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Determination of chemical composition distribution of poly(methyl methacrylate)-*graft*-polystyrene prepared from ω-*p*-vinylbenzyl polystyrene macromonomer by adsorption high-performance liquid chromatography

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Chemical composition distributions (CCDs) of poly(methyl methacrylate)-*graft*-polystyrene samples with different compositions and conversions synthesized from methyl methacrylate and ω-*p*-vinylbenzyl polystyrene macromonomer were determined by high-performance liquid chromatography using both reversed-phase and normal-phase adsorption modes. The good agreement between CCDs obtained by both modes showed that the molecular-weight effect on the CCDs is negligible. All samples have broad CCDs. As the macromonomer content increases, the CCD becomes sharper. These results are in accordance with the theoretical predictions. As the conversion increases at the same feed composition, the CCD becomes broader towards the low-macromonomer-content side, which is in contrast to the CCDs of the samples obtained previously from ω-methacryloyl polystyrene macromonomer.

(Keywords: CCD determination; PMMA-*g*-PS; h.p.l.c.)

INTRODUCTION

A large number of papers have been published on the copolymerization of macromonomers with small comonomers and the applications of graft copolymers thus prepared. Although the chemical composition distributions (CCDs) of such graft copolymers predicted theoretically have very interesting features (for example, the CCDs are very broad compared with those of statistical copolymers both monomers of which are ordinary small monomers[1,2]), only a few studies of the CCDs of such graft copolymers have been reported[3,4]. In our previous work, the CCDs of poly(methyl methacrylate)-*graft*-polystyrene samples prepared by radical copolymerization of ω-methacryloyl polystyrene (PS) macromonomer and methyl methacrylate (MMA) were determined by high-performance liquid chromatography (h.p.l.c.) of reversed-phase adsorption mode[4]. The CCDs had features in accordance with the theoretical predictions. Moreover, it was shown that the CCDs of the samples obtained from the same monomer composition become broader towards the high-macromonomer-content region, as the conversion increases.

It is very difficult, in general, to evaluate the exact monomer reactivity ratios from the compositional analysis in the copolymerization systems of conventional small monomers with macromonomers, because only data in the region of very low (molar basis) content of macromonomers can be obtained. On the other hand, the shift of the CCDs caused by the conversion is sensitive to the reactivity ratio of the small comonomer. That is, it can be illustrated from the theoretical calculation that the shift to the higher-macromonomer-content region means that the reactivity ratio of the small comonomers (r_{sc}) is larger than one ($r_{sc} > 1$), and vice versa for the reverse direction ($r_{sc} < 1$). The CCDs in the previous work clearly shifted to the higher-macromonomer-content region in accordance with the fact that the reactivity ratio of MMA (r_{MMA}) determined by the compositional analysis is somewhat larger than one ($r_{MMA} = 1.15$).

The lowering of the copolymerization reactivity of the macromonomer compared with the corresponding small monomer may be explained partially by the dynamic excluded-volume effect and also by the incompatibility effect between the macromonomer and the comonomer main chain[5,6]. However, it is difficult to draw a general picture on the copolymerization reactivity of the macromonomer at present, since various data, which

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seem to indicate different effects of the large size of macromonomers, have been reported[7]. Therefore, it is very interesting to determine the CCDs of the same kind of graft copolymer samples prepared from PS macromonomer with another reactive end-group, that is, ω-*p*-vinylbenzyl PS macromonomer.

