

## **Separation and detection of styrene–alkyl methacrylate and ethyl methacrylate–butyl methacrylate copolymers by liquid adsorption chromatography using a dichloroethane mobile phase and a UV detector**

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### **ABSTRACT**

Styrene (S)–methyl methacrylate (MMA), S–ethyl methacrylate (EMA) and EMA–*n*-butyl methacrylate (BMA) copolymers were separated according to chemical composition. Silica gel was used as the stationary phase and a mixture of 1,2-dichloroethane (DCE) and ethanol as the mobile phase. DCE was transparent at wavelengths over 230 nm and methacrylate homopolymers and copolymers could be monitored with a conventional UV detector at 233 nm. The molar absorption coefficients for both PS and PMMA at 233 nm were nearly equal and the chromatograms obtained at this wavelength reflected the relative amounts of the copolymers with different chemical compositions. A mixture of S–MMA copolymers having different compositions and PMMA was separated by a gradient elution method at constant column temperature. The initial mobile phase was a mixture of DCE and ethanol (99.0:1.0, v/v), and the ethanol content was increased to 5.0% in 20 min and then to 10.0% in another 5 min or to 10.0% in 20 min. The copolymers of S–MMA and S–EMA having higher styrene contents eluted earlier and the elution of the copolymers was in order of decreasing styrene content. Therefore, the chemical composition of the copolymers in a mixture can be determined directly from the chromatogram by knowing the retention volume of each copolymer. A mixture of PEMA, PBMA and their copolymers was also separated by a similar method. PBMA eluted earlier than PEMA. The affinity of the EMA component to the surface of silica gel was assumed to be stronger than that of the BMA component.

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### **INTRODUCTION**

Synthetic random copolymers usually have a molecular weight distribution (MWD) and a chemical composition distribution (CCD). The accurate determination of CCD is important for the characterization of copolymers and the determination of MWD. Although molecular weight averages and the MWD of a polymer can be measured by size exclusion chromatography (SEC), those of a copolymer cannot be obtained accurately without knowing the CCD of the copolymer [1]. The separation of styrene (S)–methyl methacrylate (MMA) random copolymers by high-performance liquid adsorption chromatography (LAC) has been reported in our previous papers [1–6] and the technique was applied to the separation of styrene–alkyl methacrylates and styrene–alkyl acrylate copolymers [7] and S–MMA block copolymers [8],

respectively. High-conversion S-MMA random copolymers have been characterized by a combination of LAC and SEC [5]. Fractionation by LAC gave the CCD of the copolymers and the real MWD has been obtained by fractionation by SEC followed by LAC. A LAC separation mechanism has been proposed [9].

Several attempts have been reported by other workers for the separation of copolymers according to composition by high-performance liquid chromatography (HPLC), *e.g.*, S-MMA [10,11], S-methyl acrylate [12], S-acrylonitrile [13] and S-butadiene [14]. UV absorption detector had to be utilized to monitor the copolymers in the effluent from a column. Because mobile phase gradient elution is required to elute the copolymers according to composition, a differential refractive index detector cannot be employed. Solvents such as chloroform and tetrahydrofuran used as one component of mobile phases reported in the literature, are opaque at wavelengths below 245 nm, and a comonomer unit such as MMA and acrylonitrile is transparent above 250 nm. Therefore, only the styrene content in the effluent could be detected. Consequently, chromatograms recorded on a chart were not true concentration profiles for the copolymers in the effluent but profiles proportional to the styrene content in the copolymers.

1,2-Dichloroethane (DCE) is transparent at wavelengths above 230 nm, and polymethacrylates and polyacrylates have UV absorption near wavelengths of 230 nm at the foot of the absorption band. Therefore, a combination of DCE and a UV detector will make possible the measurement of chromatograms of methacrylate copolymers and homopolymers. In this work, copolymers of S-alkyl methacrylates (methyl, ethyl and *n*-butyl) were separated using a mixture of DCE and ethanol as the mobile phase and detected using a UV detector at 233 nm. Operating variables such as the gradient elution conditions and the selection of a wavelength which has equal molar absorption coefficients for both styrene and alkyl methacrylate units were investigated. The separation system was applied for the separation of ethyl methacrylate (EMA)-butyl methacrylate (BMA) copolymers, which have no UV absorption near 254 nm.

