Chemical Composition Distribution of Poly(methyl methacrylate)-*graft*-polystyrene Prepared by a Macromonomer Technique: Effect of Graft Length

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ABSTRACT: The chemical composition distributions (CCDs) of poly(methyl methacrylate)-*graft*-polystyrene samples prepared from the polystyrene macromonomers with different molecular weights were determined by high-performance liquid chromatography (HPLC) based on the reversed-phase and normal-phase adsorption modes. The effect of graft length on the CCDs was studied and compared to theoretical prediction. Using three ω-methacryloylpolystyrene macromonomers with molecular weights ($M_n = 3.0 \times 10^3$, 5.8×10^3, and 1.24×10^4), graft copolymers of different compositions were prepared by radical copolymerization to low conversions. These were analyzed by HPLC using a reversed-phase octadecyl-modified silica-gel column and a linear gradient of tetrahydrofuran and acetonitrile. Some samples were analyzed using also a normal-phase cyano-modified silica-gel column and a linear gradient of tetrahydrofuran and *n*-heptane. The chromatograms were converted to CCDs of the samples by an optimization method. Good agreements between CCDs obtained by both modes demonstrated that the effect of the molecular weight distribution on the CCD is negligible. From the CCDs obtained in the present and previous works, it was shown that the CCD is broadened as the graft length increases, in copolymer samples with a similar composition, in accordance with the theoretical prediction of Stejskal and Kratochvíl.

Introduction

Studies of syntheses and applications of graft copolymers prepared from macromonomers and ordinary small comonomers have recently increased. For these kinds of graft copolymers, the branches are approximately uniform but the backbones are heterogeneous in the degree of polymerization. From this structural feature, very broad chemical composition distributions (CCDs) and other interesting characteristics of CCDs may result, as predicted theoretically.[1–3] However, only a few studies on the determination of CCDs of the graft copolymers have been published.[4–6] Stejskal *et al.*[4] have shown that the CCD of poly(methyl methacrylate)-*graft*-poly(dimethylsiloxane) prepared by the macromonomer technique can be determined by demixing solvent fractionation. However, the method may not be applied generally, since it is very difficult to find a suitable pair of demixing solvents for a given graft copolymer. On the other hand, high-performance liquid chromatography (HPLC) based on the adsorption mechanism can be applied readily not only for linear statistical copolymers but also for graft copolymers.[5–7]

In our previous paper,[5] HPLC based on the reversed-phase adsorption mechanism was applied to determine the CCDs of poly(methyl methacrylate)-*graft*-polystyrene (PMMA-*graft*-PS) samples, which were prepared by statistical copolymerization of a ω-methacryloylpolystyrene macromonomer and MMA. From the results, it was shown that (a) the CCDs of the graft copolymer samples were very broad even for low-conversion samples compared with those of the statistical copolymers obtained from conventional small monomers, (b) the CCD became broader as the macromonomer content decreased, and (c) the CCD became broader as the conversion increased. These results are in accordance with the results obtained in another of our studies of PMMA-*graft*-PS prepared from ω-(*p*-vinylbenzyl)polystyrene macromonomer and MMA,[6] and they agree also with theoretical predictions.[1–3]

Another important factor controlling the CCDs of the present type of copolymers may be the length of the graft, that is, the molecular weight of the macromonomer. However, the effect of graft length on CCDs has not yet been demonstrated experimentally. In the present work, the CCDs of PMMA-*graft*-PS with different graft lengths were determined by HPLC of reversed-phase and normal-phase adsorption modes and compared with theoretical predictions. It was confirmed that the shorter the graft length, the sharper is the CCD, for graft copolymers with a similar average composition, in accordance with theoretical prediction.

