Separation of Poly(styrene–Methyl Methacrylate) Block Copolymers by Liquid Adsorption Chromatography

SADAO MORI, *Department of Industrial Chemistry, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan*

Synopsis

Block copolymers P(S-*b*-MMA) prepared by using polymeric peroxide as an initiator were separated into three peaks using silica gel as an adsorbent and a mixture of chloroform and ethanol as the mobile phase. The first peak included both polystyrene homopolymer and P(S-*b*-MMA), the second peak appeared to be P(S-*b*-MMA), and the third consisted of P(S-*b*-MMA) and poly(methyl methacrylate) homopolymer. These results suggest the presence of three different block copolymers in composition and/or in structure. By removing the two homopolymers, it was found that the P(S-*b*-MMA) sample prepared in this work consisted of two components of equal amount: One was a block copolymer having a smaller MMA content and smaller molecular weight averages and the other having a higher MMA content (similar to the monomer feed ratio) and higher molecular weight. Besides these two components, one minor copolymer, which might be different from these two components but rather similar to the first one in both composition and molecular weight, appeared between these two peaks in a liquid adsorption chromatogram. These three components had both composition and molecular weight distributions.

INTRODUCTION

In our previous articles,[1-5] separation of poly(styrene–methyl methacrylate) random copolymers, P(S–MMA), according to chemical composition by liquid adsorption chromatography (LAC) was reported. Silica gel with a pore size of 30 Å was selected as an adsorbent,[1] and a mixture of chloroform and ethanol was used as the mobile phase for LAC.[2] Copolymers having more styrene eluted first and the molecular weight dependence on retention volume was not observed.[3] Low-conversion P(S–MMA) copolymers, which were supposed to have the relatively homogeneous composition, still had chemical heterogeneity and the compositional difference of the front and rear halves of an adsorption chromatogram of a copolymer was about 2%.[3] An example of the range of methyl methacrylate (MMA) content in a high-conversion copolymer (average composition, MMA 67.2%) was between 54 and 85%.[5]

Several attempts have been reported for the separation of random copolymers according to chemical composition by high-performance liquid chromatography (HPLC): P(S–MMA),[6,7] poly(styrene–methyl acrylate),[8] poly(styrene–acrylonitrile),[9] and poly(styrene–butadiene).[10] However, literature on the determination of the chemical heterogeneity of block copolymers by HPLC is limited. Two types of styrene block copolymers of interest to us are P(S–MMA) block copolymers, which have been characterized by light scattering and adsorption chromatography,[11] and poly(styrene–dimethylsilox-

Journal of Applied Polymer Science, Vol. 38, 95–103 (1989)
CCC 0021-8995/89/010095-09$04.00

ane) block copolymers, which have been characterized by size-exclusion chromatography (SEC)–low-angle laser light scattering.[12]

In the present report, styrene–MMA diblock copolymers, P(S-*b*-MMA), have been characterized by LAC and SEC. Availability and the limitations for characterization of the block copolymers by LAC are discussed.

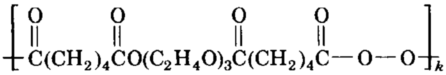
EXPERIMENTAL

A Jasco TRIROTAR-VI high-performance liquid chromatograph (Jasco Ltd., Hachioji, Tokyo 192, Japan) with an ultraviolet absorption detector (Model UVIDEC-100 VI) operated at 254 nm was used for LAC and a differential refractive index detector (Model RID-300) was connected in series for SEC. The column used for LAC was 50 mm in length and 4.6 mm i.d. and was packed with microporous silica gel of 30 Å pore diameter and a mean particle size of 5 μm (Nomura Chemical Co., Seto 489, Japan). This column was thermostatted at a specified temperature by using a column jacket in which constant temperature water was circulated. SEC columns were two Shodex KF 80M HPSEC columns (25 cm × 8 mm i.d.) (Showa Denko Co., Ltd., Minato-ku, Tokyo 105, Japan) packed with polystyrene gels for polymer analysis. The number of theoretical plates of the column was 12,000 per 25 cm, which was obtained by injecting 0.05 mL of a 1% benzene solution at a flow rate of 1.0 mL/min.