## EXPERIMENTAL

### *Apparatus*

LAC measurements were performed on a Jasco Trirotar-VI high-performance liquid chromatograph (Japan Spectroscopic, Tokyo, Japan) with a Uvidec-100VI variable-wavelength UV absorption detector. Silica gel with a pore size of 30 Å and a mean particle diameter of 5 μm was packed in a 50 mm × 4.6 mm I.D. stainless-steel tube. This column was thermostated at a specified temperature in a Model TU-300 column oven.

A Uvidec-610C UV-VIS spectrophotometer (Japan Spectroscopic) equipped with a microcomputer was used for the measurement of the UV absorption spectra of polystyrene (PS), poly(methyl methacrylate) (PMMA) and DCE, using a band width (resolution) of 2.00 nm, time constant 0.4 s, scan speed 10 nm/min and quartz cells of 1-cm path length.

### *Sample*

Copolymers of S-MMA [2] and S-ethyl methacrylate (EMA) [7], having narrow

TABLE I  
STYRENE CONTENT OF S-MMA AND S-EMA COPOLYMERS

Copolymer	Sample	Styrene content (mol-%)	Copolymer	Sample	Styrene content (mol-%)
S-MMA	I	85.5	S-MMA	VIII	26.5
	II	73.4		IX	15.2
	III	66.3	S-EMA	I	69.1
	IV	57.4		II	50.2
	V	48.7		III	30.4
	VI	42.1		IV	15.5

CCD, were the same as those prepared previously. These samples were prepared by solution polymerization in benzene at a low degree of conversion. PS, PMMA, PEMA and PBMA homopolymers and EMA-BMA copolymers were also prepared in the same manner [7].

The compositions of the styrene copolymers were measured by UV spectrophotometry and are shown as the styrene content in mole percent in Table I. The composition of EMA-BMA copolymers was not measured and only the mole percent of the feed of monomers is given, as follows: EMA-BMA I (25-75%), II (50-50%) and III (75-25%) (it was found by separate IR experiments that the copolymers had roughly the expected chemical compositions).

### Elution

The solvents used in the mobile phases were DCE and ethanol. Elution was performed in the gradient elution mode. Three different mixtures of DCE and ethanol were prepared: (A) 99.0:1.0, (B) 95.0:5.0 and (C) 90.0:10.0 (v/v). The initial mobile phase was A and the composition of the mobile phase was changed linearly to 100% B in 15 min, or to 100% B in 20 min and to 100% C in a further 5 min or to 100% C in 20 min.

Samples were dissolved in mobile phase A and the injection volume of the sample solutions was 0.1 ml. At the beginning of the elution, the gradient programme of the mobile phase composition was started first, and the sample solutions were injected 1 min after the start of the gradient programme. The flow-rate of the mobile phase was 0.5 ml/min.

## RESULTS AND DISCUSSION

### UV spectra

Fig. 1 shows the UV spectra of PS, PMMA, chloroform and DCE. PS and PMMA were each dissolved in DCE at a concentration of 0.335 g/l and the UV spectra of the polymer solutions were measured with DCE as a reference solvent. Water was used as a reference for DCE and chloroform.

PMMA has UV absorption in the low-wavelength region and the foot of the PMMA absorption band can be observed near 230 nm. The UV absorbance at 250 nm for chloroform was 0.9 and that at 229 nm for DCE was 0.90. Therefore, the UV absorption spectra of PMMA in a DCE solution can be measured near 230 nm with

