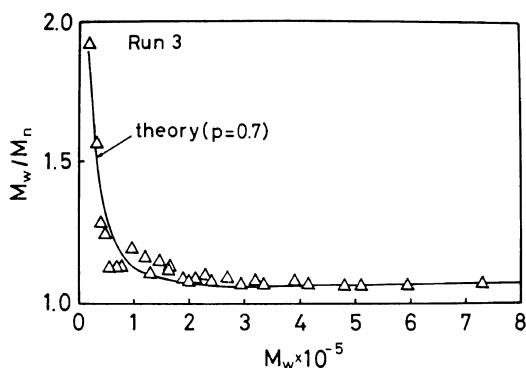


Figure 5. Plot of  $M_w/M_n$  vs.  $M_w$  of a series of the fractions obtained by SSF Run 2 ( $v_p^0=0.94\%$ ,  $n_t=20$ ) on the system of polystyrene and methylcyclohexane:  $\square$ , experimental data; full line, theoretical curve ( $p=0.7$ ).

effective value of  $p$  which gives the best concordance to the entire set of experimental data is about 0.7.

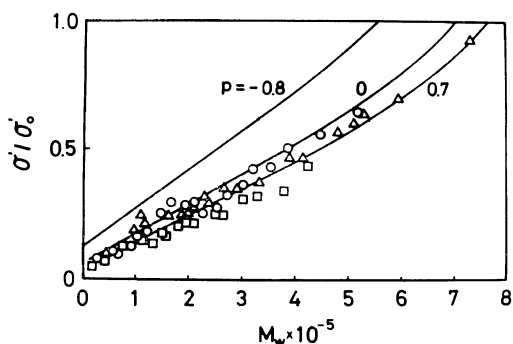
Inspection of Figures 4–7 leads us to the conclusion that all the experimental data available are thoroughly consistent with the theory developed, and that the conclusions deduced in a previous paper<sup>3</sup> were corroborated, reflecting strongly the validity of the modern theory of molecular weight fractionation as well as the adequacy of computer simulation technique developed in our laboratory. Since a significant difference does not exist between theory and experiment on any point,  $p$  can be treated as constant throughout fractionation and, moreover, the molecular weight dependence of the partition coefficient  $\sigma$  observed by the direct experiment can be reasonably ignored. The reverse, however, is not true and the determination of  $p$  from the plot like Figures 4–6 may be greatly in error. The conclusions deduced in a series of simulation studies are not so easy to verify by experimentation, but can be considered valid. We are



**Figure 6.** Plot of  $M_w/M_n$  vs.  $M_w$  of a series of the fractions obtained by SSF Run 3 ( $v_p^0=1.89\%$ ,  $n_t=30$ ) on the system of polystyrene and methylcyclohexane:  $\triangle$ , experimental data; full line, theoretical curve ( $p=0.7$ ).

now in a position to design the fractionation scheme in a way known in detail and to predict the molecular characteristics of fractions thus obtained.

The so-called monodisperse polymer samples are useful as standard materials for calibration of GPC, vapor pressure osmometry and, for establishing the structure-property—processability relations. Up to now such polymers are prepared by either an anion polymerization technique or by preparative GPC. In the former case, the kinds of polymers available are severely limited and in the latter case, the polymers thus obtained are very expensive. In addition to these considerations, the polymer samples with very narrow MWD are achieved by SSF under the usual conditions. Table IV compiles the number of fractions having  $M_w/M_n$  less than 1.10, or 1.05 in that case when the above three SSF runs are applied. Table IV indicates that



**Figure 7.** Plot of the ratio of the standard deviation  $\sigma'$  of the fractions obtained by successive solutional fractionation runs to that of the original polymer  $\sigma_0'$  vs. their  $M_w$ :  $\circ$ , experimental data of Run 1 ( $v_p^0=0.94\%$ ,  $n_t=23$ );  $\square$ , experimental data of Run 2 ( $v_p^0=0.94\%$ ,  $n_t=20$ );  $\triangle$ , experimental data of Run 3 ( $v_p^0=1.89\%$ ,  $n_t=30$ ); full line, theoretical curves  $p$  values are indicated on curves.

**Table IV.** Number of fractions having  $M_w/M_n$  less than 1.10 or 1.05, isolated by three successive solutional fractionations

Polydispersity of fractions	Run 1 ( $v_p^0=0.94\%$ , $n_t=23$ )		Run 2 ( $v_p^0=0.94\%$ , $n_t=20$ )		Run 3 ( $v_p^0=1.89\%$ , $n_t=30$ )	
	Exptl	Theory	Exptl	Theory	Exptl	Theory
$M_w/M_n < 1.10$	18	19	15	16	16	25
$M_w/M_n < 1.05$	7	9	5	7	0	10



### Additional Test of the Fractionation Theory

the agreement between experiment and theory is quite satisfactory, especially for Runs 1 and 2, which were performed at relatively low  $v_p^0$ . The usefulness of SSF for this purpose was recently demonstrated by the authors for polyethylene and cellulose diacetate.<sup>12</sup>

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