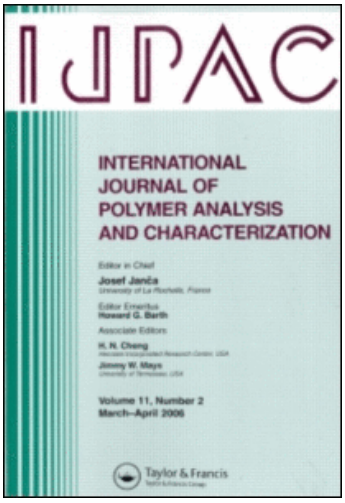

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Kawai, Tadatomo , Teramachi, Shinya , Tanaka, Susumu and Maeda, Shingo(2000) 'Comparison of Chemical Composition Distributions of Poly(methyl methacrylate)-*graft*-polydimethylsiloxane by High-Performance Liquid Chromatography and Demixing-Solvent Fractionation', International Journal of Polymer Analysis and Characterization, 5: 4, 381 — 399
To link to this Article: DOI: 10.1080/10236660008034634
URL: http://dx.doi.org/10.1080/10236660008034634

Int. J. Polym. Anal. Charact.,
2000 Vol. 5, pp. 381–399
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Comparison of Chemical Composition Distributions of Poly(methyl methacrylate)-*graft*-polydimethylsiloxane by High-Performance Liquid Chromatography and Demixing-Solvent Fractionation

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(Received 19 April 1999; In final form 22 May 1999)

Poly(methyl methacrylate)-*graft*-polydimethylsiloxane (PMMA-*graft*-PDMS) samples with different compositions were prepared by radical copolymerization of PDMS macromonomer with methyl methacrylate. The chemical composition distributions (CCDs) of the graft copolymer samples were determined by the high-performance liquid chromatography (HPLC) based on the reversed-phase adsorption mode, using a prepacked column of butyl-modified silica gel and the linear gradient elution of acetonitrile and tetrahydrofuran. The CCD of one of the graft copolymer samples was also determined by the demixing-solvent fractionation using the demixing-solvent pair of dimethylsulfoxid–tetrachloroethylene reported by Stejskal *et al.* The CCD by HPLC was in good agreement with theoretical CCD, while the CCD by the demixing-solvent fractionation was narrower than those by the HPLC and the theoretical calculation.

Keywords: Chemical composition distribution; Graft copolymer; Reversed-phase adsorption HPLC; Compositional fractionation; Demixing-solvent fractionation

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INTRODUCTION

The graft copolymers prepared by macromonomer technique are very interesting and important, as it is easy to control the length and the average number of grafts by the technique. Since it is predicted theoretically that the chemical composition distributions (CCDs) of such graft copolymers are broad even if the conversion is very low,[1–3] the determination of the CCDs of such graft copolymers is an interesting subject.

We have demonstrated that the CCDs of the graft copolymers can be determined by adsorption high-performance liquid chromatography (HPLC).[4–7] However, Stejskal *et al.*[8] reported the determination of the CCD by using demixing-solvent fractionation for poly(methyl methacrylate)-*graft*-polydimethylsiloxane (PMMA-*graft*-PDMS) prepared from the macromonomer of PDMS. This method is applicable for determining the compositional fractionation of graft or block copolymers. In the usual systems of selective solvents appropriate for compositional fractionation of copolymers, phase separation can occur only when polymers are present. Under such condition, graft copolymers cannot be separated into fractions with different compositions, since graft copolymers form generally micelles. In contrast to this, the demixing-solvent fractionation approach can avoid micelle formation and separate the sample into fractions, since phase separation depends on the nature of the solvent pair, and the polymer species are partitioned into both phases selectively.

However, the effect of molecular weight on the fractionation is inevitable, theoretically,[9] though the result by Stejskal *et al.* appears to be in good agreement with the theoretical CCD.[8] Therefore, it is of interest to compare adsorption HPLC, which was successfully used for PMMA-*graft*-polystyrene samples,[4–7] with the demixing-solvent fractionation approach.

In the present paper, the CCDs of PMMA-*graft*-PDMS samples prepared by the macromonomer technique were determined by adsorption HPLC and the CCD of a high conversion sample was determined also by demixing-solvent fractionation. The CCDs determined by both methods were compared with one another and also with the theoretical CCD.

EXPERIMENTAL

Synthesis of PMMA-*graft*-PDMS Samples

The PDMS macromonomer with methacryloyl end groups was supplied by Chisso Co. Ltd. (Japan). According to the catalog data, the molecular weight was about 10,000. The weight average molecular weight (M_w) corresponding to standard polystyrene estimated by size-exclusion chromatography (SEC) was 1.3×10^4, and M_w/M_n (M_n = number-average molecular weight) was 1.03. SEC instrument was composed of a pump model CCPE (Tosoh Co. Ltd.), a column oven model CO8000 (Tosoh), a refractive index detector model RI-8 (Tosoh), and an ultraviolet detector model UV8011 (Tosoh). SEC measurement was carried out by using two TSKgel GMH_{HR}-M columns (Tosoh) and tetrahydrofuran (THF) as the eluent. The column temperature was 30°C, the flow rate was 1.0 cm^3/min, the injection volume was 0.1 cm^3, and the sample concentration injected was 2.0 mg/cm^3.