There is a problem with the reliability of the CCDs determined by the present method. That is, the CCD may be distorted by the molecular-weight distribution, if the elution volumes of the copolymer components depend not only on chemical compositions but also on molecular weights. In the case of linear statistical copolymers, the molecular-weight (*MW*) effect was examined experimentally by using samples fractionated by molecular weight[8]. The *MW* effect was negligible in the *MW* region higher than several 10^4. For the graft copolymers, however, the *MW* effect cannot be examined directly, since samples with the same composition and the same architecture but different molecular weights cannot be obtained. The *MW* effect may be examined for samples with asymmetric CCDs by comparing the results obtained by the normal-phase and the reversed-phase modes, since the samples should elute from components of higher PS content and lower *MW* to those of lower PS content and higher *MW* in the normal-phase mode, but from components of higher MMA content and lower *MW* to those of lower MMA content and higher *MW* in the reversed-phase mode. Both CCDs should be in accordance with one another, if the *MW* effect is negligible.

In the present study, the CCDs of PMMA-*graft*-PS prepared from ω-*p*-vinylbenzyl (VB) PS macromonomer were determined by adsorption h.p.l.c. of normal-phase and reversed-phase modes, and compared with one another and also with the CCDs calculated theoretically.

EXPERIMENTAL

Synthesis of graft copolymer

The PS macromonomer having an ω-*p*-vinylbenzyl end-group was synthesized by living anionic polymerization as in a previous paper[9]. The number-average molecular weight (M_n) of the macromonomer determined by size exclusion chromatography (s.e.c.) is 4200. The s.e.c. measurement was carried out by using HLC-802A and TSK-Gel, G5000H–G3000H columns (Tosoh Co. Ltd) in chloroform at 30°C. The end functionality was 0.95, which was determined by ^{1}H n.m.r. (Gemini-200, Varian; in $CDCl_3$, 200 MHz) and confirmed by the maximum conversion in the radical copolymerization with MMA.

Graft copolymer samples were synthesized by statistical copolymerization of the PS macromonomer with MMA comonomer using 2,2′-azobisisobutyronitrile (AIBN) in benzene at 60°C. The copolymerizations were carried out with three different feed compositions (samples A–C) and three different conversions (samples B, D and E), as shown in *Table 1*. The copolymerization products were precipitated into a mixture of cyclohexane and petroleum ether (typical mixing ratio 3:2) to remove unreacted PS macromonomer. Removal of the PS macromonomer was checked by s.e.c. The isolated copolymer samples were freeze-dried in benzene. Methyl methacrylate, AIBN and solvents are commercially available. MMA monomer was dried with Na_2SO_4 after removal of the inhibitor with 5% aqueous NaOH and distilled over calcium hydride under reduced pressure just before the copolymerization. Benzene was dried with sodium wire and distilled under nitrogen atmosphere.

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 n.m.r. spectra. Conversions of the macromonomer in *Table 1* were calculated from s.e.c. 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 (u.v.) 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 20°C.

H.p.l.c. measurements

For the reversed-phase mode measurements, the h.p.l.c. instrument was composed of two LC-6A pumps, an SCL-6A controller, an SPD-6A u.v. detector (Shimadzu Corp.) and an SSC-3510 column thermostat (Senshu Scientific Co. Ltd). A prepacked column of butyl-modified silica gel (C4) was used: μbondasphere 5μ C4-100A (Waters) (column length, 15 cm; inner diameter, 0.39 cm; particle diameter of the starting silica gel, 5 μm; and micropore diameter of the silica gel, 10 nm). The eluent was a mixture of tetrahydrofuran (THF) and acetonitrile,

Table 1 Synthesis of graft copolymer samples

Sample code	Feed					Reaction time (h)	Conversion of macromonomer (wt%)	Copolymer[a]	
	Macromonomer[b] (g)	(wt%)	MMA (g)	AIBN (g)	Benzene (ml)			Macromonomer content (wt%)	M_n ($\times 10^{-4}$)
A	1.0	30.3	2.3	0.0236	10	2.0	20.2	46.6	13.8
B	1.5	50.0	1.5	0.0370	15	2.0	18.3	70.3	9.7
C	2.0	74.9	0.67	0.0501	20	2.0	16.5	82.6	6.4
D	0.5	50.0	0.5	0.0123	5	6.0	36.8	65.8	7.8
E	0.5	50.0	0.5	0.0123	5	24.0	95.9	63.0	7.3