Experimental Section

Synthesis of Graft Copolymer. Polystyrene macromonomers with methacryloyl end groups were synthesized as in previous work.[5] Two kinds of macromonomers were prepared. The number-average molecular weights (M_n) determined by size-exclusion chromatography (SEC) were 3.0×10^3 and 5.8×10^3, respectively. The ratio of weight-average and number-average molecular weights, M_w/M_n, by SEC was 1.05 for both macromonomers. The SEC measurement was carried out by using HLC-802A of Tosoh Co. Ltd. (Tokyo) and TSK-gel G5000H–G3000H columns (Tosoh Co. Ltd.) in chloroform at 30 °C. The end functionalities, which were measured by ^{1}H-NMR (Gemini-200 of Varian, in CDCl, 200 MHz), were 97% and 100% for the respective macromonomers.

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Table 1. Synthesis of Graft Copolymer Samples

sample code	feed: macromonomer g	feed: macromonomer wt %	feed: MMA (g)	feed: AIBN (g)	feed: benzene (mL)	reaction time (h)	convn (wt %): macromonomer	convn (wt %): total	copolymer: macromonomer content (wt %)
30-A	1.0170	30.6	2.3053	0.0230	11	2.5	14.4	21.0	27.5
30-B	1.4894	50.6	1.4548	0.0153	10	2.5	5.4	7.8	44.0
30-C	1.9882	74.7	0.6742	0.0073	8.9	2.5	6.6	8.3	68.6
30-D	0.4956	49.8	0.4990	0.0051	3.3	12.0	46.9	54.1	45.4
30-E	0.4979	50.2	0.4937	0.0051	3.3	48.0	85.2	92.1	48.1
30-F	2.0168	50.2	2.0046	0.0204	13.3	1.5	6.4	6.4	42.9
58-A	0.9775	30.1	2.275	0.0228	11	2.5	15.3	20.5	26.1
58-B	1.50	50.0	1.50	0.0150	10	2.5	9.3	11.3	41.5
58-C	1.9905	74.6	0.6765	0.0069	8.9	2.5	6.9	7.5	69.4

Table 2. Gradient Protocols for HPLC

No. 1 (Reversed-Phase Mode, 30- and 58-Series)								
time/min	0	5	6	21	26	27	37	52
THF/(vol %)	10	10	20	60	60	100	100	10

No. 2 (Normal-Phase Mode, 30-Series)							
time/min	0	1	16	21	22	32	46
THF/(vol %)	5	40	80	80	100	100	5

The graft copolymer samples were prepared by radical copolymerization of the macromonomers with MMA in benzene as in the previous work,[5] in which the macromonomer with $M_n = 1.24 \times 10^4$ was used. The graft copolymers were purified by precipitation into a mixture of cyclohexane and petroleum ether (volume ratio = 3:2). The purification was repeated four times for each sample. Removal of macromonomers was checked by SEC. The compositions of the copolymerization mixtures, the reaction times, the conversions, and the compositions of the graft copolymers are summarized in Table 1. The average composition of the graft copolymer was determined from ^{1}H-NMR spectra. The conversion of the macromonomer was calculated from the ratio of SEC peak areas of the unreacted macromonomer and the total crude reaction mixture detected by an ultraviolet (UV) detector. The number-average molecular weight was determined by a high-speed membrane osmometer, Model 231 of Wescan Instruments, Inc. (Santa Clara, CA), for a benzene solution at 20 °C.

HPLC Measurements. For the reversed-phase mode measurements, the HPLC instrument was composed of a controller SCL-6A, two pumps of LC-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 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). These are the same as those in the previous work.[5] The eluent was a mixture of tetrahydrofuran (THF) and acetonitrile (ACN), both of which were of chromatographic grade of Wako Pure Chemical Industries, Ltd. (Tokyo). The gradient protocol of the eluent was No. 1 in Table 2.