The graft copolymer samples were prepared by radical copolymerization of the PDMS macromonomer with methyl methacrylate (MMA) using 2,2′-azobisisobutyronitrile (AIBN) as the initiator in benzene at 60°C. The feed compositions are given together with the reaction time, the conversion and the characteristics of the graft copolymers in Table I. The polymer components in the copolymerization mixtures were precipitated with an excess amount of methanol. The PMMA-*graft*-PDMS samples were isolated by extracting the non-reacted PDMS macromonomer from the precipitated mixtures with *n*-hexane using a Soxhlet extractor for 24 h. The removal of the macromonomer was verified by SEC.

The average compositions of the graft copolymers were determined by ^{1}H-NMR at 270 MHz (JEOL EX270) in $CDCl_3$. The number average molecular weights of graft copolymers were measured by osmometry (model 230 Wescan Instrument) in benzene solution at 40°C.

MMA, AIBN and solvents were obtained commercially. They were purified by conventional methods.

HPLC Measurement

The chemical composition distributions of the graft copolymer samples were determined by reversed-phase HPLC. The HPLC instrument

TABLE I Synthesis of PMMA-*graft*-PDMS

Sample code	*Feed* (g)				*Reaction time* (h)	*Conversion* (wt%)	*PDMS contents* (wt%)		M_n[c] $\times 10^{-5}$	P_n	m_n
	Macromonomer[a]	*MMA*	*AIBN* $\times 10^3$	*Benzene* (mL)			*Feed*	*Copolymer*[b]			
S303	2.76	7.05	71.1	30	3.0	7.07	28.2	23.7	1.21	925	2.87
S503	5.10	4.98	49.6	30	3.0	10.2	50.6	35.7	1.55	1000	5.53
S703	6.87	3.02	32.3	30	3.0	9.98	69.5	55.4	1.68	758	9.31
S508	2.48	2.56	26.1	15	8.0	19.4	49.2	36.5	1.22	778	4.45
S524	2.52	2.55	26.1	15	24	38.7	49.7	38.5	1.33	822	5.12
S596	4.98	5.10	50.4	30	96	69.5	49.4	44.0	0.97	547	4.27

[a]PDMS macromonomer molecular weight 1.0×10^4 (catalog data).
[b]Determined by ^{1}H-NMR.
[c]Osmometry.
P_n: Degree of polymerization of main chain.
m_n: Number of side chains.
Polymerization temperature was 60.0°C.

was composed of two pumps model 510 (Waters), a controller model 680 (Waters), a column oven with temperature control system (Waters), a UV detector UV-8 model II (Tosoh), and an evaporative light scattering detector (ELSD) Mk III (Alltech). A prepacked butyl-modified silica gel column [μ-Bondasphere C4 (Waters), 0.39 mm × 150 mm, particle diameter 5 μm, pore diameter 100 Å] was used. The column temperature was 30°C, the flow rate was 1.0 cm^3/min, the injection volume was 0.02 cm^3 and the sample concentration injected was 0.1 mg/cm^3. The eluent combination of THF and acetonitrile, both of which were chromatographic grade from Wako Pure Chemical Industries Ltd., were used. The gradient program of the eluent was as follows:

Time (min)	0	1	16	21	22	32	42
THF (vol%)	0	40	80	80	100	100	0

The wavelength of the UV detector was 254 nm. The ELSD conditions were as follows: evaporator tube temperature 121.2°C, air pressure 100 kPa, attenuation range 1/32, and recorder range 500 mV.

Demixing-Solvent Fractionation

The demixing-solvent system was used dimethyl sulfoxide (DMSO) and tetrachloroethylene (TCE), according to Stejskal *et al.*[8] The mixtures of both solvents and the mixture containing 0.5 wt% of a high-conversion sample of the graft copolymer (S596) were placed in a series of sealed glass ampules, respectively. The TCE contents in the ampules ranged from 45 to 100 wt% in 5 wt% increments. The temperature was slowly increased and decreased between room temperature and 60°C (1°C/h). The phase separation temperature was determined visually as the point of center between the temperatures where the turbidity appeared and disappeared. From these data, the cloud points curve was constructed, as shown in Figure 1.