[a] The values measured after removal of the unreacted macromonomer
[b] M_n of the macromonomer is 4200

Table 2 M_n, m_n and P_n of graft copolymer samples

Sample code	M_n ($\times 10^{-4}$)	m_n[a]	P_n[b]
A	13.8	15.3	751
B	9.7	16.2	303
C	6.4	12.6	124
D	7.8	12.2	279
E	7.3	11.0	282

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

both of which were of chromatographic grade from Wako Pure Chemical Industries Ltd. The gradient programme of the eluent was as follows:

Time (min)	0	15	20	21	31	46
THF (vol%)	1	55	55	100	100	1

The sample fractionation was carried out in the region of the linear gradient from 1 to 55 vol% THF.

For the normal-phase mode measurements, the h.p.l.c. instrument was composed of two model 510 pumps, a model 680 controller (Waters), a model 875-UV u.v. detector (Jasco) and an HLC-802A column thermostat (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 of chromatographic grade from Wako Pure Chemical Industries Ltd. The gradient program of the eluent was as follows:

Time (min)	0	1	16	21	22	32	47
THF (vol%)	5	40	80	80	100	100	5

The sample fractionation was carried out in the region of the linear gradient from 40 to 80 vol% THF.

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 0.3 mg cm^{-3}. The wavelength of the u.v. detector was 254 nm. The present combinations of columns and solvent pairs for both modes were effective for the compositional fractionation of the samples of poly(MMA-*stat*-S)[8]. The sample measurements were carried out after recovery of baseline following several rinses with the blank gradient elutions for both modes.

RESULTS AND DISCUSSION

Average characteristics

Feed compositions, average copolymer compositions, conversions of the macromonomer and M_n values of the copolymers obtained by osmometry are shown in *Table 1*. 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 2*.

As seen in *Table 1*, the macromonomer contents of the graft copolymers are larger than those in feeds (samples A, B and C), but decrease and approach the feed value as the conversion increases (samples B, D and E). This indicates that the relative reactivity of the macromonomer is larger than that of MMA. *Tables 1* and *2* show that, as the macromonomer content increased, M_n and P_n become smaller. This may be due to the decrease in the total monomer concentration by increase in the solvent amount. Irrespective of the increase of the macromonomer content, m_n of samples A, B and C are almost the same because of decrease of P_n. The large changes of P_n and m_n are not observed also for the high-conversion samples D and E.

Chromatograms by h.p.l.c.

Figures 1 and *3* show the chromatograms for the samples A, B and C at different feed compositions obtained by the reversed-phase adsorption systems and by the normal-phase adsorption systems, respectively. The chromatograms obtained by the reversed-phase and normal-phase adsorption systems for samples B, D and E at different conversions are shown in *Figures 2* and *4*, respectively.

