Determination of Chemical Composition Distribution of Poly(methyl methacrylate)-*graft*-Polystyrene by Adsorption High-Performance Liquid Chromatography

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ABSTRACT: The chemical composition distributions (CCD) of poly(methyl methacrylate)-*graft*-polystyrene samples prepared by the macromonomer technique were determined by high-performance liquid chromatography (HPLC) in the reversed-phase adsorption mode. Three samples of different compositions at low conversions and four samples obtained at different conversions from the same monomer feed compositions were prepared. These were separated and analyzed by HPLC using reversed-phase combination of an octadecyl-modified silica gel column and a linear gradient of tetrahydrofuran and acetonitrile. The samples were eluted from components of high MMA content to components of low MMA content. The chromatograms were converted to CCDs using three samples of different compositions as standards by the optimization method. The CCDs of all samples thus determined were very broad, irrespective of the conversions, in accordance with the theoretical prediction of Stejskal and Kratochvíl.

Introduction

Studies of the copolymerization of macromonomers with small comonomers have recently increased, aiming at the synthesis of well-defined graft copolymers. However, only a few studies of the chemical composition distributions (CCDs) of such copolymers have been reported,[1-3] though relatively broad CCDs were predicted theoretically.[4,5] The properties of the copolymers may be affected by the CCD as well as the molecular weight distribution. DeSimone et al.[1,2] reported the determination of CCDs of samples of poly(methyl methacrylate)-*graft*-poly(dimethylsiloxane) by supercritical fluid fractionation and demixing solvent fractionation, and Stejskal et al.[3] used the latter method for the same purpose. However, the correct CCDs of the samples may not be obtained by the former method because of the effect of molecular weight distribution. In fact, the CCDs obtained by that method are narrower than those of the same samples obtained by the demixing solvent fractionation.[2] Theoretical and experimental CCDs obtained by the latter method are in good agreement.[3] However, the demixing solvent fractionation may not be a general method for the compositional fractionation of copolymers, since it is difficult to find a suitable pair of solvents. A major effort is required to find a fractionation system such as used by Stejskal et al.

On the other hand, high-performance liquid chromatography (HPLC) has been used successfully for the compositional separation or the determination of CCDs not only for statistical copolymers[6-12] but also for block copolymers[13-15] and a graft copolymer,[16] based on mechanisms of adsorption (normal and reversed-phase modes) and (or) phase separation. In the present work, we applied HPLC to the determination of CCDs of poly(methyl methacrylate)-*graft*-polystyrene samples prepared by radical copolymerization of polystyrene (PS) macromonomer and methy methacrylate (MMA). The results were compared with CCDs calculated theoretically.

Experimental Section

Synthesis of Graft Copolymer. The PS macromonomer having a methacryloyl end group used in the present study was synthesized by living anion polymerization of the styrene monomer with *sec*-butyllithium followed by addition of ethylene oxide and coupling with methacryloyl chloride.[17-19] The number-average molecular weight (M_n) determined by gel-permeation chromatography (GPC) was 1.24×10^4. The M_w/M_n ratio, which was also determined by GPC, was 1.06. The GPC measurement was carried out by using HLC-802 and TSK-GEL, G5000H-G3000H columns (Tosoh Co. Ltd., Tokyo) in chloroform at 30 °C. The end functionality was 0.86, which was determined by ^{1}H NMR (Gemini-200, Varian; in $CDCl_3$, 200 MHz).

Graft copolymer samples were synthesized by statistical copolymerization of the macromonomer with MMA comonomer using 2,2′-azobisisobutyronitrile (AIBN) in benzene at 60 °C. The copolymerizations were carried out with three different feed compositions and four different conversions, as shown in Table I. The copolymerization products were precipitated four times into a mixture of cyclohexane (CHX) and petroleum ether (typical mixing ratio 3:2) to remove unreacted macromonomer. Removal of the macromonomer was checked by GPC. The copolymerization products were freeze-dried in benzene. The crude sample without purification (E2 (u)) was used for comparison with the purified product E2.

Styrene, methyl methacrylate, methacryloyl chloride, ethylene oxide, AIBN, and solvents were obtained commercially. The monomers were dried with Na_2SO_4 after removal of inhibitor with 5% aqueous NaOH and distilled over calcium hydride under reduced pressure. Benzene was dried with sodium wire and distilled under nitrogen. Other solvents for the precipitation and the purification of the copolymer were used as received. Styrene used in the living anion polymerization was further purified with the sodium salt of benzophenone and distilled under high vacuum. Ethylene oxide and methacryloyl chloride were purified with CaH_2 and distilled under high vacuum.