The composition of the demixing-solvents used for the fractionation was 65 wt% of TCE from the cloud points curve (see Figure 1). In a test tube with a stopper, 85 g of the demixing-solvent was added to 3.0 g of the copolymer sample (S596). In another test tube only the demixing-solvent with the same composition was added. The solution

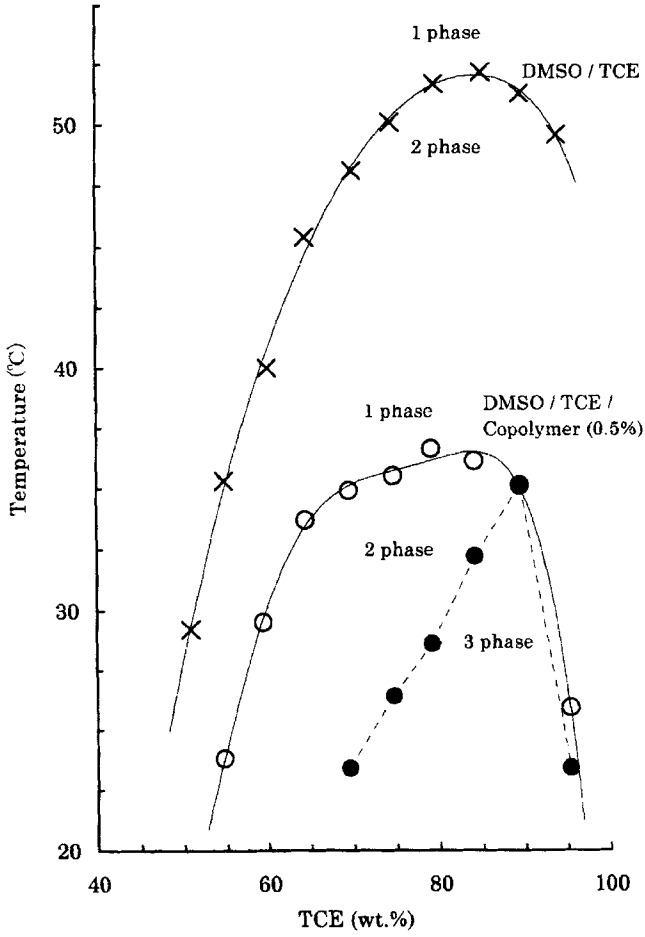

FIGURE 1 Cloud points curves of DMSO/TCE demixing-solvents pairs and the DMSO/TCE/S596 sample system.

was heated to 60°C until a clear solution was formed, then the test tubes were placed in water bath and kept at 19°C for 12 h until phase separation was completed. The upper phase was removed with a syringe and the polymer in the phase was precipitated into excess methanol. The fraction recovered was dried *in vacuo*. To the lower phase, which contained most of the copolymer sample, the upper phase in another tube containing only solvent mixture was added, and then the system was heated to 60°C until the solution became clear. The solution

TABLE II Results of demixing-solvent fractionation

Fraction code	*Fractionation temperature*	*Yield* (g)	*Weight fraction*	*PDMS* (mol%)
U-1	19	0.08774	0.0301	35.68
M-2	20	0.00881	0.0030	28.83
U-2	20	0.00457	0.0016	29.50
M-3	22	0.00725	0.0025	27.13
U-3	22	0.00288	0.0010	21.14
U-4	24	0.02587	0.0089	41.45
U-5	26	0.01732	0.0059	37.68
U-6	27	0.05246	0.0180	42.50
U-7	28	0.03934	0.0135	35.74
U-8	29	0.05043	0.0173	35.42
U-9	30	0.07283	0.0250	40.28
U-10	31	0.09570	0.0329	41.42
U-11	32	0.11939	0.0410	40.80
U-12	33	0.11560	0.0397	39.33
U-13	34	0.12398	0.0426	41.29
U-14	35	0.15724	0.0540	42.41
U-15	36	0.22964	0.0789	44.10
U-16	37	0.29255	0.1005	44.58
U-17	38	0.21930	0.0753	44.82
U-18	39	0.33984	0.1167	46.44
U-19	40	0.10016	0.0344	45.95
U-20	41	0.09359	0.0321	47.69
U-21	42	0.08184	0.0281	49.08
U-22	44	0.09042	0.0311	50.10
U-23	46	0.07498	0.0258	49.97
U-24	48	0.13782	0.0473	52.84
U-25	50	0.15311	0.0526	53.15
U-26	52	0.07829	0.0269	54.17
L-27	53	0.01335	0.0046	55.16
U-27	53	0.02548	0.0088	54.86
		2.91178	1.00	

was cooled to 20°C and kept at the temperature for 12 h. After phase separation was completed, the upper phase was removed and the polymer was recovered from the phase. The procedure was repeated, by increasing the temperature stepwise, as shown in Table II.

RESULTS AND DISCUSSION

Synthesis of PMMA-*graft*-PDMS Samples

The copolymerization condition and the characteristics of the copolymers are shown in Table I. The number-average number of graft per copolymer molecule (m_n) and the number-average degree of

polymerization of backbone (P_n) were calculated from the average composition, M_n of the copolymer and M_n of the macromonomer.

The macromonomer contents of the graft copolymer samples were smaller than those of the feeds, respectively. The difference between compositions of the feed and the copolymer became smaller as the conversion increased. The results mean that the relative reactivity of the macromonomer is lower than that of MMA. The monomer reactivity ratios were $r_{MMA} = 1.53$ and $r_{PDMS} = 0.69$, which were estimated by the Kelen–Tüdös method from the data of the low conversion samples (S303, S503 and S703) in Table I. These values were obtained from the data in the region of very low mole fraction of PDMS, because the molecular weight of the macromonomer is higher than the MMA. Therefore, the reliability of the values were not very high. These values were, however, used to calculate the theoretical CCDs.