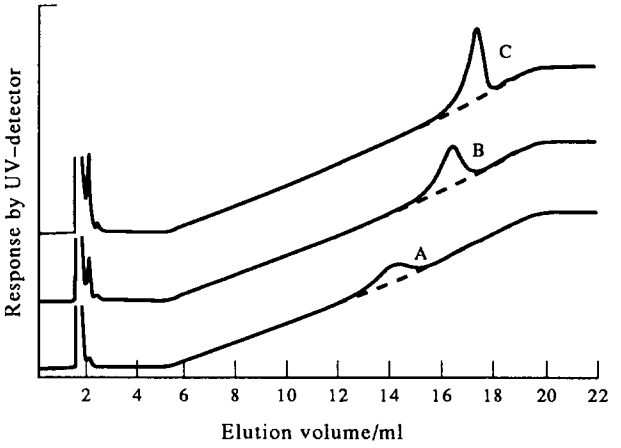

Figure 1 Chromatograms of samples A, B and C obtained by the reversed-phase mode

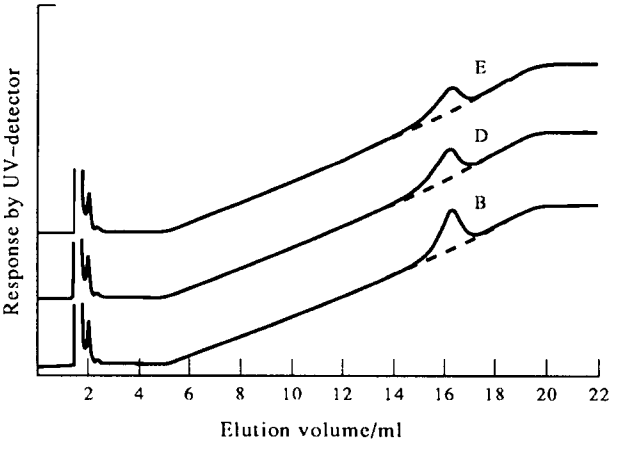

Figure 2 Chromatograms of samples B, D and E obtained by the reversed-phase mode

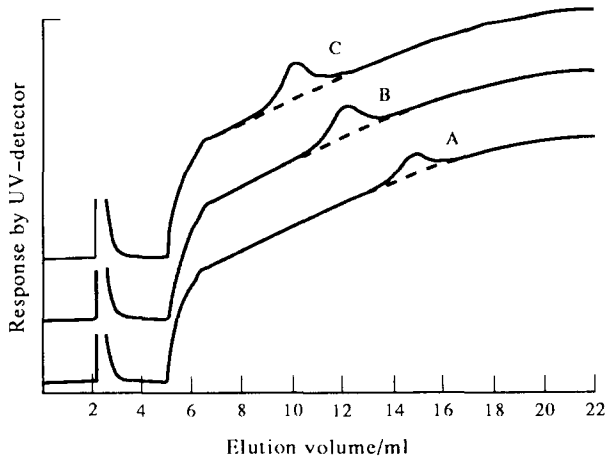

Figure 3 Chromatograms of samples A, B and C obtained by the normal-phase mode

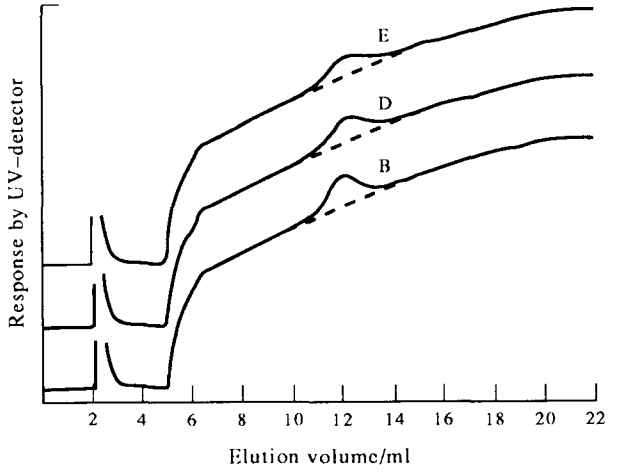

Figure 4 Chromatograms of samples B, D and E obtained by the normal-phase mode

From the chromatograms in *Figures 1* and *3*, it can be concluded that, the lower the PS macromonomer contents, the earlier the graft copolymer samples eluted in the reversed-phase mode, and the later in the normal-phase mode. This is in accordance with the case of the linear poly(MMA-*stat*-S)[8,10]. All samples in *Figures 1–4* have broad peaks irrespective of the conversion and composition.

Converting chromatograms to CCDs

The peak areas of the chromatograms of samples A–C measured by u.v. detector divided by the concentrations were approximately proportional to the PS macromonomer contents, as in the previous paper[4]. Thus, the CCDs were obtained from the chromatograms in the same manner as in the previous paper. The elution time at the peak position (V_p) for each sample is plotted against the average PS macromonomer content of the sample (X_0) in *Figures 5* and *6* (full curves).