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Table I
Synthesis of Graft Copolymer Samples

sample code	feed: macromonomer[b] (g)	feed: macromonomer[b] (wt %)[c]	feed: MMA (g)	feed: AIBN (g)	feed: benzene (mL)	reactn time (h)	conversion (wt %): total monomer	conversion (wt %): macromonomer	copolymer[a]: S content (wt %)	copolymer[a]: $10^{-4}M_n$
A	1.7400	29.9	3.5019	0.0346	16.7	2.5	16.5	11.5	27.0	5.8
B	2.3304	50.0	2.0032	0.0199	13.3	2.5	10.8	8.9	46.3	10.7
C	4.0003	77.4	1.0054	0.0205	16.7	2.5	9.8	8.8	74.4	29.2
D	1.1707	50.2	1.0004	0.0099	6.7	12.0	50.0	43.0	46.3	8.6
E1	2.3300	50.0	2.0016	0.0199	13.3	48.0	83.0	74.5	48.3	6.9
E2	2.3300	50.0	2.0010	0.0199	13.4	48.0	83.4	74.6	48.1	7.0
F	2.3306	50.0	2.0015	0.0200	13.5	1.5	6.1	4.9	44.4	10.5

[a] The values measured after removal of the unreacted macromonomer. [b] M_n of the macromonomer is 12 400; M_w/M_n = 1.06 by GPC. [c] Feed compositions corrected by the end functionality of the macromonomer (f = 0.86).

Characterization of Graft Copolymers. The compositions of the graft copolymers were determined from the relative peak intensities of the phenyl protons of styrene residues of the branches and the methoxy protons of MMA residues of the backbone in ^{1}H NMR spectra. Conversions of the macromonomer in Table I were calculated from GPC chromatograms of the crude reaction mixture using the ratio of peak area of the unreacted macromonomer to the total peak area of the copolymerization product detected with an ultraviolet (UV) detector.

Number-average molecular weights of the graft copolymers were determined using a high-speed membrane osmometer, Model 231 from Wescan Instruments, Inc., for benzene solutions at 40 °C.

HPLC Measurements. The HPLC instrument was composed of two pumps LC-6A, a controller SCL-6A, a UV detector SPD-6A (Shimadzu Corp., Tokyo) and a column thermostat SSC-3510 (Senshu Scientific Co. Ltd., Tokyo). A prepacked column of octadecyl-modified silica gel (ODS) was used; ODS-1251-K (Senshu Scientific Co. Ltd.) (column length 25 cm, inner diameter 0.46 cm, particle diameter of the starting silica gel 5 μm, and micropore diameter of the silica gel 10 nm). The column temperature was 30 °C, the flow rate 1.0 cm^3 min^{-1}, the injection volume 0.1 cm^3, and the concentration of the sample 0.3 mg cm^{-3}. The wavelength of the UV detector was 254 nm. The eluent was a mixture of tetrahydrofuran (THF) and acetonitrile (ACN), both of which were of chromatographic grade from Wako Pure Chemical Industries, Ltd. (Tokyo). The present combination of ODS column and the solvent pair was effective for the compositional fractionation of the samples of poly(MMA-*stat*-S) as reported in our previous paper.[11] The gradient program of the eluent was as follows:

time (min)	0	1	16	21	21	31	46
THF (vol %)	10	20	60	60	100	100	10

The sample fractionation was carried out in the region of the linear gradient from 20 to 60 vol % THF. The starting composition of 10 vol % was used to complete the precipitation of the samples. Since a part of the sample injected remained in the ODS column as reported elsewhere,[20] the chromatograms were obtained after recovery of a straight base line following several rinses with the blank gradient elution of the same program as that used in the measurement.