Theoretical Calculation

In general, the CCDs consist of two parts: one is the statistical CCD that originates from the statistical nature of copolymerization process, the other is the conversion CCD. The reactivities of two monomers are different from each other, in general, so that the composition of monomer feed drifts with the conversion.

For the statistical CCD of graft copolymers synthesized by the macromonomer technique, two theories are proposed by Stejskal *et al.* One is based on the statistics of random coupling of grafts to backbones,[1] the other is obtained by modification of the Stockmayer theory for statistical copolymers.[2] The modified Stockmayer theory is inadequate for samples with a small number of branches, whereas the former theory, in which the most probable distribution of degree of polymerization is assumed for the backbone, is applicable for such samples. Since the number of branches is small in the present samples, the random coupling theory was used.

According to the theory, the weight-base compositional distribution function $W(x)$ is given by the following equation:[1]

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

$$Q = \left(\frac{1}{1-r}\right)\left(\frac{1-\bar{x}}{\bar{x}}\right)\left(\frac{x}{1-x}\right), \quad r = \frac{1}{m_n + 1},$$

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, and m_n is the number-average number of grafts (PDMS) per copolymer molecule.

The conversion CCD should not be neglected for the high conversion samples, because the reactivities of two monomers are different for the present copolymer. For the conversion CCD, the weight-base compositional distribution function $g(x)$ is given by the following equation:[10]

$$g(x) = \left|\left[\frac{y}{y_0}\right]^{\alpha}\left[\frac{y-1}{y_0-1}\right]^{\beta}\left[\frac{y-b}{y_0-b}\right]^{\gamma}\left[\frac{\alpha}{y} + \frac{\beta}{y-1} + \frac{\gamma}{y-b}\right] \times \frac{[y^2(r_1 + r_2 t - 1 - t) + y(1 + t + 2r_2 t) + r_2 t]^2}{y^2(r_2 t^2 + r_1 - 2r_1 r_2 t) + 2ytr_2(r_1 - t) + r_2 t^2}\right|, \quad (2)$$

where y_0 and y are weight fractions of MMA in the monomer feed at zero time and at a given time, respectively, r_1 and r_2 are the monomer reactivity ratios of MMA (1) and PDMS (2), respectively, t is the ratio of molecular weights of the two monomers (M_{01}/M_{02}), $\alpha = r_2/(1-r_2)$, $\beta = r_1/(1-r_1)$, $\gamma = (r_1 r_2 - 1)/[(1-r_1)(1-r_2)]$, $b = t(1-r_2)/[(1-r_1) + t(1-r_2)]$. The instantaneous composition of the copolymer, x, can be calculated from y by using the copolymerization equation:

$$x = \frac{y^2(r_1 - t) + yt}{y^2[t(r_2 - 1) + r_1 - 1] + y(1 - 2r_2 t + t) + r_2 t}. \quad (3)$$

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

$$\psi = 1 - \left(\frac{y}{y_0}\right)^{\alpha}\left(\frac{y-1}{y_0-1}\right)^{\beta}\left(\frac{y-b}{y_0-b}\right)^{\gamma}. \quad (4)$$

If y_f denotes y at ψ_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 the sample was calculated by multiplying Equations (1) and (2), taking into account that x in Equation (2) is the average composition of instantaneous copolymer shown by $\bar{x}$ in Equation (1):

$$W(x) = \int_{x_0}^{x_f} W(x, \bar{x}) g(\bar{x}) \, d\bar{x}. \tag{5}$$

In these calculations, the data in Table I, $r_{MMA} = 1.53$ and $r_{PDMS} = 0.69$, were used. The theoretical CCD curves of low-conversion samples S303, S503 and S703 are shown in Figure 2(a), and the theoretical CCD curves of various conversion samples S508, S524 and S596 are shown in Figure 3(a), respectively.

CCDs by HPLC

The chromatograms obtained by the ELSD are shown in Figure 4. The PMMA-*graft*-PDMS samples were eluted from the components of higher MMA content to those of lower MMA content. Since PMMA is a polar constituent and PDMS is a non-polar constituent, the present elution order is according to reversed-phase adsorption mechanism. That is, the present graft copolymers were separated according to their chemical compositions. In our previous paper, we reported that the molecular weight dependency of the separation is negligible in the range of high molecular weight for adsorption.[11] The molecular weights of the present samples are highly sufficient to ignore the molecular weight dependency.

The response of the ELSD depends on many factors such as the number of particles, the average particle size, the particle size distribution and the refractive index, which depend upon experimental conditions. Therefore, the chromatograms cannot be converted into CCDs in a straightforward manner. In this paper, the relationships between the response and the polymer concentrations at respective elution volumes were determined phenomenologically to convert the chromatograms to the CCDs.