The mobile phase for LAC was a mixture of chloroform and ethanol. The composition of the mobile phase was regulated by linear gradient elution. Ethanol used as a stabilizer in chloroform was removed before use and the content of ethanol in the mobile phase was controlled strictly. The flow rate was 0.5 mL/min. The mobile phase for SEC was tetrahydrofuran (THF) and the flow rate was 1.0 mL/min. Samples for LAC were dissolved in the initial mobile phase for linear gradient elution in a concentration of 0.1% and an injection volume was 0.1 mL. Samples for SEC were dissolved in THF in a concentration of 0.1% and an injection volume was 0.2 mL.

A calibration curve of SEC columns was constructed by determining the peak retention volume of polystyrene standards (Pressure Chemical Co., Pittsburgh, PA). The ordinate was the scale of log molecular weight of polystyrene, and the abscissa was the scale of retention volume. Molecular weight averages of the block copolymers calculated in this experiment were polystyrene equivalent ones.

Samples used in the present work were styrene–MMA block copolymers prepared at Chemicals and Explosives Laboratory, Nippon Oil and Fats Co., Ltd., Taketoyo, Aichi 470-23, Japan. These copolymers were similar to a shrinkage suppressor (a brand name Modiper-MS) commercially available from Nippon Oil and Fats Co., Ltd., Japan. The initiator for polymerization was polymeric peroxide (PPO)[13] prepared from adipoyl chloride and triethylene glycol:



$$\left[\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}O(C_2H_4O)_3\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}-O-O\right]_k, \qquad k = 5\text{–}6$$

MMA monomers were first polymerized with this initiator at 65°C; then styrene (S) monomers were added, and a polymerization process was continued at 75°C. Three samples of P(S-*b*-MMA) of different compositions were prepared by changing monomer concentrations and were designated as MS-9, MS-7, and MS-5.

The main product might be a diblock copolymer $(S)_m$–$(MMA)_n$ and a triblock copolymer $(S)_l$–$(MMA)_n$–$(S)_m$, and two homopolymers, polystyrene (PS) and poly(methyl methacrylate) (PMMA), would be produced as byproducts. These homopolymers were extracted by the following extraction scheme. Sample MS-5 was subjected to Soxhlet extraction, first with cyclohexane for 100 h to remove PS, then with acetonitrile for 100 h to remove PMMA, and finally with benzene for 180 h to dissolve the block copolymers. The final extract was poured into methanol to precipitate the block copolymers. This refined final product was designated as MS-50B.

RESULTS AND DISCUSSION

Table I gives the monomer feed and the MMA content of the samples used in this work. The MMA content of the samples was measured by using an infrared spectrophotometer. The samples were cast on a KBr disk from a chloroform solution and absorbances at 1728 cm^{-1} (a carbonyl group characteristic band) and at 698 cm^{-1} (a phenyl group characteristic band) were determined. A calibration curve of the ratio of these two absorbances and the content of P(S–MMA) copolymers was constructed by using low conversion P(S–MMA) random copolymers of known composition.[5] The relative standard deviation by infrared analysis was between 1 and 3%. Samples of MS-5, MS-7, and MS-9 included PS and PMMA homopolymers, and therefore MMA contents of these samples were nearly equal to the values of the monomer feed. The MMA content of sample MS-50B represented an average composition of block copolymers in MS-50B.