Fractionation of Sample E2(u). Sample E2(u) was fractionated by preparative column elution fractionation to separate the unreacted polystyrene macromonomer. The glass column was covered with a water jacket through which water from a constant-temperature bath (30 °C) was circulated. The effective length and the inner diameter were 105 and 4.2 cm, respectively. Glass beads with an average diameter of ~0.4 mm were used as support for the precipitated phase. The beads were purified with boiling aqueous HCl and concentrated HNO_3 and washed with distilled water and acetone. A solution of 0.5004 g of E2(u) dissolved in 293 cm^3 of a 1:1 mixture of dichloromethane (DCM) and CHX (where DCM is a good solvent for both parent homopolymers, whereas CHX is a solvent for PS but a precipitant for PMMA) was slowly evaporated at room temperature to deposit the copolymer on the glass beads. The glass beads coated with the sample were then dried in vacuo, passed through a sieve, and filled into the column as a slurry with a mixture of *n*-hexane (NHX) and CHX (volume ratio 8:2), which was the start eluent for the fractionation. Each fraction was eluted with a mixture of the solvents, whose composition was varied stepwise as shown in Table II. The equibration time and the flow time for each fraction were 2.5 and 1 h, respectively. The fractions were concentrated by a rotary evaporator, precipitated with a large excess of methanol, and dried in vacuo. Each fraction was analyzed by ^{1}H NMR and HPLC.

Table II
Column Fractionation of Sample E2(u)

fractn no.	vol % of solvents: NHX	CHX	DCM	wt % of fractn	note[a]
1	80	20	0	4.8	macromonomer (PS)
2	55	45	0	5.7	PS and P(PS)
3	40	60	0	2.6	PS and P(PS)
4	20	80	0	1.3	PS and P(PS)
5	0	100	0	30.4	graft copolymer
6	0	100	0	21.9	graft copolymer
7	0	0	100	33.3	graft copolymer
sum				100.0	

[a] By ^{1}H NMR and HPLC (see text).

Table III
M_n, m_n, and P_n of Graft Copolymer Samples

sample code	$10^{-4}M_n$	m_n[a]	P_n[b]
A	5.8	1.26	424
B	10.7	4.00	578
C	29.2	17.52	764
D	8.6	3.21	464
E1	6.9	2.69	359
E2	7.0	2.71	366
F	10.5	3.79	587

[a] m_n, number-average number of grafts per copolymer molecule. $m_n = XM_n/M_{nS}°$ (X, weight fraction of the graft part; $M_{nS}°$, M_n of the macromonomer). [b] P_n, number-average degree of polymerization of backbone. $P_n = m_n + (1-X)M_n/M_M°$ ($M_M°$, molecular weight of MMA).

Results and Discussion

Average Characteristics. Feed compositions, average copolymer compositions, conversions of the total monomers and the macromonomer, and M_n's of the copolymers obtained by osmometry are shown in Table I. The number-average number of grafts per copolymer molecule (m_n), the number-average degree of polymerization of the backbone (P_n) calculated from the average composition, and the M_n are given in Table III.

As seen in Table I, the macromonomer contents of the copolymers are a little smaller than those of the monomer feeds, but tend to approach each other as the conversion increases. Thus, the reactivity ratio of the macromonomer is smaller than that of MMA.

Tables I and III show that as the macromonomer content increased, M_n and P_n became larger, though the concentration of the initiator in the feeds remained almost

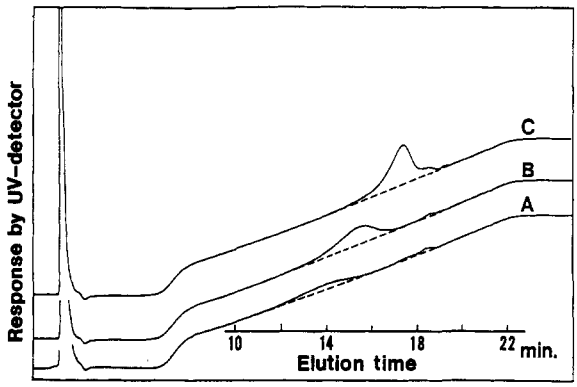

Figure 1. Chromatograms of samples A–C.

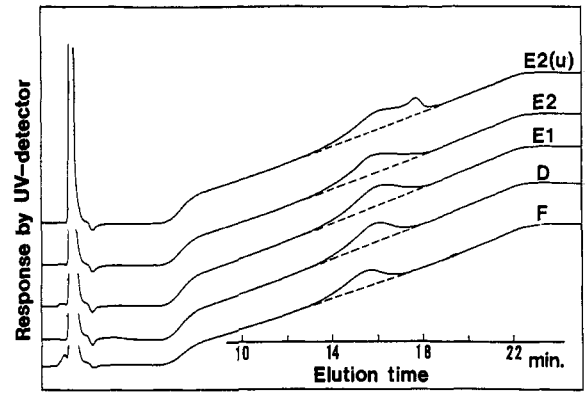

Figure 2. Chromatograms of samples F, D, E1, E2, and E2(u).

constant. This may be related to the gel effect, where the termination reaction is inhibited at increasing concentrations of macromonomer, which increases the viscosity of the reaction mixture and the density of branching of the propagating radicals.[19]

Chromatograms by HPLC. The chromatograms of the graft copolymers A–C with different compositions are shown in Figure 1. The chromatograms of samples F, D, E1, and E2 obtained at different conversions from the same food compositions are shown in Figure 2, including the result of the unpurified sample, E2(u).