In general, it is known that both logarithmic plots of ELSD responses vs. polymer concentrations are linear.[12] However, in the

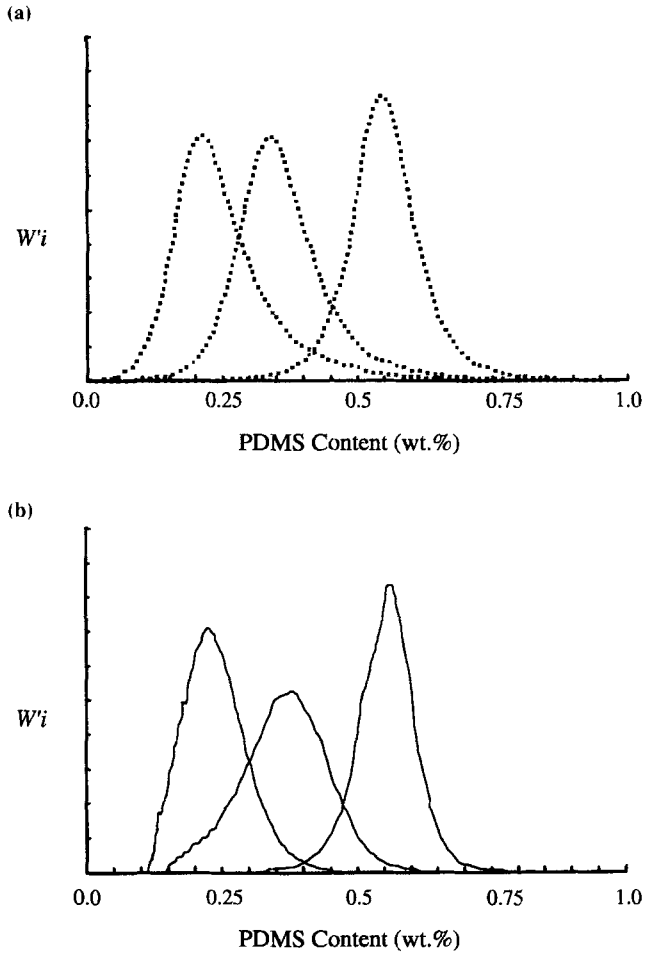

FIGURE 2 Chemical composition distribution curves of low-conversion samples, S303, S503 and S703 (a) theoretical calculation, (b) determined by HPLC.

present work, the plots of total peak areas of chromatograms (responses) vs. the polymer concentrations injected were approximated by straight lines passing through the origins for the respective samples, since the polymer concentrations were very low. The respective response factors (response/concentration = R) were plotted against the copolymer compositions (average PDMS content, $\bar{X}_0$). The relationship is illustrated

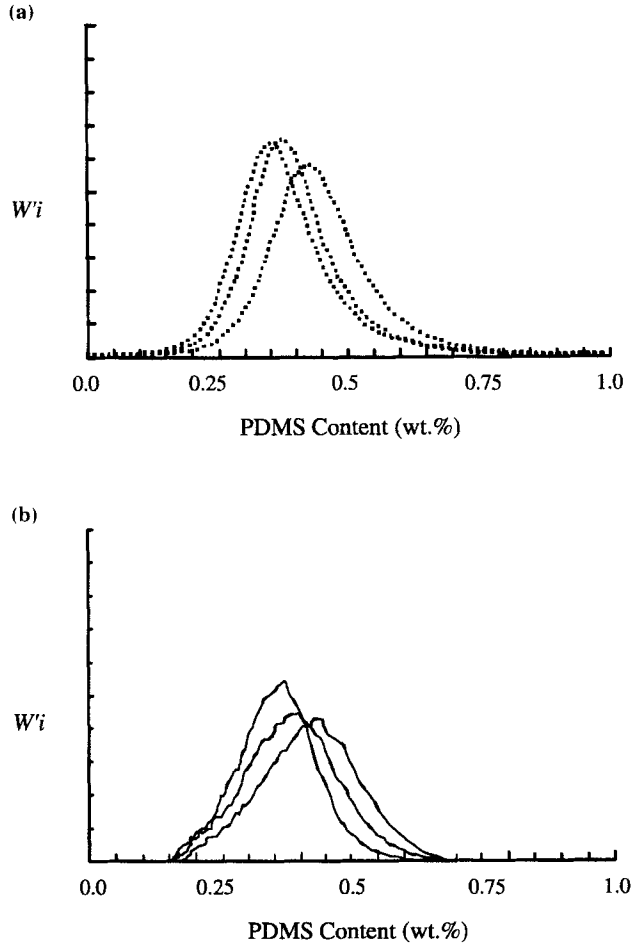

FIGURE 3 Chemical composition distribution curves of high-conversion samples, S508, S524 and S596 (a) theoretical calculation, (b) determined by HPLC.

in Figure 5 can be approximated by

$$R = p \times \bar{X}_0 + q. \tag{6}$$

The elution time at the peak position (V_p) for each sample was plotted against X_0, as shown in Figure 6 (dashed line). The relationship