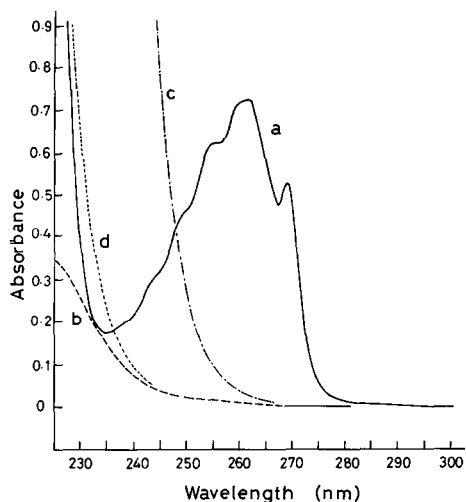


Fig. 1. UV absorption spectra of (a) PS and (b) PMMA homopolymers, (c) chloroform and (d) DCE. Solvent for PS and PMMA, DCE; reference for PS and PMMA, DCE; reference for chloroform and DEC, water; concentration for PS and PMMA, 0.335 g/ml.

a better signal-to-noise ratio. If the UV absorption of the copolymers in the effluent is monitored at a wavelength at which the absorption coefficient for PS is equal to that for PMMA, then the chromatograms of S-MMA copolymers express the concentrations of the copolymers in the effluent. To examine a wavelength at which PS and PMMA have the same absorption coefficient, PS and PMMA solutions at the same molar concentration were prepared and the UV absorption spectra of the solutions were measured as shown in Fig. 1.

Although a wavelength at which the absorption coefficient of PS was equal to that of PMMA could not be found, the wavelength of 233 nm was assumed to have nearly equal absorption coefficients. The absorbance at 233 nm for PS in Fig. 1 was 0.200 and that for PMMA was 0.195. Therefore, even if it was assumed that both homopolymers in Fig. 1 had the same absorbance at 233 nm, the relative error was within 3%. The only disadvantage of the use of a wavelength of 233 nm for monitoring the copolymer concentration in the effluent was that the UV absorption coefficient of PS at 233 nm was 28% of that at 254 nm. This drawback, however, can be partly overcome because the chromatograms obtained at 233 nm were the sum of the UV absorptions for PS and PMMA. Moreover, the attenuation for the UV detector could be increased to obtain reasonable peak heights for the copolymers.

### Elution

When chloroform in the mobile phase was replaced with DCE, a large volume of ethanol was required to elute S-MMA copolymers from the column [3], although the elution behaviour of the copolymers in the DCE-ethanol system was similar to that with chloroform-ethanol as the mobile phase; an increase in the ethanol content in the mobile phase and/or a decrease in the column temperature was effective in eluting the copolymers which were retained in the column. At a column temperature of 10°C, for example, a PMMA homopolymer was eluted from the column completely using DCE-ethanol (95:5, v/v) as the mobile phase.

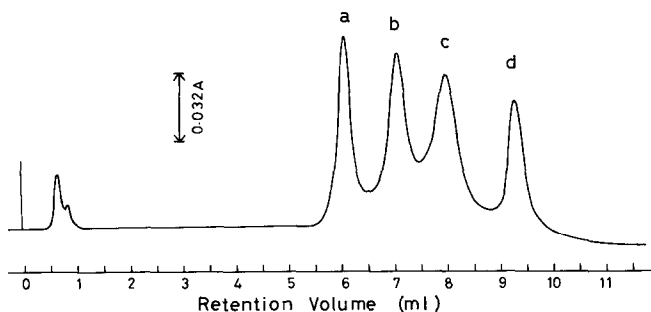


Fig. 2. LAC of S-MMA copolymers and PMMA. Column temperature, 10°C; sample, (a) S-MMA VI, (b) S-MMA VIII, (c) S-MMA IX, (d) PMMA; detection, 233 nm, 0.32 a.u.f.s.; sample concentration, *ca.* 0.01% each; gradient, 100% A to 100% B in 15 min.

A mixture of S-MMA VI, VIII and IX and PMMA was separated at a column temperature of 10°C and the result is shown in Fig. 2. The gradient elution conditions were as follows: the initial mobile phase was mixture A and the composition of the mobile phase was changed linearly from 100% A to 100% B in 15 min. The sample concentrations of the copolymers and PMMA were about 0.01% each. The peak height for each sample was nearly equal and a PMMA peak can also be seen in Fig. 2. Under these elution conditions, S-MMA copolymers I, II and III eluted at  $V_0$  (the exclusion limit, *ca.* 0.6 ml), and copolymers IV and V eluted near copolymer VI.