For the normal-phase mode measurements, chromatograms were obtained only for the 30-series samples, where the HPLC instrument consisted of two pumps of Model 510, a controller Model 680 (Waters), a UV detector UV-8 Model II (Tosoh), and a column thermostat HLC-802A (Tosoh). A prepacked column of cyano-modified silica gel (CN) was used: TSK-gel CN-80TS (Tosoh; column length 15 cm, inner diameter 0.46 cm, particle diameter of the starting silica gel 5 μm, and micropore diameter of the silica gel 8 nm). The eluent was a mixture of THF and *n*-heptane, both of which were chromatographic grade from Wako Pure Chemical Industries, Ltd. The gradient protocol of the eluent was No. 2 in Table 2.

For both modes, 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 0.5 mg cm^{-3}. The wavelength of the UV detector was 254 nm. Since a part of the sample injected remained in the column as reported elsewhere,[8] the respective chromatograms were obtained after the recovery of the base line by repeating the blank elutions of the same protocols as those used in the measurements.

Table 3. Characteristics of Graft Copolymer Samples

sample code	macromonomer content (wt %)	M_n ($\times 10^{-4}$)	m_n[a]	P_n[b]
30-A	27.5	11.7	10.73	858
30-B	44.0	11.1	16.28	637
30-C	68.6	11.2	25.62	377
30-D	45.4	11.0	16.64	617
30-E	48.1	8.1	13.00	433
30-F	42.9	9.2	13.17	537
58-A	26.1	9.2	4.14	683
58-B	41.5	9.8	7.00	580
58-C	69.4	6.2	7.42	197

[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. The average composition (weight fraction of styrene monomeric units), the number-average molecular weight, the number-average degree of polymerization of the backbone (P_n), and the number-average number of grafts per copolymer molecule (m_n) are summarized in Table 3 for the respective samples.

For all samples, the macromonomer contents of the copolymers are a little smaller than those of the monomer feeds (Table 1). The conversions of the macromonomers are smaller than those of the total monomers. This tendency was observed both in the present study and in a previous study.[5] For the 30-series samples obtained from the same feed composition at different conversions, the composition of the copolymer tends to approach the feed composition as the conversion increases.

Reactivity ratios $r_{MMA} = 1.15$ and $r_{macro} = 0.001$ were estimated from data for the low-conversion samples of 30-, 58-, and 124-series by the Kelen–Tüdós method.[9] The accuracy of the value r_{macro} is low, since the value was calculated only for data in the region of very low mole fraction of the macromonomer. Although various data on the copolymerization reactivities of the macromonomers have been reported,[10] it appears from these results that the copolymerization reactivity of the methacryloyl end group in the macromonomer is not exactly equal to that of MMA but is rather similar to those of ethyl methacrylate (EMA) or butyl methacrylate (BMA).[11]

Determination of CCDs. The chromatograms obtained by the reversed-phase mode are shown in Figures 1–3 for samples 30A–C, 30D–F, and 58A–C, respectively, and those for samples 30A–C by the normal-phase mode are shown in Figure 4. From the chromatograms in Figures 1, 3, and 4, it can be concluded that the lower the PS macromonomer contents, the earlier the samples elute in the reversed-phase mode

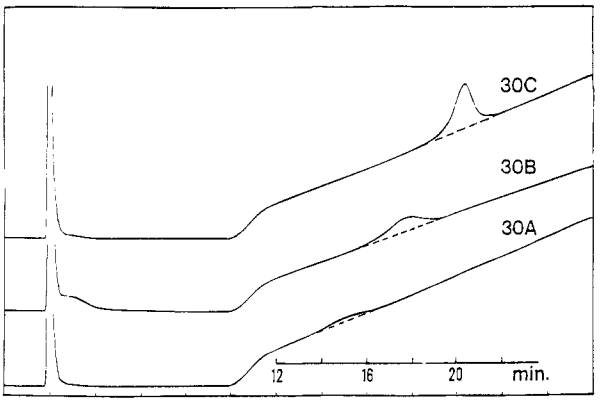

Figure 1. Chromatograms obtained by the reversed-phase mode for samples 30-A–C.

