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## Liquid adsorption chromatography of styrene copolymers of methacrylates and acrylates

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### SUMMARY

Styrene copolymers with methyl, ethyl and *n*-butyl methacrylate and acrylate were prepared by solution polymerization at a low degree of conversion. These copolymers were separated according to composition by gradient elution using silica gel as the stationary phase and chloroform–ethanol as the mobile phase. The initial mobile phase was chloroform–ethanol (99:1, v/v) and the final one (93:7, v/v), the composition changing linearly. Acrylate- or methacrylate-rich copolymers were eluted later and required a higher ethanol content in the mobile phase. The retention volume of the copolymers was influenced by column temperature in such a way that the copolymers tended to be retained in the column longer at high temperatures. The resolution between two adjacent peaks was improved with increase in column temperature. For copolymers having the same styrene content, those having smaller alkyl ester groups tended to be retained in the column longer than those having longer alkyl ester groups at the same column temperature.

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### INTRODUCTION

Most synthetic copolymers generally have a chemical composition distribution (CCD) in addition to a molecular weight distribution (MWD). Size-exclusion chromatography (SEC) can be used for the determination of the MWD of synthetic polymers, but it is not always easy to obtain accurate molecular weight averages for copolymers by SEC, because the separation of polymers by SEC is achieved according to the sizes of the molecules in solution and the molecular weights of copolymers are not always directly proportional to molecular size<sup>1</sup>. SEC with dual detectors is a well known method for determining the CCD. However, this technique is incapable of determining a real CCD, because components eluted in the same retention volume might have different compositions with the same molecular size. Therefore, only the average composition can be detected<sup>2</sup>.

To obtain both the MWD and the CCD, the determination of the MWD independent of composition and the separation of copolymers by composition independent of molecular weight are required. Recent developments in high-performance liquid chromatography (HPLC) have permitted the separation of copol-

ymers according to their chemical compositions. Styrene–methyl methacrylate<sup>3–5</sup>, styrene–acrylate<sup>6</sup>, styrene–acrylonitrile<sup>7</sup> and styrene–butadiene<sup>8</sup> copolymers have been separated by HPLC according to their compositions.

In previous papers<sup>4,9–12</sup>, the separation of styrene–methyl methacrylate copolymers according to chemical composition by liquid adsorption chromatography (LAC) was reported. A molecular weight dependence on the separation of these copolymers by LAC was not observed. The aim of this work was to apply this LAC technique to the separation of several types of styrene–acrylate and styrene–methacrylate copolymers according to their composition and to explain the usefulness of LAC for the separation of styrene copolymers having carbonyl groups as one component.

## EXPERIMENTAL

### *Apparatus*

LAC was performed on a Jasco Trirotar-VI high-performance liquid chromatograph with a Uvidec-100 VI ultraviolet absorption detector operated at 254 nm (Japan Spectroscopic, Tokyo, Japan). The column (50 mm × 4.6 mm I.D.) was packed with silica gel with a pore size of 30 Å and a mean particle diameter of 5 μm (Nomura Chemical, Aichi, Japan). The number of theoretical plates was 1600, obtained by injecting 5 μl of a 0.5% benzene solution in chloroform containing 1% ethanol. The column was thermostated at a specified temperature in a Model TU-100 column oven (Japan Spectroscopic).

### *Samples*

Methyl methacrylate (MMA), ethyl methacrylate (EMA), *n*-butyl methacrylate (BMA), methyl acrylate (MA), ethyl acrylate (EA) and *n*-butyl acrylate (BA) were used as comonomers, and were copolymerized with styrene (S) by solution polymerization at a low degree of conversion. A total volume of 25 ml of a mixture of freshly distilled styrene monomer and methacrylate or acrylate monomer at a specified molar ratio was dissolved in 25 or 50 ml of benzene and 20 or 40 mg of azobisisobutyronitrile (AIBN) were added. Polymerization was performed at 60°C for 10 h under a nitrogen atmosphere. The polymerization products were purified by a solution-precipitation approach by dissolving the products in chloroform, followed by precipitating them in methanol. This approach was repeated twice and the products were dried under vacuum.

The composition of the copolymers was measured by ultraviolet spectroscopy at 260 nm and the results are listed in Table I. A calibration graph was constructed with polystyrene. Polystyrene-equivalent molecular weight averages of the copolymers measured by SEC were between  $1.0 \cdot 10^5$  and  $3.0 \cdot 10^5$  for the weight-average molecular weight ( $\bar{M}_w$ ) and  $0.5 \cdot 10^5$  and  $1.5 \cdot 10^5$  for the number-average molecular weight ( $\bar{M}_n$ ), and the values of  $\bar{M}_w/\bar{M}_n$  were between 1.6 and 1.7 (Table I).

