Separation of poly(styrene–vinyl acetate) block copolymers by liquid adsorption chromatography

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SUMMARY

Poly(styrene–vinyl acetate) block copolymers, prepared by using a polymeric peroxide as an initiator, were characterized by liquid adsorption chromatography (LAC) and size-exclusion chromatography (SEC). The copolymers were separated according to their chemical composition by LAC using silica gel as an adsorbent and a mixture of 1,2-dichloroethane (DCE) and ethanol as the mobile phase with a 20-min linear gradient from DCE–ethanol (98:2, v/v) to DCE–ethanol (85:15, v/v). The column temperature was 30°C. The copolymers were separated by LAC according to the composition in order of increasing vinyl acetate content. The copolymers were fractionated by LAC and SEC in order to determine the relationship between the composition and molecular weight. The LAC fractions were subjected to SEC and the SEC fractions to LAC. The range of composition for the copolymers was between 40 and 90% (w/w) styrene regardless of the monomer feed. There are positive trends in the composition and the molecular weight averages that the copolymer fractions containing more styrene have lower molecular weights, although the copolymers have chemical compositions and molecular weight distributions that are independent of each other.

INTRODUCTION

Copolymers in general have a molecular weight distribution and a chemical composition distribution, and the determination of both distributions is very important for the characterization of the copolymers. The separation of poly-(styrene–methyl methacrylate) random copolymers[1–5], P(S–MMA), and the block copolymers[6], P(S–b–MMA), according to chemical composition by liquid adsorption chromatography (LAC) has been reported in the previous papers. For the random copolymers, those having more styrene eluted first and the molecular weight dependence on retention volume was not observed[2,3]. Although the separation of the block copolymers was not directly proportional to the composition, LAC was found to be a useful technique for the characterization of the block copolymers.

Several attempts have been reported for the separation of random copolymers such as P(S–MMA)[7] and poly(styrene–acrylonitrile)[8] copolymers according to chemical composition by high-performance liquid chromatography (HPLC). However, the reports on the determination of the chemical heterogeneity of block copolymers by HPLC are limited and only one type of styrene block copolymer could be found in the literature apart from our report, *i.e.*, P(S–MMA) block copolymers were separated by LAC and characterized by light scattering[9].

In this work, styrene–vinyl acetate block copolymers, P(S–b–VAc), were characterized by LAC and size-exclusion chromatography (SEC). The separation was in order of increasing vinyl acetate content and molecular weight.

EXPERIMENTAL

Apparatus

A Model Trirotar-VI high-performance liquid chromatograph (Japan Spectroscopic, Tokyo, Japan) was used for both LAC and SEC. A Model Uvidec-VI UV absorption detector (Japan Spectroscopic) was used for LAC and a Model SE-61 differential refractive index detector (Showa Denko, Tokyo, Japan) for SEC. The UV detector was operated at 254 nm. The column used for LAC (50 mm × 4.6 mm I.D.) was packed with silica gel of pore diameter 30 Å and particle size 5 μm (Nomura Chemical, Aichi, Japan). The column was thermostated at a specified temperature in a Model TU-300 column oven (Japan Spectroscopic).

SEC columns were two Shodex A80M HPSEC columns (50 cm × 8 mm I.D.) (Showa Denko) packed with polystyrene gel for polymer separation.

Samples

The samples used were styrene–vinyl acetate block copolymers, P(S–b–VAc), prepared at the Chemicals & Explosives Laboratory, Nippon Oil & Fats, Aichi, Japan. Vinyl acetate monomer was first polymerized with a polymeric peroxide as the initiator, then styrene monomers were added and the polymerization process was continued. Three samples of P(S–b–VAc) of different compositions were prepared by changing the monomer concentrations; the styrene feed for P(S–b–VAc) I was 90 wt.-%, that for P(S–b–VAc) II was 70 wt.-% and that for P(S–b–VAc) III was 50 wt.-%.

The products were subjected to Soxhlet extraction, first with cyclohexane to remove polystyrene (PS), then with methanol to remove poly(vinyl acetate) (PVAc). The residues consisted of P(S–b–VAc) as the main product and small amounts of residual PS and PVAc homopolymers. The composition of the purified products was measured by NMR spectroscopy. The styrene contents of the copolymers were I, 90 wt.-%; II, 48 wt.-%; and III, 49 wt.-%.