For the results obtained by the reversed-phase mode, the relationship was approximated by a linear equation. However, this equation cannot be used to convert each position (V_i) to the composition (X_i) as it stands, since the compositions at the peak positions do not necessarily correspond to the average compositions of the respective samples. As a first approximation, V_i was converted to X_i by a linear equation. Then, the peak height of the position was converted to the relative concentration of the component. The average macromonomer content of each sample (X_I) was calculated from these results. Next, the average elution volume (V_I) for each sample was obtained from the equation by substituting X_I for X_0. Using the linear equation between V_I and X_0, V_i was converted to X_i and then the average macromonomer content (X_{II}) was calculated. Then, the same procedure was repeated several times. The average macromonomer contents thus calculated approached but did not necessarily agree with the original values. In the third calculation, the equation converged and the values nearest to X_0 were obtained for the respective samples. Then, the equation (broken curve in *Figure 5*) was used to calculate the CCDs for all samples. The ordinates of the CCDs were normalized by taking into account the slope of the equation. The CCDs thus obtained for samples A–C and samples B, D and E are illustrated in *Figures 7* and *8*, respectively. In the figures, the subpeaks of the chromatograms corresponding to pure PS were excluded and the distribution curves were renormalized.

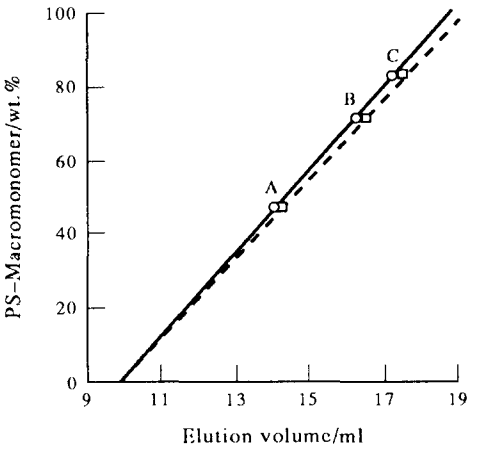

Figure 5 Calibration curves between elution volume and PS macromonomer content of the first equation (□) and the third equation (○) for the results by the reversed-phase mode

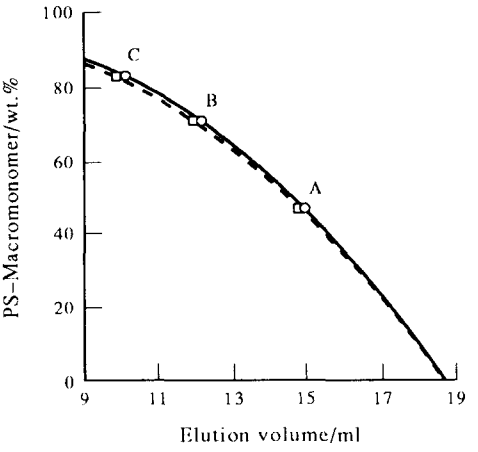

Figure 6 Calibration curves between elution volume and PS macromonomer content of the first equation (□) and the eighth equation (○) for the results by the normal-phase mode

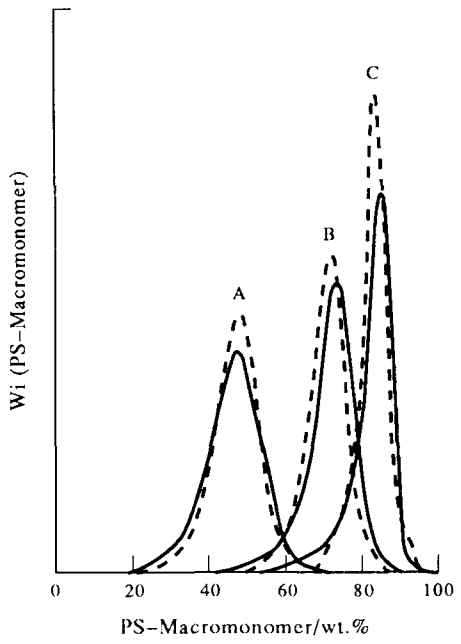

Figure 7 Experimental CCDs of samples A, B and C synthesized from the monomer feeds of different compositions at low conversions: (——) reversed-phase mode; (– – –) normal-phase mode