### *Gradient elution*

The mobile phase was a linear gradient of chloroform–ethanol. The initial mobile phase (A) was chloroform–ethanol (99.0:1.0, v/v) and the final one (B) chloroform–ethanol (93.0:7.0, v/v), the composition changing linearly from 100%

TABLE I  
COMPOSITION AND MOLECULAR WEIGHT AVERAGES OF SAMPLE COPOLYMERS

Sample	Styrene content (mol%)	Molecular weight <sup>a</sup>		Sample	Styrene content (mol%)	Molecular weight <sup>a</sup>	
		$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$			$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$
S-MMA	I	64.6	12.4	S-MA	I	65.7	10.7
	II	47.3	12.2		II	51.3	12.5
	III	28.7	12.2		III	35.6	17.8
	IV	14.7	12.6		IV	19.0	20.1
S-EMA	I	69.1	9.5	S-EA	I	68.6	12.2
	II	50.2	12.0		II	52.6	10.9
	III	30.4	13.5		III	36.7	20.2
	IV	15.5	22.9		IV	20.7	23.8
S-BMA	I	69.6	9.4	S-BA	I	75.5	8.7
	II	50.3	13.8		II	59.2	10.7
	III	30.7	14.2		III	41.0	12.9
	IV	14.5	18.6		IV	15.8	22.9

<sup>a</sup> Polystyrene-equivalent molecular weight.

A to 100% B in 30 min. The flow-rate of the mobile phase was 0.5 ml/min. The sample copolymers were dissolved in solution A at a total concentration of 0.1% (w/v) and the injection volume was 0.1 ml. The sample solutions were injected 1 min after the start of the gradient elution programme.

## RESULTS AND DISCUSSION

In the LAC of S-MMA copolymer, the retention volume of the copolymers was affected considerably by the ethanol content in the mobile phase and by the column temperature<sup>9,10</sup>. However, the separation of the copolymers according to composition was not possible with isocratic elution conditions. Gradient elution conditions were required at a constant column temperature. Higher ethanol contents in the mobile phase and lower column temperatures were required to separate MMA-rich copolymers. In the present experiments, several gradient elution conditions, *i.e.*, the initial and the final compositions of the mobile phase and the gradient period, were examined at different column temperatures in order to separate various styrene copolymers with acrylate or methacrylate having different compositions. The optimized gradient elution conditions are given under Experimental.

Figs. 1-3 show examples of the separation of mixtures of S-MMA (Fig. 1), S-MA (Fig. 2) and S-BA (Fig. 3) copolymers at different column temperatures. Peak elution was retarded with increasing column temperature, as observed in previous studies<sup>9,10</sup>.

Fig. 1 shows the LAC of a mixture of four S-MMA copolymers of different composition. The mixture was separated into four peaks, indicating the separation was performed according to composition. The gradient elution conditions in the present experiment were different from those used in previous work<sup>10</sup> and the ethanol content in the mobile phase at the retention volume, *ca.* 7-8 ml, was lower in this work than in the previous studies. As a result of the lower ethanol content, the retention volume of

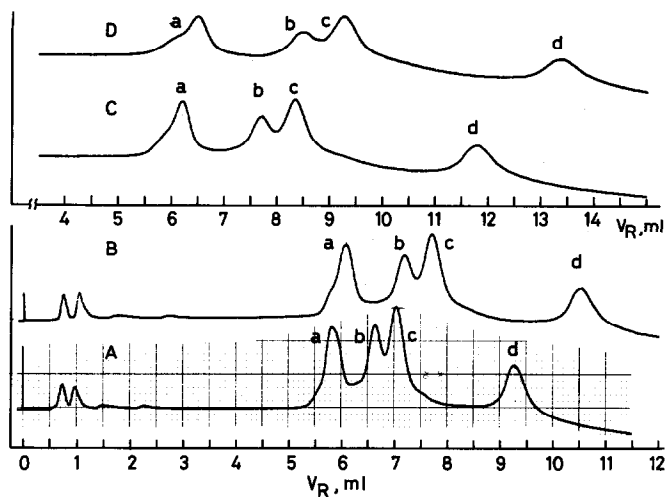


Fig. 1. Chromatograms of S-MMA copolymers. Column temperature: (A) 40; (B) 50; (C) 60; (D) 70°C. S-MMA sample: a = I; b = II; c = III; d = IV. UV attenuation: 0.16 a.u.f.s.

the copolymers increased and the width of the blind zone<sup>10</sup>, defined as a space in which no peak appears between  $V_0$  (the interstitial volume of the column) and the point where the most weakly adsorbed solute appears, increased together. As the final ethanol content in the mobile phase was nearly twice that in previous work, sample copolymers with a high MMA content (S-MMA IV, peak d) could be eluted even at high column temperature, such as 70°C. The difference in retention volume between the first two peaks increased with increasing column temperature and the resolution between two peaks, S-MMA I and II (peaks a and b), was improved considerably at