Elution

The mobile phase for LAC was a mixture of 1,2-dichloroethane (DCE) and ethanol. The composition of the mobile phase was regulated by linear gradient elution. The initial mobile phase (A) was DCE–ethanol (98:2, v/v), the composition of the final mobile phase (B) was DCE–ethanol (85:15, v/v) and the composition of the mobile phase was changed from 100% A to 100% B in 20 min linearly. The copolymer samples

were dissolved in DCE at a concentration of 0.1% and the sample solutions were injected onto the column 1 min after from the start of the gradient elution. The column temperature was 30°C. The flow-rate of the mobile phase was 0.5 ml/min and the injection volume of the sample solutions was 0.1 ml. Isocratic elution was also performed for the selection of the elution conditions by changing the composition of the mobile phase and the column temperature.

The mobile phase for SEC was tetrahydrofuran (THF) at a flow-rate of 1 ml/min. The copolymer samples were dissolved in THF at a concentration of 0.1% and the injection volume was 0.2 ml.

Fractionation

In order to estimate the chemical heterogeneity of the block copolymers, the LAC traces were divided into ten fractions as shown in Fig. 2 by dividing the retention volume every 0.5 ml from 4.5 to 9.5 ml. The sample concentration was 0.4% and the injection volume was 0.2 ml. Fractionation was repeated 15 times and corresponding fractions were combined. One portion of the fractions was used for the determination of composition and the other for the determination of molecular weight averages.

SEC traces for the copolymers were divided into six fractions as shown in Fig. 3 by dividing the retention volume every 2 ml from 21 to 33 ml. Fractionation was repeated five times and corresponding fractions were combined. The mobile phase was DCE–ethanol (95:5, v/v); the sample concentration was 0.4% and the injection volume was 0.2 ml. Solvent in the fractions was removed and the residues were dissolved in DCE.

RESULTS AND DISCUSSION

Selection of eluton conditions

The reactivity ratios between the two monomers, styrene (M_1) and vinyl acetate (M_2), are $r_1 = 55 \pm 10$ and $r_2 = 0.01 \pm 0.01$. These two values are significantly different and hence a styrene–vinyl acetate random copolymer cannot be obtained by usual polymerization techniques. Therefore, in this study, the block copolymers were used as the test samples to select the elution conditions.

At a column temperature of 30°C, the elution behaviour of the copolymers was examined by changing the ethanol content in DCE as the mobile phase. Isocratic elution was performed. When DCE and mixtures of DCE and ethanol up to 98:2 (v/v) were used as the mobile phase, all the copolymers were retained in the column, excect for a small peak, which was assigned to styrene, at the interstitial volume of the column system. At a concentration of 3% (v/v) ethanol in the mobile phase, the peak height at the interstitial volume (about 0.5 ml) increased to some extent, and it increased with increasing ethanol content in the mobile phase. However, no peaks were observed after the interstitial volume. This observation was similar to that observed for styrene–methyl methacrylate copolymers[2], where all the block copolymers and polystyrene appeared at the interstitial volume on increasing the ethanol content in the mobile phase.

Linear gradient elution was then attempted for eluting the copolymers at different retention volumes according to their chemical compositions, with a 20-min gradient from DCE–ethanol (98:2, v/v) to DCE–ethanol (85:15, v/v). All the

copolymers and PVAc were retained in the column and only PS could be eluted from the column with the initial mobile phase. With increase in the ethanol content, the copolymers appeared from the column in order of increasing vinyl acetate content. The results are shown in Fig. 1. DCE alone was also injected as a sample solution to check the baseline drift.

The first peak, appearing at $V_R = 0.5$–1.0 ml, was residual PS wich remained in the samples despite the extraction process. The second peak was UV-sensitive impurities produced during polymerization. Most of the impurities were removed by the purification process by dissolving the copolymers in chloroform, followed by precipitation in methanol. The peak at $V_R = 2.5$ ml and the breakthrough at $V_R = 4.0$–4.5 ml were impurities or the baseline drift originated in the DCE solvent, as shown in Fig. 1 D. The block copolymers appeared between 4.7 and 9.3 ml. Only one broad and leading peak was observed for every sample. The chromatograms were similar for the three samples. A PVAc homopolymer must appear at the end of the chromatogram, *i.e.*, around 9.0 ml, although it cannot be observed with a UV detector at 254 nm.