To separate all the components of a mixture of S-MMA copolymers I-IX and PMMA simultaneously, the column temperature was increased to 50°C and the gradient elution conditions were improved as follows: the initial mobile phase was mixture A and the composition of the mobile phase was changed from 100% A to 100% B in 20 min and then to 100% C in a further 5 min. The results are shown in Fig. 3. The chromatograms obtained at 254 nm are also shown for comparison. S-MMA copolymer I appeared at the exclusion limit and is not shown in Fig. 3. The peak for

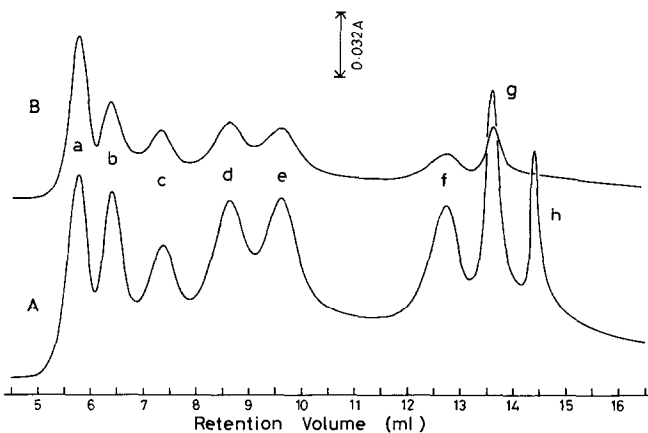


Fig. 3. LAC of S-MMA copolymers and PMMA. Column temperature, 50°C; sample, (a) S-MMA II, (b) S-MMA III, (c) S-MMA IV, (d) S-MMA V, (e) S-MMZ VI, (f) S-MMA VIII, (g) S-MMA IX, (h) PMMA; sample concentration, *ca.* 0.01% each; detection, (A) 233 nm, 0.16 a.u.f.s., (B) 254 nm, 0.32 a.u.f.s.; gradient, 100% A to 100% B in 20 min and to 100% C in a further 5 min.

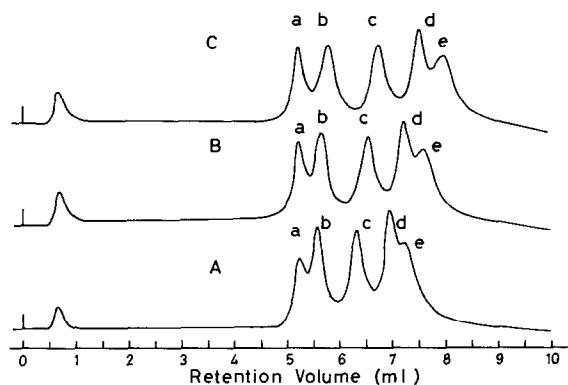


Fig. 4. Chromatograms of S-EMA copolymers and PEMA. Column temperature, (A) 50°C, (B) 60°C, (C) 70°C; sample, (a) S-EMA I, (b) S-EMA II, (c) S-EMA III, (d) S-EMA IV, (e) PEMA; sample concentration, *ca.* 0.01% each; detection, 233 nm, 0.32 a.u.f.s.; gradient, 100% A to 100% C in 20 min.

PMMA disappeared at 254 nm. The peak intensity of every component at 233 nm was higher than that at 254 nm, although the attenuation of the UV detector was not the same. This is because peaks obtained at 233 nm include both components S and MMA in the copolymers, although the UV absorption coefficient for the styrene component at 254 nm is higher than that at 233 nm.

Fig. 4 shows the chromatograms for a mixture of four S-EMA copolymers and PEMA at three different column temperatures. The retention volumes of the peaks increased with increasing column temperature, except for S-EMA copolymer I, and as a result the resolution between copolymers I and II and that between IV and PEMA was improved. The gradient elution conditions were as follows: the initial mobile phase was mixture A and the composition of the mobile phase was changed from 100% A to 100% C in 20 min.