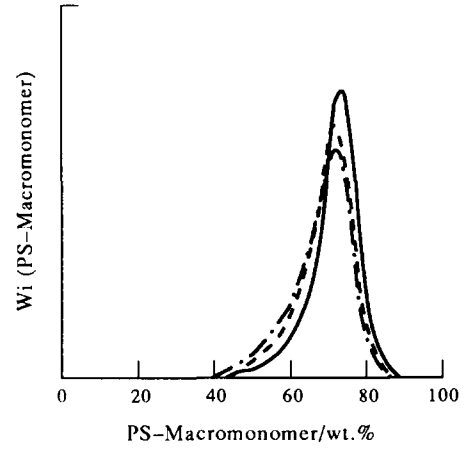

Figure 8 Experimental CCDs of samples B, D and E synthesized from the monomer feeds of the same composition at different conversions obtained by the reversed-phase mode: (——) B; (– – –) D; (–·–·–) E

For the results by the normal-phase mode, since a linear equation did not converge, a quadratic equation was used for the calibration as shown in *Figure 6* (full curve). A similar procedure to the case of the reversed-phase mode was performed. Since the equation converged in the eighth calculation, the equation (broken curve in *Figure 6*) was used to calculate the CCDs for all samples. The ordinates of the CCDs were normalized by taking into account the slope of the calibration equation (dX/dV). The CCDs thus obtained for samples A–C and samples B, D and E are illustrated in *Figures 7* and *9*, respectively.

The differences between the average compositions calculated by the last equations and those by ^{1}H n.m.r. (shown in *Table 1*) are 0.3–5.5% for the results by the reversed-phase mode and 0–3.7% for the normal-phase mode, respectively. The certainty of the CCDs thus determined is not very high; however, the CCDs may be sufficiently useful for the present discussion.

Theoretical calculation of CCD

Theoretical CCDs were calculated in the same manner as in the previous work[4], for comparison with the CCDs obtained experimentally. A copolymer sample synthesized by statistical copolymerization has both the statistical CCD and the conversion CCD. Both CCDs were calculated not only for high-conversion samples D and E but also for low-conversion samples A–C (conversions 16.5–20.2%, see *Table 1*).

For the statistical CCDs, the theory based on the statistics of random coupling of grafts to backbones proposed by Stejskal and Kratochvíl[1] was used; for the conversion CCD, the weight-base compositional distribution function introduced by Stejskal *et al.*[11] was used.

The total CCD of each sample was calculated by multiplying both distribution functions. The reactivity ratios were estimated from the data for samples A–C in *Table 1* by the Kelen–Tüdös method[12] as $r_A = 0.47$, $r_B = 1.32$. The latter value is not reasonable from the viewpoint of copolymerization kinetics, as explained in the latter section. Moreover, from the calculation procedure, the reliability of the value is very low. Therefore, the value used in the previous paper[4] ($r_B = 0.001$) was used in the actual calculations. For the total conversions, the values estimated from the macromonomer conversions and the macromonomer contents in the respective samples were used. For the other parameters, the experimental values shown in *Tables 1* and *2* were used. The CCDs of samples A–C and samples B, D and E thus calculated are shown in *Figures 10* and *11*, respectively, which can be compared with the experimental CCDs in *Figures 7–9*.