LAC chromatograms of block copolymers MS-9, MS-7, and MS-5 separated at column temperature of 30°C are shown in Figure 1. The initial mobile phase (A) for linear gradient elution was chloroform/ethanol 99.0/1.0 (v/v) and the final mobile phase (B) was 95.5/4.5 (v/v). The composition of the mobile phase was changed from 100% A to 100% B in 15 min and kept to 100% B until the end of the separation. A sample solution was injected 1 min after from the start of gradient. Three peaks can be observed for every sample. Peak 1 must include a PS homopolymer, and a PMMA homopolymer must appear at the rear end of peak 3, though it cannot be observed by a UV

TABLE I
Monomer Feed and Methyl Methacrylate Content
of Styrene–Methyl Methacrylate Block Copolymers

Sample	Monomer feed (wt %) MMA	Monomer feed (wt %) Styrene	MMA content (wt %)
MS-9	10	90	7.8
MS-7	30	70	24.4
MS-5	50	50	48.1
MS-50B	50	50	30.7

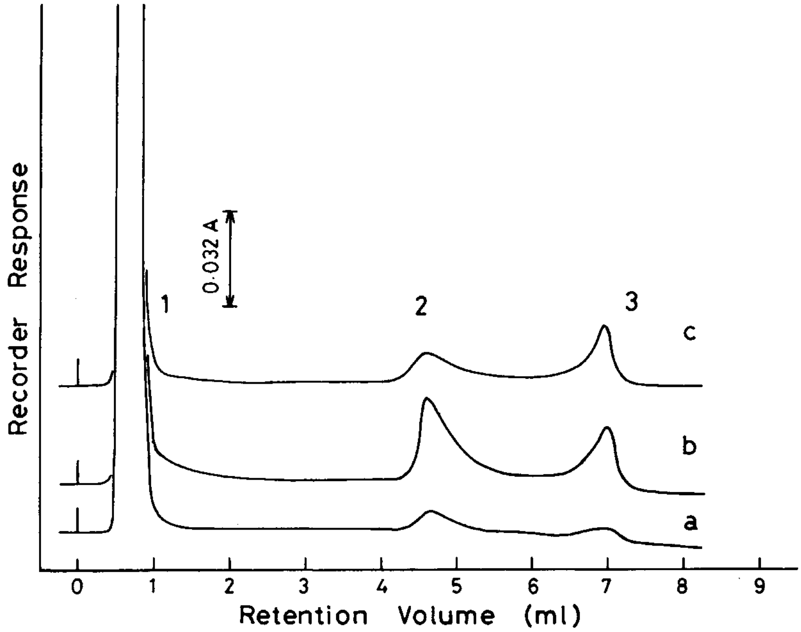


Fig. 1. LAC chromatograms of P(S-*b*-MMA) copolymers. Samples: (a) MS-9; (b) MS-7; (c) MS-5; column temperature, 30°C; sample concentration, 0.1 wt %; injection volume, 0.1 mL; detector attenuation, UV × 0.32 AUFS. For the gradient elution condition, see the text.

detector. Chromatograms were similar in three samples; that is, peaks 1, 2, and 3 of different samples appeared at the same retention volumes, respectively.

Figure 2 is LAC chromatograms of the sample MS-50B, which is assumed not to include homopolymers. Chromatograms were also measured at different column temperature. Similar chromatograms to that in Figure 1(c) were obtained, but peak 1 in Figure 2 became narrower, signifying that some solutes, probably PS, do not appear in peak 1.

In order to ascertain that peak 1 in Figure 2 includes a PS homopolymer or consists of only copolymers, chloroform without ethanol was used as the initial mobile phase and LAC of MS-50B was performed. The results are shown in Figure 3. The gradient elution condition for Figure 3(a) was as follows. The initial mobile phase was pure chloroform and kept for 3 min. After 3 min, linear gradient elution was performed from pure chloroform to chloroform/ethanol 99.0/1.0 (v/v) in 5 min and then to chloroform/ethanol 95.5/4.5 (v/v) in 15 min. A sample solution was injected 1 min after the start of this elution pattern. The gradient elution condition for Figure 3(b) and (c) was that the initial mobile phase was pure chloroform and kept for 3 min, and the linear gradient elution was performed from this mobile phase to chloroform/ethanol 95.5/4.5 (v/v) in 20 min. With pure chloroform as the initial mobile phase, only PS eluted at a retention volume of about 1 mL, which corresponds to the interstitial volume in the column, and P(S–MMA) copolymers of any composition were retained in the column.[4] The copolymers eluted at retention volumes where the mobile phase included ethanol of appropriate content.