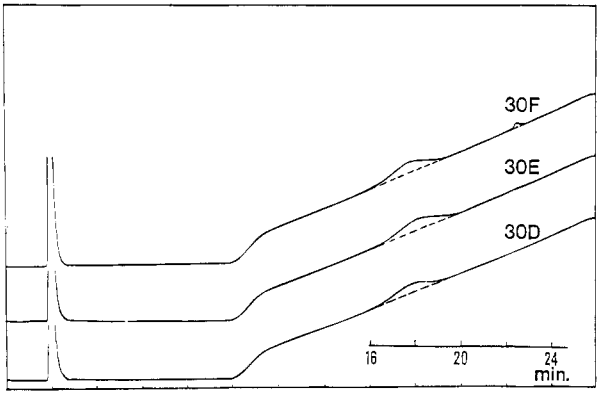

Figure 2. Chromatograms obtained by the reversed-phase mode for samples 30-D–F.

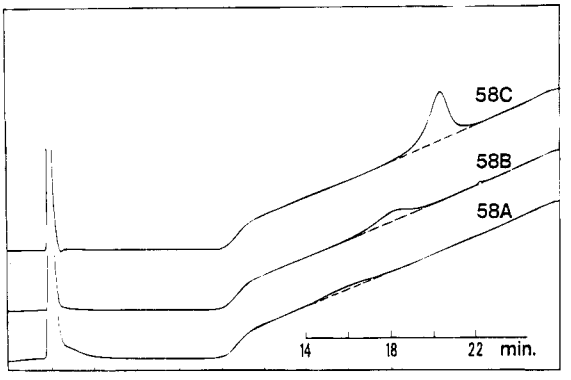

Figure 3. Chromatograms obtained by the reversed-phase mode for samples 58-A–C.

and the later in the normal-phase mode. This is in accordance with results in our previous papers.[5,6] Also in the present case, it was shown that the total peak areas measured by a UV detector were proportional to the products of the sample concentrations and the macromonomer contents (weight fraction), as in the previous work. Thus, the chromatograms were converted to the CCDs in the same manner as in the previous paper.[5]

The relationships between the elution time at the peak position (V_p) of each low-conversion sample (A–C) and the average macromonomer content of the sample (X_0) were approximated by linear equations for the reversed-phase mode and by a quadratic equation for the normal-phase mode. Each position of the chromatogram (V_i) was converted to the composition (X_i) by the equation, and the peak height of the position was converted to the relative concentration of the component. The average composition (X_I) was calculated for

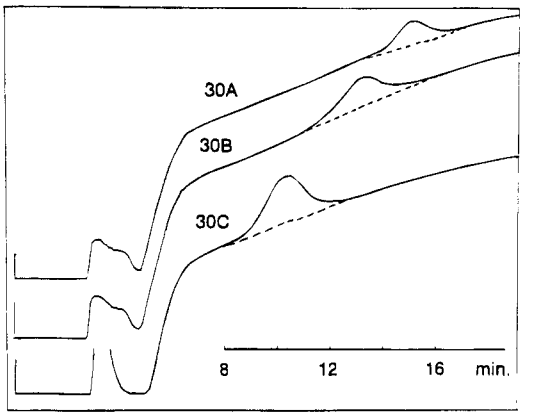

Figure 4. Chromatograms obtained by the normal-phase mode for samples 30-A–C.

each sample from these results as a first approximation. Then, the average elution time (V_I) for each sample was calculated using the equation substituting X_I for X_0. Using the equation between V_I and X_0, the average composition (X_{II}) was calculated in the same manner. This procedure was repeated several times. The average compositions thus calculated approached, but did not necessarily agree with, the original values. The equations converged in the fourth iteration for the 30-series, in the third iteration for the 58-series by the reversed-phase mode, and in the sixth iteration for the 30-series by the normal-phase mode. These equations were then used to calculate the CCDs for all samples of the respective series. Ordinates of the CCDs were normalized by taking into account the slopes of the calibration equations. In Figure 5 (solid line), the CCDs thus determined for low-conversion samples (A–C) of both series were illustrated together with the CCDs for the low-conversion samples of the 124-series reproduced from the previous paper.[5] The CCDs for the 30-series samples A–C by the normal-phase mode are shown in Figure 6 together with those by the reversed-phase mode. The CCDs of the different-conversion samples of 30-series (30-D–F) by the reversed-phase mode were shown in Figure 7.