Discussion of CCDs

The experimental CCDs determined by the reversed-phase mode are almost in agreement with those determined by the normal-phase mode for low-conversion samples as well as for high-conversion samples. The good agreement between both CCDs even for the high-

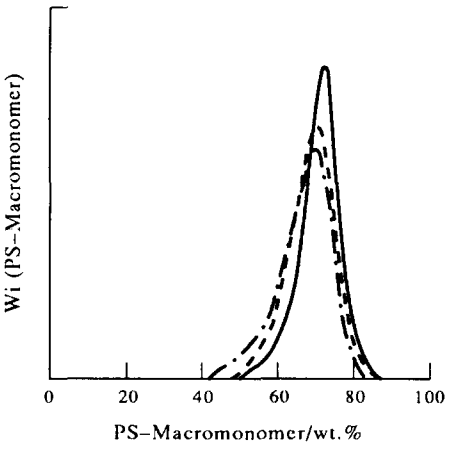

Figure 9 Experimental CCDs of samples B, D and E synthesized from the monomer feeds obtained by the normal-phase mode: (——) B; (– – –) D; (–·–·–) E

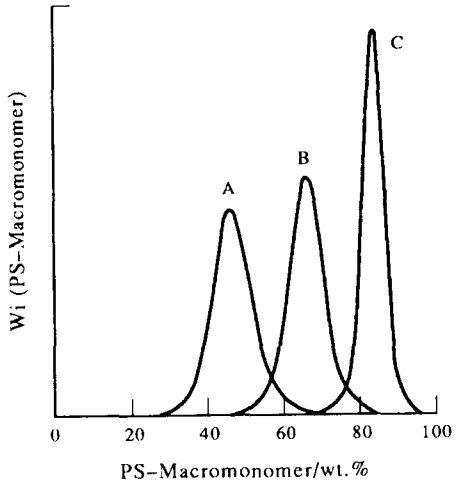

Figure 10 Theoretical CCDs of samples A, B and C

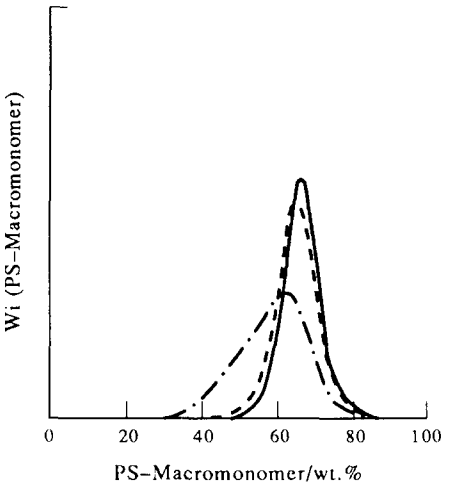

Figure 11 Theoretical CCDs of samples B, D and E: (——) B; (– – –) D; (–·–·–) E

conversion samples with asymmetric CCDs indicates that the *MW* effect on the CCDs obtained in the present method is negligible, or not serious even if it exists, as in the case of the corresponding statistical linear copolymers[8].

It is seen in *Figure 7* that the CCDs are very broad for low-conversion samples (A–C). The broad CCDs are similar to the results obtained for PMMA-*graft*-PS prepared from ω-methacryloyl PS macromonomer in our previous paper[4], but differ from the CCDs of statistical copolymers of small monomers[8,13]. The broad CCD is one of the features of the graft copolymers prepared by the macromonomer technique. Furthermore, it is seen in *Figure 7* that the CCD becomes sharper as the macromonomer content increases. These features are in agreement with theoretical predictions[1,2] as shown in *Figure 10*.

The effect of conversion on CCDs is seen in *Figures 8* and *9* for the samples obtained from the monomer feeds of the same composition at different conversions, where the CCD becomes broader towards the low-macromonomer-content side, as the conversion increases. This corresponds to the fact that the macromonomer content of the copolymer sample, which is higher than that of the initial monomer feed, drifts towards the feed composition as the conversion increases. This means that the rate of consumption of the macromonomer is larger than that of MMA, resulting in the decrease in the instantaneous feed composition of the macromonomer.