From the chromatograms in Figure 1, it can be concluded that the earlier the graft copolymer samples eluted, the lower their S contents were, in accordance with the case of poly(MMA-*stat*-S) reported in the previous paper.[11] In both figures, all samples have broad peaks irrespective of the conversion and the composition, differing from the results of poly(MMA-*stat*-S).

The chromatogram of E2(u) was very similar to that of a mixture of sample E2 and a standard PS of $M_n = 1.02 \times 10^4$. The position of the subpeak at 17–18 min in the chromatogram of E2(u) was also almost the same as that of the standard PS by single injection. (These chromatograms were not illustrated here.) Thus, the very small subpeak around 17–18 min in the chromatogram of sample A can be ascribed to the unreacted macromonomer. However, the subpeaks observed at 18–19 min in the chromatograms of samples A–C and F may not be ascribed to the macromonomer.

The molecular weight dependency of the peak position was studied for standard PS samples under the same condition as that of the HPLC measurement. The peak position varied from 17.6 to 18.7 min in the order of molecular weight in the range of $M_n = 1.02 \times 10^4$–1.78×10^5, leveling off in the higher molecular weight region. Chromatograms of some of the fractions of sample E2(u) obtained by the column elution fractionation are shown in Figure 3. The chromatogram of F-1 shows a single peak

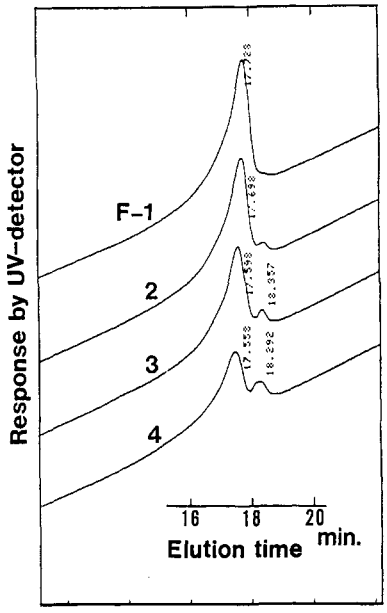

Figure 3. Chromatograms of fractions of sample E2(u).

very similar to that of the standard PS ($M_n = 1.02 \times 10^4$), while the chromatograms of F-2–4 have two peaks. In these chromatograms, the main peaks are at 17.6 min according to the position of the macromonomer, whereas the subpeaks are around 18.3. The chromatograms of F-5–7 were almost the same as that of sample E2. In the ^{1}H NMR spectra, the fractions from F-1 to F-4 did not show the methoxy proton peaks of the MMA monomeric units even integration of 200–300 times, whereas the other fractions showed the methoxy proton peaks. It can be concluded that F-1 is the unreacted macromonomer and the fractions F-2–4 are PS containing not only the macromonomer but also a small amount of higher molecular weight PS, which corresponds to the subpeak at 18–19 min. This may be branched PS prepared by homopolymerization of the PS macromonomer, P(PS).

Converting Chromatograms to CCDs. The total peak areas of the chromatograms (containing the subpeaks) of samples A–C measured by UV detector divided by the concentrations were plotted against the S contents of the samples. Since the plot was linear passing through the origin, it may be concluded that the height of the chromatogram from the base line (h_i) at the respective elution times (V_i) is proportional to the product of the S content (X_i) and its relative concentration (H_i). The elution time at the peak position (V_p) for each sample was plotted against the average S content of the sample (X_o), as in Figure 4 (solid line). The relationship was approximately linear, i.e.

$$X_o = a_o V_p + b_o \tag{1}$$

However, this equation cannot be used for the calibration to convert V_i to X_i, as it stands, since the compositions at the peak positions do not necessarily correspond to the average compositions of the respective samples.