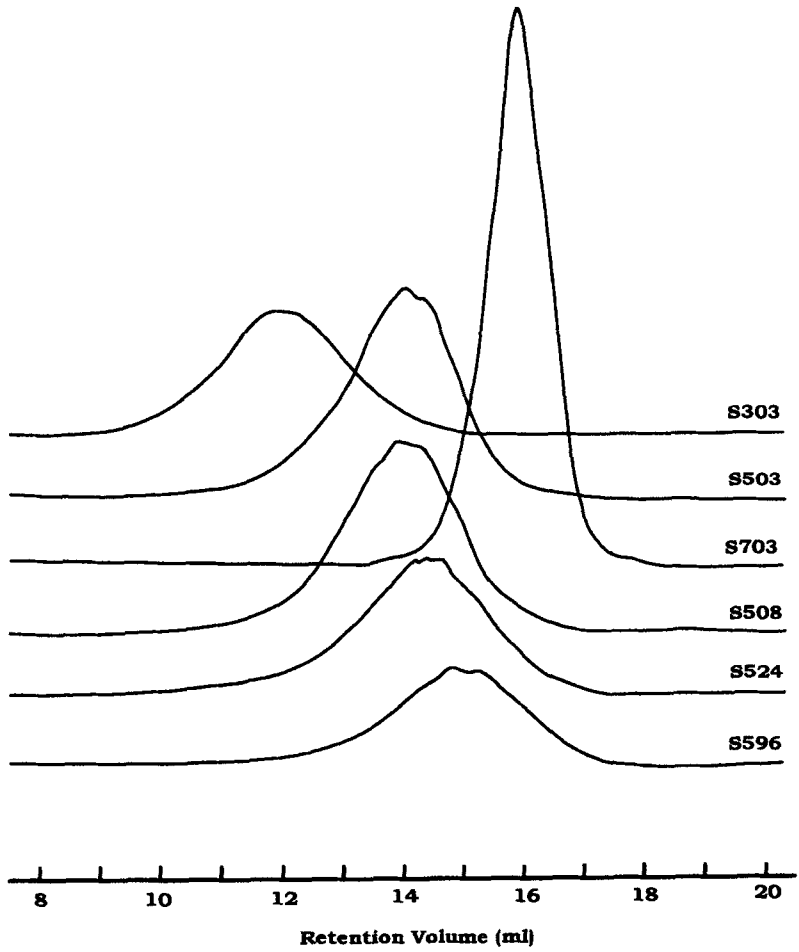

FIGURE 4 Chromatograms of PMMA-*graft*-PDMS samples.

is approximated by

$$\bar{X}_0 = a_0 \times V_p^2 + b_0 \times V_p + c_0. \tag{7}$$

However, this equation cannot be used to convert the chromatograms into the CCD curves, since the compositions at the peak positions do not necessarily correspond to the average compositions of the samples. To obtain a quantitative CCD, the chromatogram was divided by

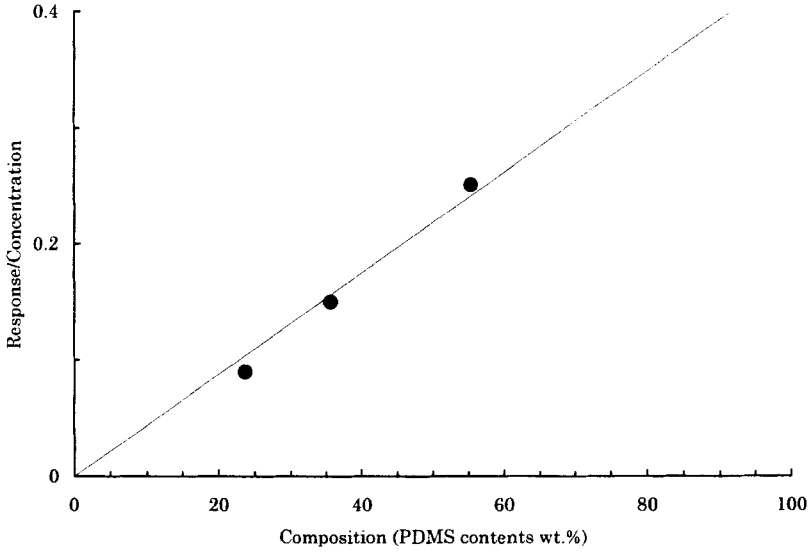

FIGURE 5 The dependency of the response factor on the copolymer composition for the samples, S303, S503 and S703.