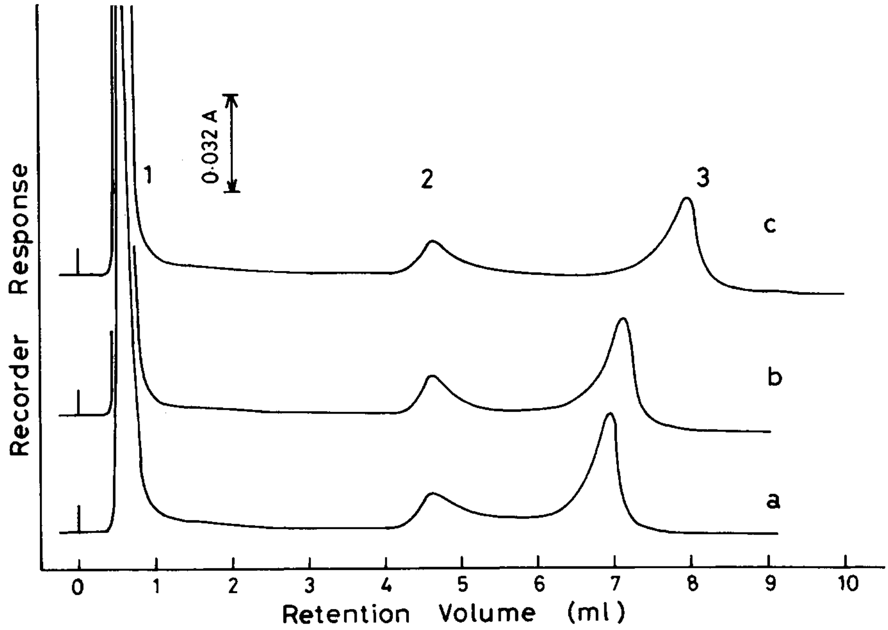


Fig. 2. LAC chromatograms of P(S-*b*-MMA) copolymer MS-50B at different column temperatures (°C): (a) 30; (b) 35; (c) 40. Other conditions were the same as in Figure 1.