The calibration equation was obtained as follows: As a first approximation, V_i was converted to X_i by using eq 1, and the average S content of each sample (X_I) was calculated from the chromatogram by

$$H_i = h_i / X_i \tag{2}$$

$$X_I = \sum X_i H_i / \sum H_i \tag{3}$$

Next, the average elution time (V_I) for each sample was

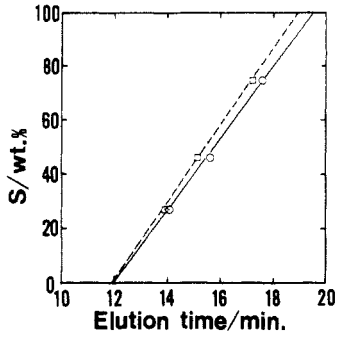

Figure 4. Calibration curves between elution time and S content of the first equation (⊙) and the fifth equation (⊡).

obtained with eq 1 by substituting X_I for X_o, and then X_o was plotted against V_I to obtain

$$X_o = a_I V_I + b_I \quad (1')$$

Again, V_i was converted to X_i by eq 1', and then the average S content (X_{II}) was calculated by use of eqs 2 and 3 for each sample. Then, V_{II} was obtained by use of eq 1'. The same procedure was repeated several times. In the procedure, the subpeaks were included in the calculation of the average compositions, since the average compositions of the samples containing components of the subpeaks were measured by ^{1}H NMR. In the calculation for sample A, since H_i diverged toward infinity as X_i approached 0, the value of H_i in the low region of X_i (lower than 8%) was assumed to be the value obtained by smooth extrapolation from the values in the higher region of X_i. If the homopolymer PMMA was contained in the sample, it could not be detected by the UV detector, but the proportionality between the peak areas divided by the concentrations and the S contents showed that no PMMA was present. The average S contents thus calculated approached the original values, but did not necessarily agree with these values. In the fifth calculation, the equation converged and the values nearest to X_o's were obtained for the respective samples. Then, the fifth equation (broken line in Figure 4) was used to calculate the CCDs for all samples. Ordinates of the CCDs were normalized by taking into account the slope of the equation.

The average compositions calculated by the equation are within 0.1–3.2% of the experimental values in Table I. Although the certainty of the CCDs thus calculated is not very high, the CCDs may be sufficiently useful for discussion.

First, a quadratic equation was assumed for the calibration equation, since three samples can be used for reference. However, the coefficient of the quadratic term oscillated between positive and negative and the equation did not converge, unlike the liner equation.

The CCDs thus obtained for samples A–C are illustrated in Figure 5, those for samples F, D, and E1 are in Figure 6, and those for samples E1 and E2 are in Figure 7. In the figures, the subpeaks of the chromatograms corresponding to pure PS were excluded and the distribution curves were renormalized. For sample C, however, the subpeak was not excluded, since the subpeak was not separated from the main peak.

Discussion of the CCDs. It is clear from these figures that the CCDs are very broad not only for high-conversion samples (D, E1, and E2) but also for low-conversion samples (A–C and F). The broad CCDs are similar to the result for poly(methyl methacrylate)-*graft*-poly(dimethylsiloxane) by Stejskal et al.[3] but differ from CCDs of statistical copolymers of small monomers.[9,11] Thus, a broad CCD is a feature of the graft copolymers prepared by the macromonomer technique, in accordance with theoretical predictions.[4,5] Moreover, as the macromonomer content is increased, the CCD becomes sharper for low-conversion samples, as shown in Figure 5.

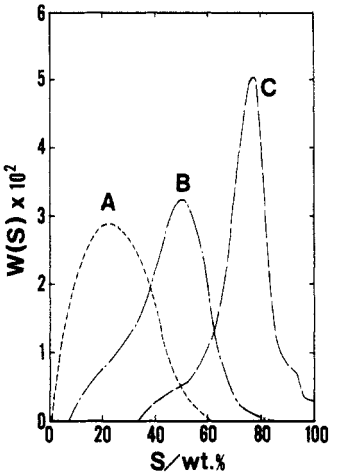

Figure 5. Experimental CCDs of samples A–C synthesized from the monomer feeds of different compositions at low conversions.

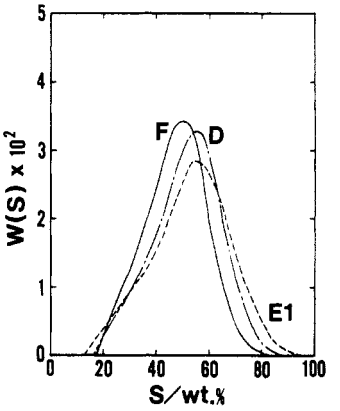

Figure 6. Experimental CCDs of samples F, D, and E1 synthesized from the monomer feeds of the same composition at different conversions.