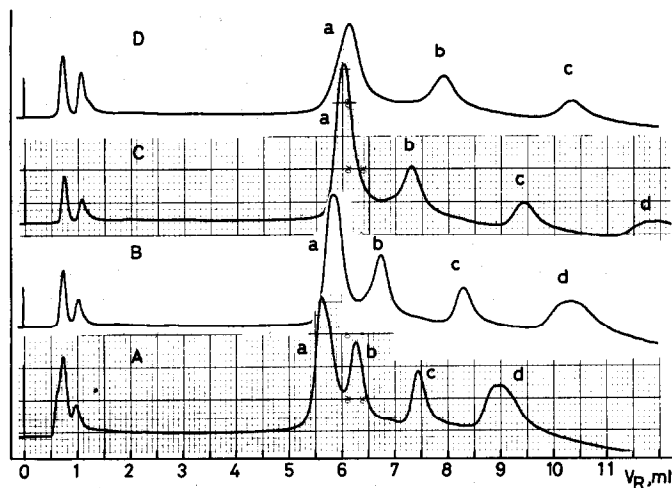


Fig. 2. Chromatograms of S-MA copolymers. Column temperature: (A) 40; (B) 50; (C) 60; (D) 70°C. S-MA sample: a = I; b = II; c = III; d = IV. UV attenuation: 0.16 a.u.f.s.

a column temperature of 70°C. However, the resolution between peaks b and c (S-MMA II and III) was unchanged and the peak widths became broad with increasing column temperature.

The LAC of a mixture of S-MA copolymers at different column temperatures is shown in Fig. 2. The peak retention volume of the copolymers increased and the resolution between adjacent peaks was improved with increasing column temperature. Each of the peaks is symmetrical and the CCD of the sample copolymers is less broad than that for the S-MMA copolymers in Fig. 1. Copolymer S-MA IV (peak d) at a column temperature 70°C eluted at a retention volume of 14.5 ml, and therefore the peak is not shown in Fig. 2D.

Fig. 3 shows examples of the separation of a mixture of S-BA copolymers. Copolymer S-BA I eluted at the interstitial volume (retention volume,  $V_R = 0.6$  ml) even at a column temperature of 70°C. The ethanol content in the initial mobile phase should be lowered to less than 1% in order to retain copolymer S-BA I in the column. The resolution between adjacent peaks of S-BA II, III and IV was improved with increasing column temperature. Peak separation of S-BA III and IV was not observed at column temperatures of 40 and 50°C, but these peaks were separated at 60°C.

The plot of column temperature *versus* retention volume can also explain the separation of a mixture of the copolymers. Fig. 4 and 5 show these plots for S-EMA and S-BMA copolymers. In Fig. 4, the difference in retention volume between two copolymers of different composition increases with increasing column temperature and a corresponding improvement in resolution is observed. The dashed line for

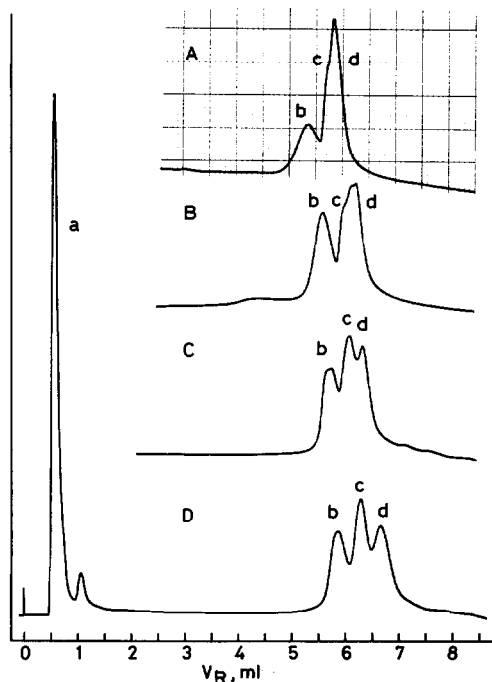


Fig. 3. Chromatograms of S-BA copolymers. Column temperature: (A) 40; (B) 50; (C) 60; (D) 70°C. S-BA sample: a = I; b = II; c = III; d = IV. UV attenuation: 0.16 a.u.f.s.

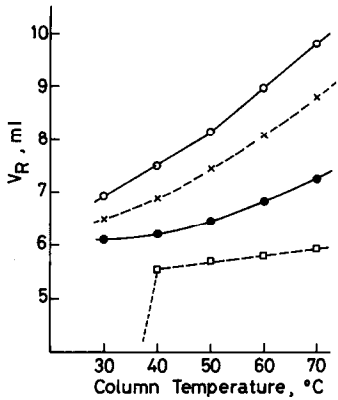


Fig. 4. Plots of retention volume vs. column temperature for S-EMA copolymers. S-EMA sample:  $\square$  = I;  $\bullet$  = II;  $\times$  = III;  $\circ$  = IV.