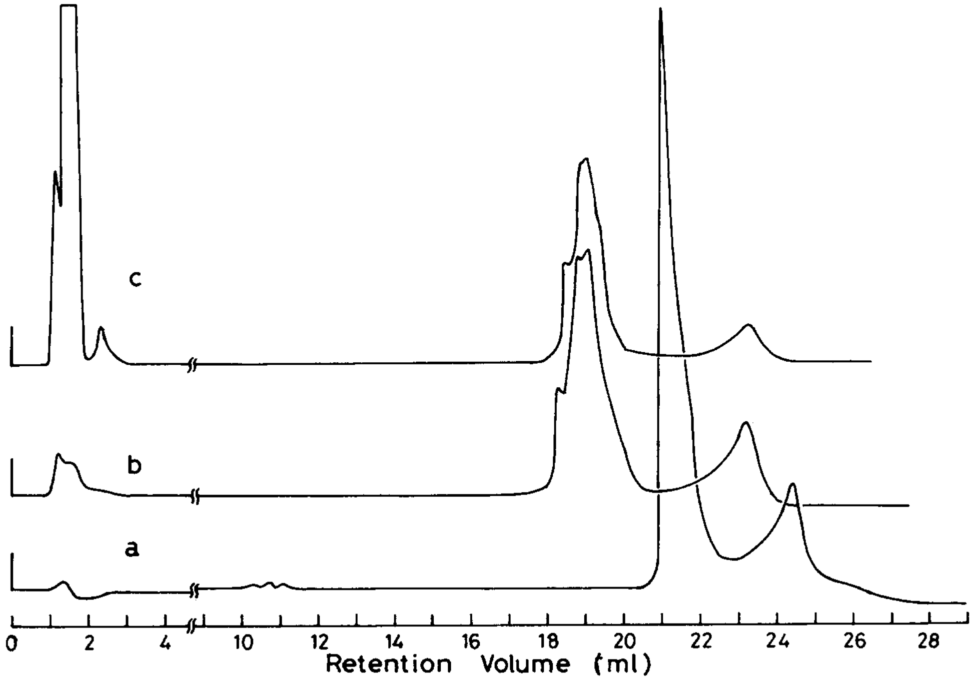


Fig. 3. LAC chromatograms of P(S-*b*-MMA) copolymers MS-50B and MS-5 obtained using pure chloroform as the initial mobile phase. Sample: (a, b) MS-50B; (c) MS-5. For the gradient elution condition, see the text. Other conditions were the same as in Figure 1.

In Figure 3(a), there is no peak as peak 1 in Figure 2(a), which proves that a PS homopolymer was extracted completely from the original sample MS-5. The second peak in Figure 3(a) is probably the same as peak 3 in Figure 2(a). Peaks 1 and 2 in Figure 2(a) appear to be combined into the first peak in Figure 3(a). By changing the gradient elution condition, the first peak in Figure 3(a) was divided into three peaks as in Figure 3(b). Therefore, peaks 1 and 2 in Figure 2(a) might include at least copolymers of three different compositions. From Figure 3(a), it was confirmed that sample MS-50B did not include a PS homopolymer and the first peak in Figure 3(c) consists of a PS homopolymer and small amount of impurities. Moreover, peak 1 in Figures 1 and 2 consists of a PS homopolymer and P(S–MMA) copolymers.

Peak 1 in Figures 1 and 2 eluted at the interstitial volume (in this case $V_R = 1$ mL). It means that solutes in the peak 1 did not adsorb on the surface of silica gel. Peak 3 in Figure 2 increased retention volume with increasing column temperature as in the results of previous papers.[2,3] Peak 2 in Figure 2 appeared at the end of a blind zone[3] and unchanged retention volume, although column temperature was changed. Therefore, peak 2 and peak 3 might be different not only in composition, but also in the structure of the solutes.

Peaks 1, 2, and 3 in Figure 1(b) and in Figure 2(c) were fractionated, and the composition of each fraction was measured by infrared spectroscopy and molecular weight averages by SEC. The results are shown in Table II. Fraction 1 corresponds to peak 1, fraction 2 to peak 2, and fraction 3 to peak 3, respectively. Peak amount in Table II means a percentage of each peak area to the total peak area corrected for the MMA content. Peak area is proportional to the styrene content and the correction should be applied to each peak by knowing the MMA content for the calculation of the amount of each fraction. Fraction 1 of MS-7 includes a PS homopolymer, and, therefore, the net MMA composition of copolymers in the fraction 1 must be higher than this value. Similarly, fraction 3 of MS-7 includes a PMMA homopolymer, and the net MMA composition of block copolymers in fraction 3 must be smaller than this value.

TABLE II
Composition and Molecular Weight Averages of Fractions of P(S-*b*-MMA) Copolymers, MS-7 and MS-50B

Sample	Composition MMA (wt %)	Peak amount	Molecular weight average $\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-5}$
MS-7				
Unfractionated	24.4		6.41	2.03
Fraction 1	7.8	57	5.20	1.66
Fraction 2	7.3	11	6.37	2.22
Fraction 3	59.0	32	8.23	3.80
MS-50B				
Unfractionated	30.7		6.69	3.05
Fraction 1	15.1	43	5.29	2.27
Fraction 2	16.9	9	5.67	2.30
Fraction 3	51.9	48	7.80	4.09

The composition and molecular weight averages for fractions 1 and 2 of MS-50B were similar, and therefore, it can be said that block copolymers of MS-50B consist of two parts of equal amount: a block copolymer having a smaller MMA content and smaller molecular weight averages, and the other having a higher MMA content (roughly corresponds to the monomer feed) and higher molecular weight. However, reinjection of each fraction of peaks 1 and 2 to a LAC system showed that each fraction appeared at the original retention volume, respectively. Moreover, infrared spectra of both fractions were different, meaning that both fractions were not identical copolymers. Similarly, infrared spectra of fractions 1 and 3 were different from each other and also from those of P(S–MMA) random copolymers. Details are now under study. Fraction 3 (peak 3) appears to be a diblock copolymer.