The differences between the average compositions thus calculated and the original ones are −1.4 to +2.9% for the 30-series and −3.2 to +4.8% for the 58-series, respectively, in the results by the reversed-phase mode. The differences are 0–0.1% for the 30-series in the results by the normal-phase mode. Although the certainty of the absolute values for the CCDs is not very high, the CCDs thus obtained may be adequate for the following discussion.

Calculation of Theoretical CCD. For comparison, the theoretical CCDs were calculated by the same manner as in the previous paper.[5] Copolymer samples have, in general, both statistical and conversion CCDs. For calculation of the statistical CCDs, the theory based on the statistics of random coupling of grafts to backbones proposed by Stejskal and Kratochvíl[1] was used. The conversion CCDs were calculated using the weight-base compositional distribution function introduced by Stejskal *et al.*[12] The total CCD of each sample was calculated by multiplying both distribution functions. In these calculations, $r_A = 1.15$ and $r_B = 0.001$, the same as in the previous work,[5] and the values of average copolymer composition, the average number of grafts per molecule (m_n), the original feed composition, and the total conversion for each sample shown in Tables 1 and 3 were used. The CCDs thus calculated for the low-

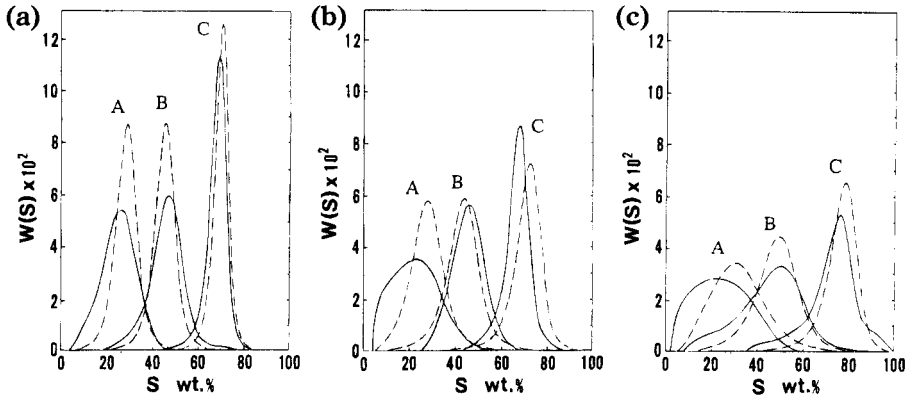

Figure 5. Experimental CCDs obtained by the reversed-phase mode and the theoretical CCDs: (—) experimental; (– –) theoretical. (a) 30-series, (b) 58-series, (c) 124-series.

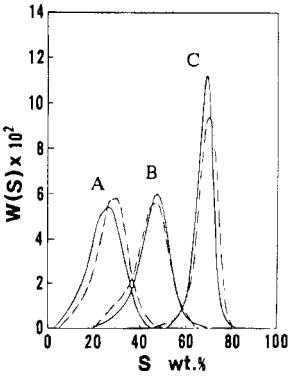

Figure 6. Experimental CCDs obtained by the reversed- and normal-phase modes for samples 30-A–C: (—) reversed-phase mode; (– –) normal-phase mode.