LAC traces for the three samples were also obtained at different column temperatures. Similar chromatograms to those in Fig. 1 were obtained, but the retention volumes of the peaks for the copolymers decreased with increasing column temperature. A PVAc homopolymer does not have UV absorption at 254 nm, and therefore these chromatograms represented styrene only.

Fractionation by LAC

In order to determine the compositions and molecular weights of the block copolymers appearing at different retention volumes in the chromatograms in Fig. 1, the copolymers were fractionated by LAC into nine or ten fractions. LAC results for the copolymers are shown in Fig. 2. The sample load was eight times larger than that in
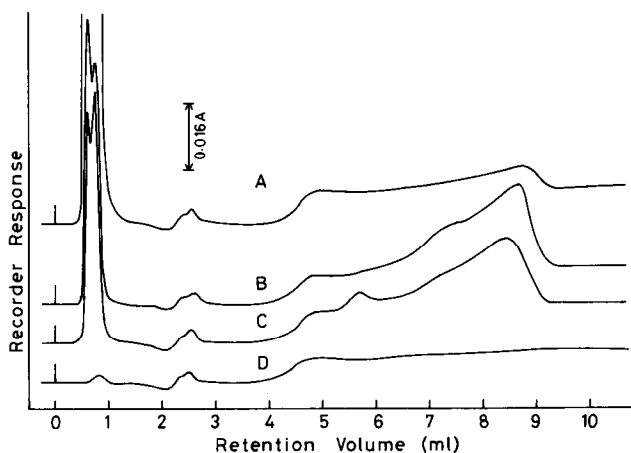

Fig. 1. LAC results for P(S–b–VAc) copolymers obtained with linear gradient elution. Samples: (A) P(S–b–VAc) I; (B) P(S–b–VAc) II; (C) P(S–b–VAc) III; (D) DCE. Sample size, 0.1%, 0.1 ml injected; linear gradient from DCE–ethanol (98:2) to DCE–ethanol (85:15) in 20 min; UV detection at 254 nm, 0.16 a.u.f.s.; column temperature, 30°C.
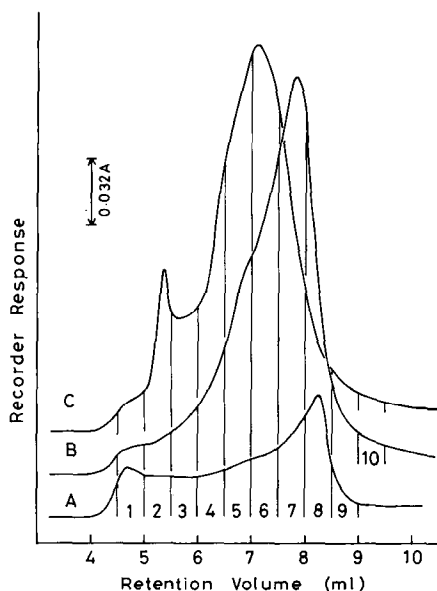
Fig. 2. LAC results and points for fractionation of P(S–b–VAc) copolymers. Samples: (A) P(S–b–VAc) I; (B) P(S–b–VAc) II; (C) P(S–b–VAc) III. Sample size, 0.4%, 0.2 ml injected; UV detection at 254 nm, 0.32 a.u.f.s.; other conditions as in Fig. 1.

Fig. 1 and, as a result, the peak retention volume and the breakthrough volume for the copolymers decreased.

The composition of the copolymers in LAC fractions was measured by infrared spectroscopy. Fractions were dried on a potassium bromide disk and the casting film formed on the disk was subjected to measurement of infrared spectra. The absorbances at 1601 cm^{-1} (a phenyl characteristic band) and 1739 cm^{-1} (a C=O characteristic band) were determined and the styrene content was calculated as follows:

$$\text{Absorbance at 1601 cm}^{-1} = 0.0075C + 0.0027 \tag{1}$$

$$\text{Absorbance at 1739 cm}^{-1} = 0.1420C' + 0.00166 \tag{2}$$

$$\text{Styrene content in the copolymer (wt.-\%)} = \frac{C}{C + C'} \cdot 100 \tag{3}$$

where C and C' are the styrene concentration in the solution and the vinyl acetate concentration in the solution, respectively.