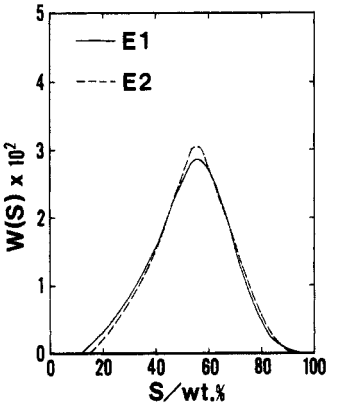

Figure 7. Experimental CCDs of samples E1 and E2 synthesized under similar conditions.

When the samples obtained from the monomer feeds of the same composition at different conversions are compared, the CCD becomes broader as one moves toward high S content, as the conversion increases (Figure 6). This may reflect the reactivity ratios of the macromonomer and MMA.

It is clear from Figure 7 that two samples synthesized under similar conditions (E1 and E2) have almost the same CCD. Samples B and F, which are low-conversion samples from the monomer feeds of the same composition, also have very similar CCDs (see Figures 5 and 6).

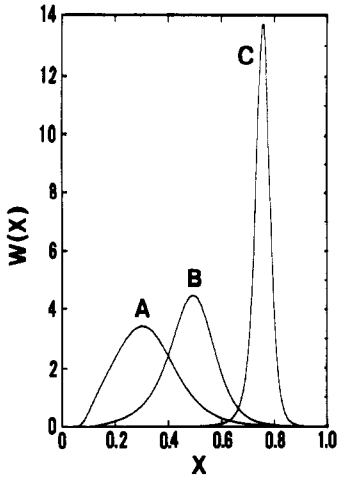

Figure 8. Theoretical CCDs of samples A–C calculated by using only the theory of the statistical CCD.

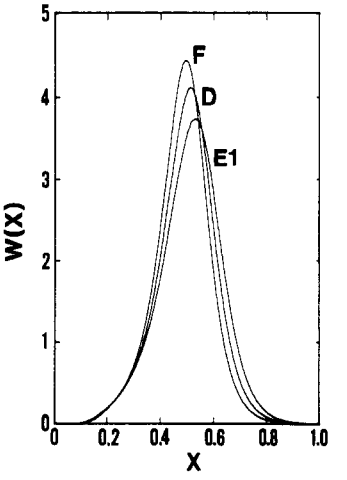

Figure 9. Theoretical CCDs of samples F, D, and E1 calculated by the combination of theories of the statistical CCD and the conversion CCD.

Theoretical Calculation of CCD. Theoretical CCDs were calculated for comparison with the CCDs obtained experimentally. It is known that a copolymer synthesized by statistical copolymerization has generally both the statistical CCD originating from the statistical nature of copolymerization and the conversion CCD caused by the drift of the monomer composition during the copolymerization process unless the copolymerization is azeotropic or the reactivity ratios are both unity. However, since the conversion CCD is negligible for low-conversion samples, only the statistical CCDs were calculated for samples A–C.

For the statistical CCD of graft copolymer synthesized by the macromonomer technique, two theories were proposed by Stejskal and Kratochvíl.[4,5] One theory is based on the statistics of random coupling of grafts to backbones, the other is obtained by modification of the Stockmayer theory statistical copolymers.[21] The latter theory is inadequate for samples with a small number of branches, whereas the former theory is applicable even to such samples. Since the number of branches is very small in the present samples, as shown in Table III, the former theory, where the most probable distribution of degree of polymerization was assumed for the backbone, was used for the present calculation, though the distribution of degree of polymerization of the backbone for the present samples is uncertain.

According to this theory,[4] the weight-base compositional distribution fraction $W(x)$ is given by

$$W(x) = \frac{r^2\bar{x}}{1-r^2\bar{x}}\left(\frac{1-\bar{x}}{(1-r)\bar{x}}+Q\right)\sum_{m=1}^{\infty} m^2\frac{[m(1-r)Q\exp(-Q)]^m}{m!}\frac{dQ}{dx}$$

$$Q = \frac{1}{1-r}\frac{(1-\bar{x})x}{\bar{x}(1-x)} \qquad (4)$$

where composition x is given by the weight fraction of the backbone part (MMA in the present calculation), $\bar{x}$ is the average value of x, m is the number of grafts in each copolymer molecule, and $r = 1/(m_n + 1)$. In these calculations, the parameters in Tables I and III were used. The calculated CCDs of samples A–C are shown in Figures 8 and 10, where an assumed molecular weight was used for sample C.