SEC chromatograms and chemical heterogeneity measured by using a SEC/UV-RI system for samples of MS-50B and MS-7 fractionated and unfractionated are shown in Figures 4 and 5, respectively. It is clear that there are differences in the shape of chromatograms and chemical heterogeneity distributions between fractions 1 and 2 in both samples. A typical difference

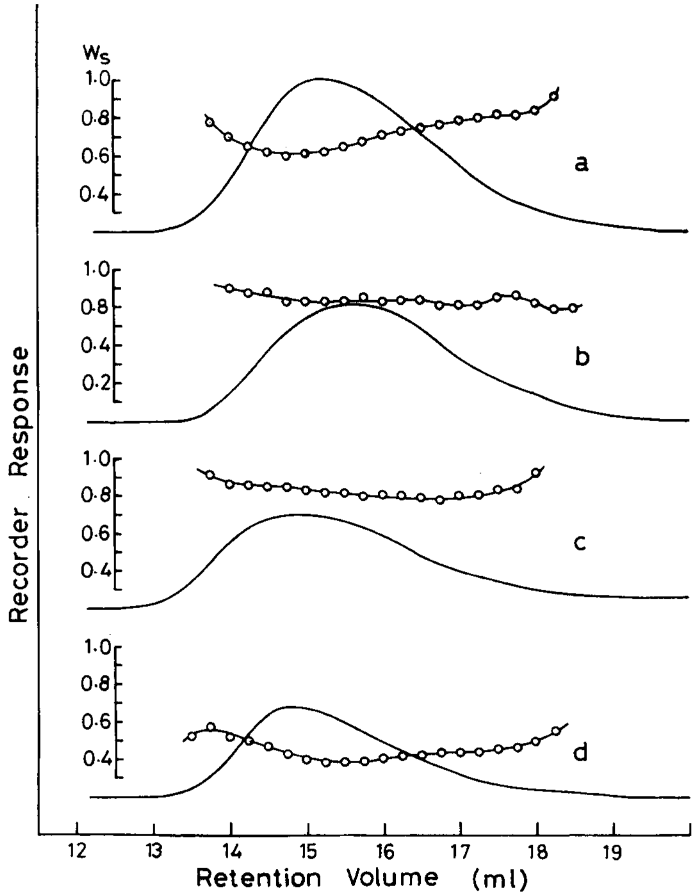


Fig. 4. SEC chromatograms of P(S-*b*-MMA) copolymer MS-50B fractionated and unfractionated. Sample: (a) unfractionated; (b) fraction 1; (c) fraction 2; (d) fraction 3; W_S = styrene weight fraction.