The tendencies of the broadening of the experimental CCDs in *Figures 8* and *9* are in agreement with the theoretical ones in *Figure 11*. The theoretical CCDs are, however, broader than the experimental ones. This difference depends on the values of r_A and r_B used for the calculation of the theoretical CCDs.

The values of r_A (=0.47) and r_B (=1.32) were evaluated from the copolymerization data using the Kelen–Tüdös method[12]. The value of r_A is almost the same as that determined for the copolymerization of ω-methacryloyl PS macromonomer with styrene[6]. However, the value of r_B is not reliable, since all values of the molar basis macromonomer contents are extremely low. From the viewpoint of copolymerization mechanism, $r_B \gtrsim 1$ is not acceptable. For the terminal model, r_A and r_B are defined as follows:

$$r_A = k_{AA}/k_{AB} \qquad r_B = k_{BB}/k_{AB} \tag{1}$$

The values of $k_{AA} = k_p(\text{MMA}) = 515\,\text{l mol}^{-1}\,\text{s}^{-1}$ (ref. 14) and $k_{BB} = k_p(\text{VB–PS}) = 4\text{–}5\,\text{l mol}^{-1}\,\text{s}^{-1}$ (ref. 9) were reported in the literature. From $r_A = 0.47$ determined in the present work, $k_{AB} = k_{AA}/0.47 = 515/0.47 \simeq 1100$. The value of k_{BA} is not known. However, if $k_{AB} \simeq k_{BA}$ is assumed, r_B can be evaluated as follows:

$$r_B = k_{BB}/k_{BA} \simeq (4\text{–}5)/1100 \simeq 0.0036\text{–}0.0045 \tag{2}$$

Since it is reasonable that k_{BA} is larger than k_{AB}, the actual value of r_B should be smaller than the above value. In the actual calculation of *Figure 11*, $r_B = 0.001$ was used as mentioned in the subsection on 'Theoretical calculation of CCD'.

The theoretical CCDs are, actually, little affected by the value of r_B used for the calculation in the region of low macromonomer content. The value of r_A, therefore, is the main factor determining the shift direction and the shape of CCDs in the region of low macromonomer content. The increase in the value of r_A gives narrower theoretical CCD curves than those in *Figure 11*.

The shift directions with conversion and also the shapes of CCDs in *Figures 8* and *9* are opposite and different from the results of PS macromonomer with ω-methacryloyl end-group in the previous work[4]. This indicates that r_A $(=k_{AA}/k_{AB}) < 1$ (or $k_{AA} < k_{AB}$) for the present copolymerization system with ω-*p*-vinylbenzyl PS macromonomer and $r_A \gtrsim 1$ (1.15) (or $k_{AA} \gtrsim k_{AB}$) for the previous system with ω-methacryloyl PS macromonomer, respectively. Thus, it is seen that the reactivity of the macromonomer is affected strongly by the kind of reactive end-group.

CONCLUSION

It was demonstrated that the graft copolymer samples of ω-*p*-vinylbenzyl PS macromonomer and MMA can be separated according to their chemical compositions by h.p.l.c. using both normal-phase and reversed-phase modes. The CCDs determined from the h.p.l.c. data obtained by both modes are in good agreement with each other.

This agreement indicates that the *MW* effect on the CCDs is negligible under the h.p.l.c. conditions in the present work.

CCDs determined by the present method are described well by the theoretical calculation using the copolymerization data and M_n values obtained by osmometry.

It is also indicated that the relative copolymerization reactivity of the macromonomer to the small comonomer can be examined by the shift of the CCD peak with conversion. The peak shifts in this study (end-group *p*-vinylbenzyl) and in the previous study (end-group methacryloyl) indicate the strong effect of the intrinsic reactivity of the polymerizable end-group on the copolymerization reactivity of the macromonomers.

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