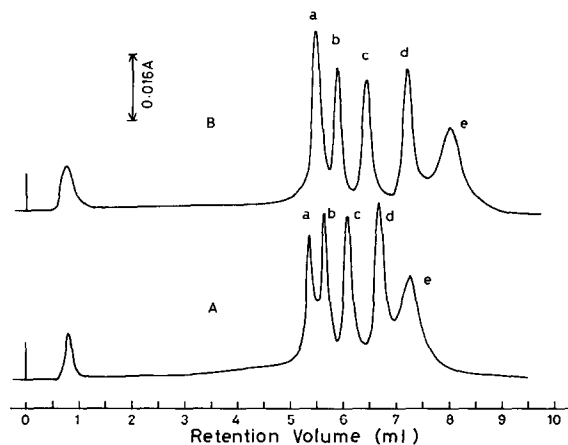


Fig. 5. Chromatograms of EMA-BMA copolymers, PEMA and PBMA. Column temperature, (A) 50°C, (B) 70°C; sample, (a) PBMA, (b) EMA-BMA I (25:75), (c) EMA-BMA (50:50), (d) EMA-BMA III (75:25), (e) PEMA; sample concentration, *ca.* 0.01% each; detection, 233 nm, 0.16 a.u.f.s.; gradient, 100% A to 100% C in 20 min.

TABLE II  
REPRODUCIBILITY OF RETENTION VOLUME WITH GRADIENT ELUTION

Copolymer	Sample	Mean and S.D. of retention volume (ml)							
		First day		Second day		Third day		Overall	
		Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
S-MMA	II	5.767	0.005	5.663	0.009	5.450	0.041	5.626	0.134
	III	6.420	0.008	6.435	0.026	6.230	0.024	6.367	0.099
	IV	7.370	0.0	7.480	0.056	7.297	0.004	7.382	0.082
	V	8.627	0.021	8.807	0.076	8.653	0.037	8.696	0.094
	VI	9.587	0.029	9.827	0.077	9.723	0.021	9.712	0.110
	VIII	12.667	0.047	12.937	0.062	12.887	0.012	12.830	0.126
PMMA	IX	13.600	0.0	13.730	0.043	13.680	0.008	13.670	0.059
	—	14.400	0.0	14.570	0.057	14.520	0.008	14.500	0.079

Fig. 5 shows the chromatograms of a mixture of PEMA, PBMA and their copolymers at different column temperatures. The gradient elution conditions were the same as in Fig. 4. As these polymers and copolymers do not have UV absorption at 254 nm, it is not possible to measure the chromatograms for these polymers and copolymers using a UV detector when tetrahydrofuran or chloroform is used as one component of the mobile phase. There has been only one report so far on the separation of mixtures of poly(alkyl methacrylates) or poly(alkyl acrylates) [15] in which a solvent-evaporative mass detector (an evaporative light-scattering detector) was used to detect the polymers in the effluent. In our system, a conventional UV detector can be employed and a special detector or detection system is not required.

The possibility of the separation of alkyl methacrylate and alkyl acrylate copolymers according to composition was pointed out in a previous paper [7], where a chloroform-ethanol mobile phase was used. On replacing chloroform in the mobile phase with DCE, a conventional UV detector could be used to monitor the concentrations of these copolymers in the effluent from a column and the possibility predicted in the previous paper [7] was proved in this work.

#### *Reproducibility of gradient elution*

Determination of the chromatograms shown in Fig. 3 was repeated three times a day for 3 days and the retention volumes of each component were measured. The results are given in Table II, with means and standard deviations for each day together with the mean and standard deviation for each set of nine measurements. The standard deviation of the retention volume for each component was between 0.06 and 0.14 ml. The range of data for each component obtained on the same day was between 0 and 0.18 ml and that obtained during the 3 days was between 0.23 and 0.39 ml.

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