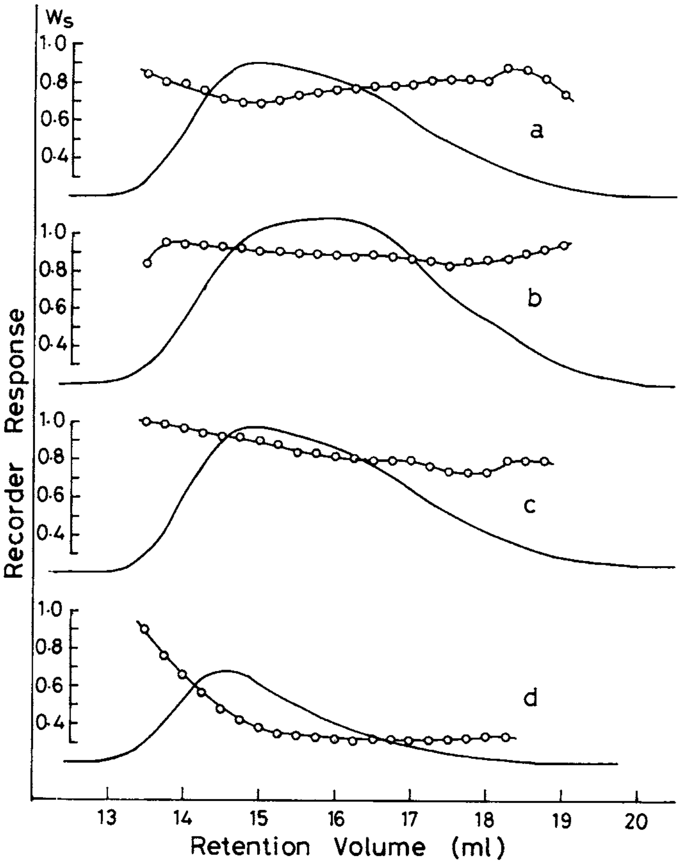


Fig. 5. SEC chromatograms of P(S-*b*-MMA) copolymer MS-7 fractionated and unfractionated. Sample: (a) unfractionated; (b) fraction 1; (c) fraction 2; (d) fraction 3; W_S = styrene weight fraction.

between fraction 3 of MS-7 and that of MS-50B is a chemical heterogeneity distribution. Fraction 3 of MS-7 includes a PMMA homopolymer and a sharp decline of W_S (styrene weight fraction) curve is observed.

Peaks 1 and 3 in Figure 2 and/or chromatograms in Figure 4(b) and (d) represent two main components in a block copolymer P(S-*b*-MMA) in this work. It was found that both components had a composition distribution as well as a molecular weight distribution. These results explain the LAC–SEC system is very valuable for characterization of block copolymers. However, similar LAC chromatograms were obtained for block copolymers MS-5, MS-7, and MS-9 of different composition (different monomer feed), which might imply that block copolymers of different composition might appear at the same retention volume. Detailed examinations for availability and the limitations of LAC for characterization of block copolymers are required. LAC of MS-7 and MS-9 extracted PS and PMMA homopolymers are now under investigation.

The author wishes to express his gratitude to Mr. H. Ishigaki and Mr. S. Suzuki at Nippon Oil and Fats Co. for sample preparation and to Mr. Y. Uno for his technical assistance.

References

1. S. Mori, Y. Uno, and M. Suzuki, *Anal. Chem.*, **58**, 303 (1986).

2. S. Mori and Y. Uno, *Anal. Chem.*, **59**, 90 (1987).

3. S. Mori and Y. Uno, *J. Appl. Polym. Sci.*, **34**, 2689 (1987).

4. S. Mori, *J. Chromatogr.*, **411**, 355 (1987).

5. S. Mori, *Anal. Chem.*, **60**, 1125 (1988).

6. M. Danielewicz and M. Kubín, *J. Appl. Polym. Sci.*, **26**, 951 (1981).

7. G. Glöckner and J. H. M. van den Berg, *J. Chromatogr.*, **352**, 511 (1986).

8. S. Teramachi, A. Hasegawa, Y. Shima, M. Akatzuka, and M. Nakajima, *Macromolecules*, **12**, 992 (1979).

9. G. Glöckner, J. H. M. van den Berg, N. L. J. Meijerink, T. G. Scholte, and R. Koningsveld, *Macromolecules*, **17**, 962 (1984).

10. H. Sato, H. Takeuchi, S. Suzuki, and Y. Tanaka, *Macromol. Chem., Rapid Commun.*, **5**, 719 (1984).

11. T. Tanaka, M. Omoto, N. Donkai, and H. Inagaki, *J. Macromol. Sci.*, **B17**, 211 (1980).

12. T. Dumelow, S. R. Holding, L. J. Maisey, and J. V. Dawkins, *Polymer*, **27**, 1170 (1986).

13. Y. Oshibe, M. Nakayama, and T. Yamamoto, *Polym. Prepr. Jpn.*, **31**(2), 266 (1982).

Received March 16, 1988
Accepted June 1, 1988