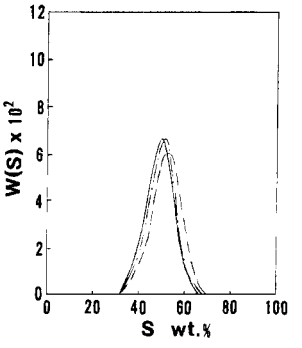

Figure 7. Experimental CCDs obtained by the reversed-phase mode for samples 30-D–F. (—) F (conversion 6.4 wt %); (– · –) D (54.1 wt %), (– –) E (92.1 wt %).

conversion samples of the respective series are illustrated by dashed lines in Figure 5 together with the experimental results (solid line). In Figure 8, the CCDs for the different conversion samples of the 30-series are shown, which should be compared with those in Figure 7.

Discussion of CCD. The experimental CCDs of the 30-series samples determined by the reversed-phase and the normal-phase modes are almost in agreement with one another as shown in Figure 6. Such agreement was demonstrated also for the samples prepared for ω-(*p*-vinylbenzyl)polystyrene macromonomer in the previous paper.[6] This agreement indicates that the molecular weight (MW) effect on the CCDs obtained by the present method is negligible. If the MW effect were significant, the samples should be eluted out from the components of higher PS content and lower MW to those of lower PS content and higher MW in the normal-phase mode, while from the components of higher MMA content and lower MW to those of lower MMA content and higher MW in the reversed-phase mode. Therefore, if both CCDs agree with one another, the MW effect is negligible and the CCDs are not distorted by the MW distributions.

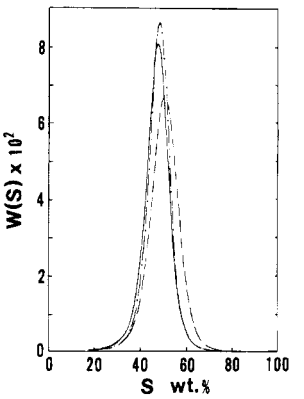

Figure 8. Theoretical CCDs for samples 30-D–F: (—) F (conversion 6.4 wt %); (– · –) D (54.1 wt %); (– –) E (92.1 wt %).

To see the effect of the graft length on the CCD, the CCDs of the samples with similar macromonomer contents (indicated by the same symbols A–C, respectively) were compared with one another in Figure 5. It was proved experimentally (solid lines) that the CCD became broader as the graft length (the molecular weight of the macromonomer) increased, in samples of similar average composition. The same conclusion was drawn also from the theoretical calculations (dashed lines).

Qualitatively, the agreements between both CCD curves are fairly good. However, when quantitatively comparing the experimental CCDs with theory, the experimental ones are somewhat broader. This may be ascribed in part to the peak broadening in HPLC and in part to the uncertainty of the monomer reactivity ratio, the average number of grafts, and degree of polymerization of the backbone used in the calculation. The peak positions are not in good agreement between the two curves. This may be ascribed both to the accuracy of the calibration discussed in the section on determination of CCDs and the values of the reactivity ratio used in the calculation. For sample A, the theoretical CCDs shift to a higher macromonomer content region than the experimental CCDs, losing a large part of the lower macromonomer content region. This may be caused by the theoretical problem pointed out in our previous paper.[5]

The features of the CCD mentioned in the Introduction were confirmed again for the present samples. That is, (a) the CCDs of the present samples are very broad compared with those of low-conversion samples of linear statistical copolymers,[13-15] (b) the CCD becomes broader as the macromonomer content decreases, and (c) the CCD becomes broader toward the region of higher macromonomer content as the conversion increases, which agrees with the arguments debated in the section on average characteristics.

Conclusions

(1) The CCDs of the graft copolymers from ω-methacryloylpolystyrene macromonomer and MMA were determined by HPLC using both reversed-phase and normal-phase modes. The CCDs obtained by the two modes are in good agreement, indicating that the effect of the molecular weight distribution on the CCD is negligible under the present conditions of the HPLC measurement.

(2) The CCDs of the samples obtained from the macromonomers of different molecular weights became broader as the graft length increased when comparing copolymers with equal average composition, as predicted theoretically.

(3) Other characteristics of the CCDs determined in the present work were well described by a theoretical calculation using M_n and reactivity ratio data.

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