Eqns. 1 and 2 were obtained with PS and PVAc solutions of several known concentrations by measuring the absorbance and by the least-squares method. The styrene contents in the LAC fractions are given in Table I. Molecular weight averages of the copolymers in the LAC fractions were measured by SEC and the values are also given in Table I. A calibration graph for SEC was constructed with polystyrene standards, and therefore the molecular weights obtained were all polystyrene equivalent molecular weight averages.

Although the three copolymer fractions of the same fraction number were not

TABLE I

STYRENE CONTENT AND MOLECULAR WEIGHT AVERAGES FOR LAC FRACTIONS

Sample	Fraction No.	Styrene content (wt.-%)	Molecular weight	
			$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$
I	1	87.4	1.46	2.41
	2	86.0	1.53	2.67
	3	87.2	1.75	2.68
	4	84.6	1.65	2.49
	5	82.3	1.78	2.56
	6	74.1	1.92	2.89
	7	66.3	2.42	3.60
	8	44.6	3.31	5.25
	9	33.8	3.70	5.69
	Unfractionated	90.0	1.29	3.09
II	1	90.2	–	–
	2	90.6	–	–
	3	88.8	0.91	1.51
	4	85.0	1.06	2.24
	5	86.3	1.37	2.22
	6	82.9	1.59	2.40
	7	74.5	2.14	3.14
	8	50.8	3.37	5.52
	9	47.4	3.20	6.60
	10	45.4	3.35	6.36
	Unfractionated	48.0	1.68	6.66
III	1	86.4	0.78	1.70
	2	74.7	0.83	1.79
	3	76.2	1.37	3.08
	4	80.2	1.44	2.90
	5	81.8	1.64	2.93
	6	76.5	1.89	3.07
	7	58.8	2.37	3.70
	8	54.5	2.60	4.83
	9	39.1	2.35	4.89
	10	39.0	2.46	4.79
	Unfractionated	49.0	1.75	5.10

consistent with respect to styrene content and molecular weight averages, there are positive trends in the compositions and molecular weight averages. Thus the vinyl acetate content and molecular weight averages of the copolymers increased with increasing fraction number (retention volume), the composition range for the three copolymers was between 40 and 90 wt.-% styrene regardless of the styrene in the feed and the copolymer fractions that contain more styrene have lower molecular weights.

Both the molecular weight distributions and the chemical composition distributions of these fractions were broad. The results from LAC and SEC for the fractions indicated that for the block copolymers the two types of distribution are independent of each other, although there is a relationship between the compositions and the molecular weight averages.
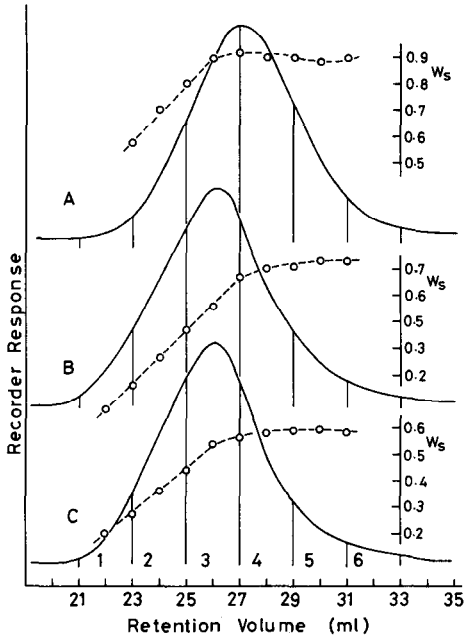
Fig. 3. SEC results and points for fractionation of P(S–b–VAc) copolymers. Samples: (A) P(S–b–VAc) I; (B) P(S–b–VAc) II; (C) P(S–b–VAc) III. Sample size, 0.4%, 0.2 ml injected; UV detection at 254 nm, 0.32 a.u.f.s. ○, Styrene weight fraction, W_s. Figures on the chromatogram C represent the fraction numbers.
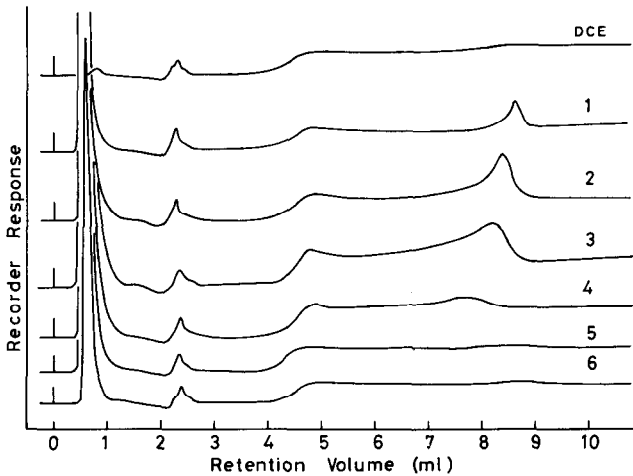