The conversion CCD should not be neglected for the middle- and high-conversion samples, because the reactivities of the two monomers are different for the present copolymer. For the conversion CCD, the weight-base compositional distribution fraction $g(x)$ is given by[22,23]

$$g(x) = \left|\left(\frac{y}{y_0}\right)^{\alpha}\left(\frac{y-1}{y_0-1}\right)^{\beta}\left(\frac{y-a}{y_0-a}\right)^{\gamma}\left(\frac{\alpha}{y}+\frac{\beta}{y-1}+\frac{\gamma}{y-a}\right)\times \frac{[y^2(r_Bt+r_A-1-t)+y(1+t-2r_Bt)+r_Bt]^2}{y^2(r_A+r_Bt^2-2r_Ar_Bt)+2ytr_B(r_A-t)+r_Bt^2}\right| \qquad (5)$$

where y and y_0 are weight fractions of MMA in the monomer feed at a given time and at zero time, respectively, r_A and r_B are the reactivity ratios of monomers A (MMA) and B (PS macromonomer), respectively, t is the ratio of molecular weights of the two monomers (100.11/12400), $\alpha = r_B/(1-r_B)$, $\beta = r_A/(1-r_A)$, $\gamma = (r_Ar_B-1)/[(1-r_A)(1-r_B)]$, and $a = t(1-r_B)/[t(1-r_B)+(1-r_A)]$. The instantaneous composition of the copolymer, x, can be calculated from y by using the copolymerization equation:

$$x = \frac{y^2(r_A-t)+yt}{y^2[t(r_B-1)+r_A-1]+y(1-2r_Bt+t)+r_Bt} \qquad (6)$$

If the conversion is not 100%, $g(x)$ must be normalized to the final conversion, ϕ_f. The relationship between the conversion, ϕ, and y is given by

$$\phi = 1-\left(\frac{y}{y_0}\right)^{\alpha}\left(\frac{y-1}{y_0-1}\right)^{\beta}\left(\frac{y-a}{y_0-a}\right)^{\gamma} \qquad (7)$$

If y_f denotes y at ϕ_f calculated by the above equation, the conversion CCD should have a range from x_0 to x_f, corresponding to y_0 and y_f, respectively. The total CCD of each sample was calculated by multiplying eqs 4 and 5, taking into account that x in eq 5 is the average composition of the instantaneous copolymer shown by $\bar{x}$ in eq 4. The reactivity ratios were estimated from the data for samples A–C and F in Table I by the Kelen–Tüdós method[24] as $r_A = 1.15-1.53$ and $r_B = 6\times10^{-5}$–1.3×10^{-3}. The reliability of the values is not very high, since all values of the base-molar macromonomer content are extremely low. In the actual calculations, $r_A = 1.15$ and $r_B = 0.001$ were used. For the other parameters, the experimental values shown in Tables I and III were used. The CCDs of samples F, D, and E1 thus calculated are shown in Figure 9, which should be compared with the CCDs in Figure 6. (The comparison between the theoretical CCDs of samples E1 and E2 is not illustrated, since the difference between the two CCDs was negligible.)

Comparison between Theoretical and Experimental CCDs. The experimental CCDs shown in Figure 5

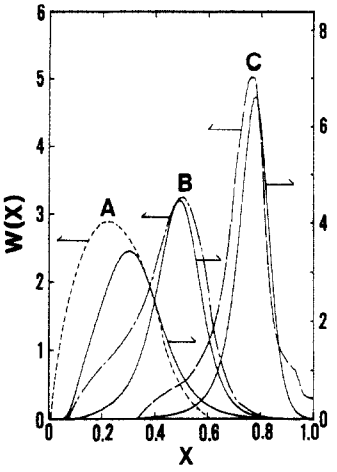

Figure 10. Theoretical CCDs (solid lines) for samples A and B (same as those in Figure 8) and for sample C, calculated by using an assumed value of M_n (7.2×10^4), and experimental CCDs (same as those in Figure 5) (broken lines).

and the theoretical CCDs in Figure 8 for low-conversion samples A–C have the common feature that the CCD of sample A extends a long tail toward the higher S content but have no long tail toward the lower S content, whereas the CCDs of samples B and C have longer tails in the lower S-content region. Also, as the macromonomer content increases, the CCD becomes sharper. The experimental CCDs are broader than the theoretical ones for all samples. This discrepancy may be due to the peak broadening in HPLC, which is important here just as it is in size-exclusion chromatography. The CCDs of poly(MMA-*stat*-S) determined by Sato et al. using HPLC were also broader than the theoretical.[9] Moreover, the CCDs may be spread by molecular weight dependence of sample elution and also by possible association of PS grafts at the verge of precipitation in the column.