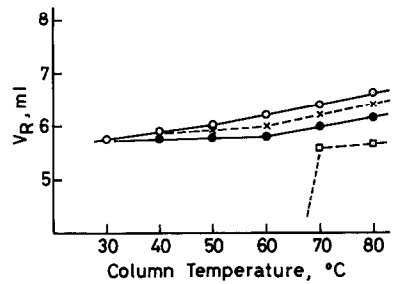


Fig. 5. Plots of retention volume vs. column temperature for S-BMA copolymers. S-BMA sample:  $\square$  = I;  $\bullet$  = II;  $\times$  = III;  $\circ$  = IV.

S-EMA I means that this copolymer eluted at the interstitial volume at a column temperature of 30°C. In Fig. 5, the difference in retention volume between two copolymers of different composition seems to be small, but the resolution was improved at elevated column temperature. Pairs of copolymers S-BMA II and III and S-BMA III and IV were not separated below a column temperature of 60°C but were separated above 70°C. Copolymer S-BMA I eluted at the interstitial volume below a column temperature of 60°C. The plots of column temperature *versus* retention volume for S-EMA and S-BMA demonstrate that, for copolymers with the same styrene content and at the same column temperature, those which have smaller alkyl ester groups (S-EMA in this instance) eluted later than those having larger alkyl ester

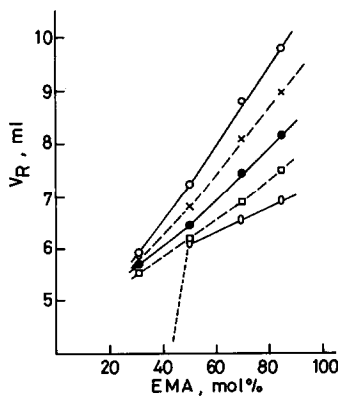


Fig. 6. Plots of retention volume vs. EMA content for S-EMA copolymers at different column temperatures.  $\circ$  = 70;  $\times$  = 60;  $\bullet$  = 50;  $\square$  = 40;  $\circ$  = 30°C.

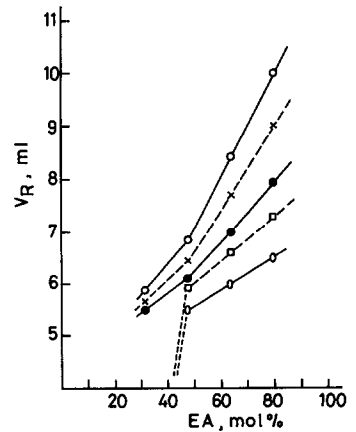


Fig. 7. Plots of retention volume vs. EA content for S-EA copolymers at different column temperatures.  $\circ$  = 70;  $\times$  = 60;  $\bullet$  = 50;  $\square$  = 40;  $\circ$  = 30°C.

groups (S-BMA). This tendency was generally observed for other styrene copolymers with acrylate and methacrylate.

The relationship between copolymer composition and retention volume at different column temperatures is shown in Figs. 6 and 7 for S-EMA and S-EA copolymers. The retention volume increased both with increasing EMA and EA content in the copolymers and with increasing column temperature. Copolymer S-EMA I at a column temperature of 30°C and S-EA I at 30 and 40°C eluted at the interstitial volume. The plots of composition *versus* retention volume show that, for copolymers with the same styrene content, S-EMA and S-EA were not resolved in most instances. Resolution is observed when the column temperature is 30°C for copolymers having an EA or EMA content of more than 50 mol-% and when column temperature is above 60°C for copolymers having an EA or EMA content of more than 80 mol-%.

## CONCLUSIONS

The LAC technique has been applied to the separation of styrene-acrylate and styrene-methacrylate copolymers. These copolymers were separated according to their composition by a gradient elution technique with increasing ethanol content in the ethanol-chloroform mobile phase. As the final ethanol content in the mobile phase was nearly twice that in previous work, sample copolymers with low styrene content could be eluted even at high column temperatures. As observed in previous studies on styrene-methyl methacrylate copolymers, the retention volumes of styrene-acrylate and styrene-methacrylate copolymers were retarded with increasing column temperature and copolymers having more styrene eluted earlier than those having less styrene. The difference in retention volume between two peaks increased with increasing column temperature and a corresponding improvement in resolution was observed. With copolymers with the same styrene content, those having smaller alkyl ester groups eluted later than those having larger alkyl ester groups. Similarly, copolymers of styrene-acrylate and styrene-methacrylate having the same alkyl ester groups and the same styrene content were not resolved in most instances.

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