Fig. 4. LAC results for SEC fractions of P(S–b–VAc) I copolymers. Figures on the chromatograms represent the fraction numbers. For LAC conditions, see text.
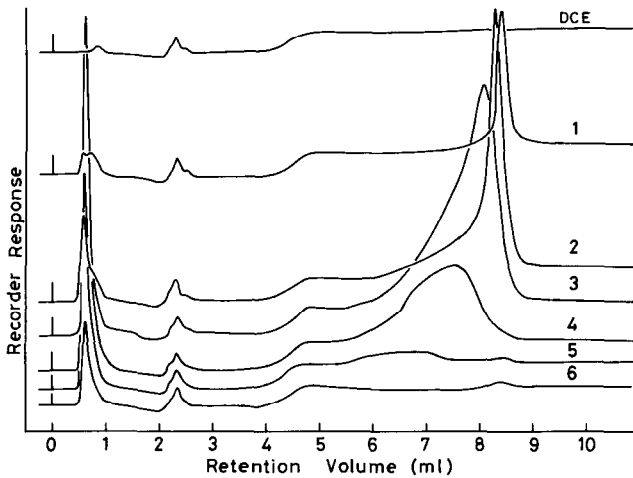
Fig. 5. LAC chromatograms for SEC fractions of P(S–b–VAc) II copolymers. Figures on the chromatograms represent the fraction numbers. For LAC conditions, see text.

Fractionation by SEC

In order to discuss in more detail the relationship between the molecular weight and chemical composition distributions, the block copolymers were fractionated by SEC and the fractions were subjected to LAC. SEC results for the copolymers are shown in Fig. 3. Styrene weight fractions calculated point by point were obtained by using a dual detection system (UV and refractive index) and are also shown in Fig. 3. Although the SEC–dual detection system does not give accurate information on the chemical heterogeneity of copolymers[10], the results show the trend in the relationship between composition and molecular weight. Similarly to the results in Table I, the
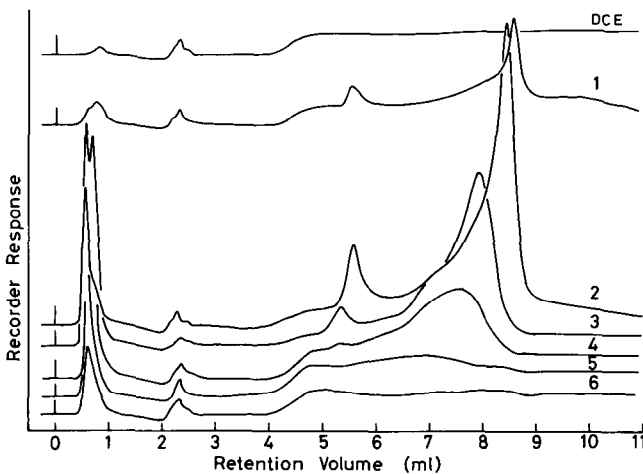
Fig. 6. LAC chromatograms for SEC fractions of P(S–b–VAc) III copolymers. Figures on the chromatograms represent the fraction numbers. For LAC conditions, see text.

portions of the copolymers that contained more styrene eluted later in SEC and had lower molecular weights.

The SEC traces were divided into six fractions and the SEC fractions were subjected to LAC; the results are shown in Figs. 4–6. Fractions having higher molecular weight contain more vinyl acetate. The chemical composition distribution of each fraction was different. Fractions having a higher molecular weight have a narrow chemical composition distribution and fraction 4 had the broadest chemical composition distribution.

A PVAc homopolymer shows UV absorption below 250 nm and the wavelength of maximum absorbance is 237 nm. Therefore, if the wavelength of the UV detector was set at 237 nm, vinyl acetate traces were observed in addition to styrene traces, although the absorption coefficient of PVAc 237 nm was only 22% of that of PS. In this work, however the wavelength at 254 nm was selected in order to obtain a higher sensitivity for the styrene traces.

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