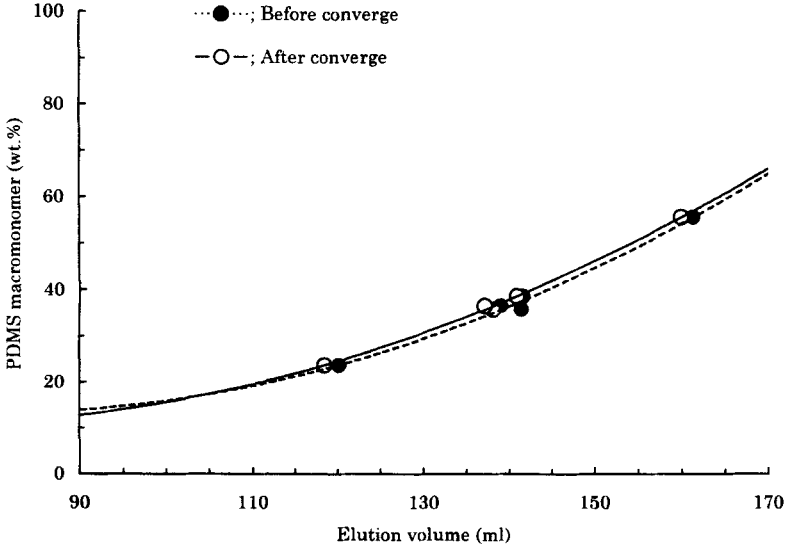

FIGURE 6 Elution volume vs. composition calibration curves of the PMMA-*graft*-PDMS samples.

equal intervals at the respective elution volume (V_i). The V_i was converted to the composition (X_i) by using the Equation (7), and the height of the chromatogram from the base line (h_i) at each position was changed to the relative concentration (H_i) using

$$H_i = h_i / R_i, \tag{8}$$

where R_i was calculated from X_i by Equation (6).

The average composition of each sample ($\bar{X}_\mathrm{I}$) was calculated from the chromatogram by

$$W_i = \frac{H_i}{\sum H_i}, \tag{9}$$

$$\bar{X}_\mathrm{I} = \sum X_i \times W_i. \tag{10}$$

Then, the average elution volume (V_I) for each samples was calculated using Equation (11) substituting $\bar{X}_\mathrm{I}$ for $\bar{X}_0$, and then V_I was plotted against $\bar{X}_0$ to obtain

$$\bar{X}_0 = a_\mathrm{I} \times V_\mathrm{I}^2 + b_\mathrm{I} \times V_\mathrm{I} + c_\mathrm{I}. \tag{11}$$

Again, V_i was converted to X_i by Equation (11), and the average composition ($\bar{X}_\mathrm{II}$) was calculated by Equations (8)–(10), and then V_II for each sample was obtained from $\bar{X}_\mathrm{II}$ by Equation (11). The same procedure was repeated several times. The average composition thus calculated approached but did not necessarily agree with the original values. In the 4th calculation, the equation converged and the values nearest to the X_0 values were obtained for the respective samples. Then the equation (solid line 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 equation. The obtained CCDs for low-conversion samples (S303, S503 and S703) are shown in Figure 2(b) and the CCDs of high-conversion samples (S508, S524 and S596) are shown in Figure 3(b). The average compositions thus calculated are in good agreement with the original values by ^{1}H-NMR, considering the approximation in the calculation and the experimental error of the NMR method. The differences are 0–2.0%, as shown in Table III.

TABLE III Chemical compositions of PMMA-*graft*-PDMS samples (PDMS contents wt%)

Sample code	*S*303	*S*503	*S*703	*S*508	*S*524	*S*596
NMR	23.7	35.7	55.4	36.5	38.5	44.0
HPLC calibration	23.7	36.4	55.4	35.7	38.5	42.0

The experimental CCDs of low-conversion samples are shown in Figure 2(b). The CCDs are very broad. The experimental CCDs of sample S703 and S303 are in good agreement with the theoretical CCDs, but the experimental CCD of S503 is broader than the theoretical one. The disagreement may be caused from the experimental error of the value of M_n obtained by osmometry, which was used to calculate the theoretical CCD.

The experimental CCDs of different conversion samples obtained from the monomer feeds of almost same compositions are shown in Figure 3(b). The CCDs became broader in the high macromonomer content region as the conversion increased. The tendency agreed with that of the theoretical CCDs. The direction of broadening corresponds to the fact that the average composition of the copolymer approaches the feed composition as the conversion increases, and also is not in conflict with the values of the reactivity ratios obtained from the copolymerization data.

Demixing-Solvent Fractionation

The cloud points curves for the demixing-solvent pairs of DMSO and TCE, and the demixing-solvent pairs containing a high-conversion sample of the copolymer (S596, 0.5 wt%) are shown in Figure 1. Both curves are very similar to those by Stejskal *et al.*,[8] although the copolymer samples are different with one another in terms of molecular weight and the composition.

The fractionation data are summarized in the Table II. The recovery was 96.8%. The PDMS content increased excepting some reversals, as the fractionation temperature increased. The middle phase appeared in the second and the third steps of the fractionation, since the polymer concentration of the solution for the fractionation was higher than that for the determination of the cloud points curve (0.5 wt%). The copolymer components in the middle phases were recovered as fractions.