In the experimental CCDs, the peak height gradually increases with the macromonomer content. On the other hand, in theoretical CCDs, the height of the CCD of sample C is exceptionally large; i.e., the CCD of sample C is very sharp compared to that of samples B and A. The theoretical ratio of the heights of CCDs of samples C and B is 2.67, whereas it is 1.54 experimentally. If the degree of polymerization of the backbone is decreased, the CCD is broadened. In Figure 10, the theoretical CCD calculated for sample C by assuming $M_n = 7.2 \times 10^4$, which was selected for the height ratio of 1.5, and the same CCDs for samples A and B as those in Figure 8 are shown together with the experimental results (broken lines). The difference between theoretical and experimental CCDs is similar for B and C. However, the assumed value of M_n is only about a quarter of the experimental value. It is not clear why the theoretical CCD calculated by using the experimental value of M_n is much sharper than the experimental one only for sample C, since M_n is measured with good reliability.

For sample A, the theoretical CCD loses a large part in the lower S-content region and shifts to the higher S-content region as compared with the experimental result, though the positions of both CCDs are not very different for samples B and C. The discrepancy between both CCDs of sample A may be due to a problem in the theory. The summation in eq 4 is carried out from $m = 1$ to ∞, omitting components with no graft in the calculation. Thus, the theoretical average composition, $\bar{x}_{th}$ is obtained by integration of $xW(x)\,dx$, leading to

$$\bar{x}_{th} = \int_0^1 xW(x)\,dx = \frac{(1-r^2)\bar{x}}{1-r^2\bar{x}} \qquad (8)$$

where $\bar{x}$ is the average composition. The smaller the value of m_n is, the larger the difference between $\bar{x}$ and $\bar{x}_{th}$ is. Another reason for the discrepancy for sample A may arise because the main peak is shifted to the lower S-content side in the experimental CCD, as a result of the comparatively large amount of PS in sample A mentioned in the section Chromatograms by HPLC.

The experimental CCDs of samples B and C have shoulders on the tails in the lower S-content sides, though the theoretical CCDs have no shoulder. The reason for the shoulders in the experimental CCDs is not obvious. However, the accuracy of the determination of the relative concentration, H_i, is not high in the tail region, since the very small value of h_i is converted to the larger value of H_i dividing h_i by X_i, which is smaller than unity. Moreover, the shoulders may also arise from the uncertainty of the calibration in the section Converting Chromatograms to CCDs, the molecular weight dependency, and the association as mentioned above. The shoulder of sample C in the higher S-content region is the result of the subpeak due to pure PS.

When Figures 6 and 9 are compared for samples F, D, and E1 obtained at different conversions, the theoretical CCDs agree with the experimental results that the CCD becomes broader toward the high S-content region as the conversion increases. This may arise from the difference between the reactivities of the macromonomer and the small monomer, MMA. In our previous paper,[17] we stated that the reactivity ratio of the macromonomer was almost the same as that of the small methacrylate monomers. However, from the present results, it can be concluded that the reactivity of the macromonomer end group is similar to that of methacrylates with a longer ester group. Diffusion control may also contribute to the lower reactivity ratio. Comparing Figures 6 and 9, the experimental CCDs are broader than the theoretical for these samples also. The differences between both CCDs may be ascribed partially to the inaccurate values of monomer reactivity ratios.

In conclusion, HPLC by reversed-phase adsorption mode yields approximate CCDs for poly(methyl methacrylate)-*graft*-polystyrene prepared by the macromonomer technique, even though the certainty of the results is not very high. The graft copolymers have broad CCDs compared with statistical copolymers of the corresponding small monomers, as predicted theoretically. Moreover, from the CCDs of the samples obtained at different conversion, it was indicated that the reactivity of the macromonomer having a methacryloyl end group is smaller than that of MMA.

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