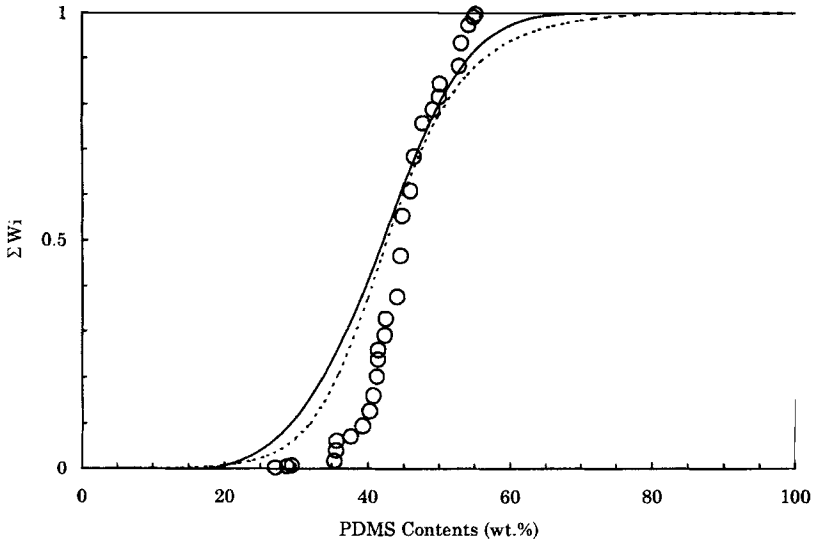

FIGURE 7 Integral curves of chemical composition distribution of S596; ...: theoretical calculation, –: determined by HPLC, ○: demixing solvent fractionation.

The average PDMS content calculated from the value of the fractions and the original sample are 45.0 and 44.0 wt%, respectively. The integral CCD curve constructed from the fractionation data is illustrated in Figure 7.

Comparison among CCDs

In Figure 7, the dotted line is the theoretical CCD, the solid line is the CCD curve obtained by adsorption HPLC, and the open circles are the results by demixing-solvent fractionation. The three CCDs are similar with one another qualitatively. However, comparing the CCDs quantitatively, the CCD by the adsorption HPLC appears to be in good agreement with the theoretical one, while the CCD by the demixing-solvent fractionation is narrower than the theoretical one. The difference between the CCDs by the demixing-solvent fractionation and by the theory is more significant in the region of lower backbone content. Strictly speaking the agreement between CCDs obtained by the theoretical calculation and adsorption HPLC is beyond our expectation, taking into account that the reactivity ratios used in the theoretical

calculation is not highly credible and the compositional dependency of the response factor used to convert the chromatograms to the CCDs was only phenomenological.

For the demixing-solvent fractionation, it is inevitable from the principles of the fractionation that the CCD is narrower than the true one. According to Podešva *et al.*[9] the partition coefficient k of the component with a degree of polymerization P and chemical composition w between two phases is given by

$$\ln k = P(\sigma - \Omega w), \tag{12}$$

$$\sigma = (\varphi_1' - \varphi_1'')\left[\left(1 - \frac{1}{\xi}\right)0.65 + \chi_{12}(1 - \varphi_1' - \varphi_1'') - (\delta_2 - \delta_1)(2\delta_B - \delta_1 - \delta_2)\frac{V_1}{RT}\right],$$

$$\Omega = 2(\varphi_1' - \varphi_1'')(\delta_2 - \delta_1)(\delta_A - \delta_B)\frac{V_1}{RT},$$

where φ_i, P and $\bar{P}$ are the volume fraction of component i, the degree of polymerization of a given copolymer species, and number-average degree of polymerization of the whole copolymer, respectively; 1 and 2 indicate two solvent components; A and B show the constituent monomer units; $\xi = V_2/V_1$ is the ratio of molar volume of the solvents; χ_{12} is the interaction parameter between components 1 and 2; and δ_i is Hildebrand solubility parameter of component i. From the equation, fractionation of copolymers must occur depending upon both chemical composition and molecular weight. Therefore, CCDs of copolymers with both distributions of P and w obtained by demixing-solvent fractionation should be narrower than the true CCDs, according to the present results.

In the results of Stejskal *et al.*[4] however, both CCDs by demixing-solvent fractionation and theory appear to be in good agreement with one another, excepting the region of low backbone content. However, the theory used in the calculation was the modified Stockmayer theory that is effective for only graft copolymers having many grafts, though their sample has only 5.1 grafts per molecule. According to our model calculations,[3] the CCD by the modified Stockmayer theory[2] becomes narrower than the CCD by random coupling theory[1] which is appropriate even for samples of small m_n, as m_n decreases. In the region of

lower backbone content, the difference between both CCDs cannot be neglected for a similar sample to the present one with $m_n = 5$. This may be the cause of the apparent agreement in their results.

CONCLUSION

1. The CCDs of the PMMA-*graft*-PDMS prepared by the macromonomer technique were determined by gradient reversed-phase HPLC. The CCDs obtained were in fairly good agreement with the theoretical CCDs.
2. The CCD of a high-conversion sample was determined also by demixing-solvent fractionation. The CCD was compared with the HPLC results and with the theoretical CCD. The CCD determined by HPLC was in good agreement with the theoretical one, while the CCD by demixing-solvent fractionation was narrower than those by HPLC and the theoretical calculation.

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