Liquid adsorption chromatography of styrene–alkyl methacrylate copolymers and ethyl methacrylate–butyl methacrylate copolymers

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Mixtures of styrene–methyl methacrylate copolymers and poly(methyl methacrylate), styrene–ethyl methacrylate copolymers and poly(ethyl methacrylate), styrene–butyl methacrylate copolymers and poly(butyl methacrylate), and an ethyl methacrylate–butyl methacrylate copolymer (1:1) and its homopolymers, were separated by liquid adsorption chromatography according to their compositions. Silica gel of 30 Å pore size was used as the stationary phase and mixtures of 1,2-dichloroethane and ethanol were used as the mobile phases. The composition of the mobile phase was regulated by gradient elution. An ultraviolet absorption detector at 233 nm was used to detect the copolymers and the homopolymers in the effluent.

(Keywords: liquid adsorption chromatography; methacrylate copolymers; methacrylate homopolymers; separation by composition; ultraviolet absorption)

INTRODUCTION

It is commonly known that synthetic random copolymers have a chemical composition distribution (CCD) as well as a molecular weight distribution (MWD). Although MWD of homopolymers can be calculated rapidly and precisely by size exclusion chromatography (s.e.c.), accurate information on the MWD of copolymers cannot be obtained by s.e.c. alone[1]. Moreover, the CCD of copolymers cannot be given correctly by an s.e.c./u.v.–differential refractive index dual detector system[2]. Information on the CCD and the MWD of copolymers should be obtained by separating the copolymers by composition independently of molecular weight, and then determining the MWD of each fraction or *vice versa*. This is the principle of cross-fractionation which can be performed by a combination of several chromatographic methods.

High performance liquid chromatography (h.p.l.c.) is an attractive technique for the separation of copolymers according to their compositions. Several separation techniques of copolymers by h.p.l.c. have been reported, e.g. styrene–methyl methacrylate copolymers (P(S–MMA)) on a silica gel column[3] or a poly(acrylonitrile) gel column[4], styrene–methyl acrylate copolymers on a silica gel column[5], styrene–acrylonitrile copolymers on a silica-ODS column[6], and styrene–butadiene copolymers on a poly(acrylonitrile) gel column[7].

The separation of P(S–MMA) random copolymers by liquid adsorption chromatography (l.a.c.) on a silica gel column using a mixture of chloroform and ethanol as the mobile phase has been reported in previous papers[8–13], and the technique was applied to the separation of styrene–alkyl methacrylate and styrene–alkyl acrylate copolymers[14], S–MMA block copolymers[15], and styrene–vinyl acetate block copolymers[16]. A u.v. detector at 254 nm or 260 nm was used to monitor the copolymer concentration in the effluent from a column. The solvents used as mobile phases in these previous investigations were opaque in the short wavelength region, in which a comonomer unit such as MMA may have u.v. absorption, therefore chromatograms recorded on a chart were not true concentration profiles for the copolymers in the effluent, and only the styrene trace could be observed.

1,2-Dichloroethane (DCE) is transparent at wavelengths >230 nm (absorbance at 230 nm in a 1 cm cell is 0.4), and poly(methyl methacrylate) (PMMA) has u.v. absorption at this wavelength as the base of the u.v. absorption band. If chloroform is replaced by DCE and if there is a wavelength at which the absorption coefficient of PMMA is the same as that of polystyrene (PS), then true concentration profiles for the copolymers in the effluent will be obtained.

In the present report, a mixture of DCE and ethanol was used and operational variables such as the gradient elution conditions for the separation of a mixture of P(S–MMA) random copolymers and PMMA, a mixture of poly(styrene–ethyl methacrylate) (P(S–EMA)) and PEMA, and a mixture of poly(styrene–butyl methacrylate) (P(S–BMA)) and PBMA have been investigated. Separation and detection of a mixture of PMMA, PEMA, PBMA and P(EMA–BMA) copolymer were demonstrated.

EXPERIMENTAL

A h.p.l.c. model Trirotar-VI (Japan Spectroscopic Co., Hachioji, Tokyo 192, Japan) was used with a variable

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wavelength u.v. detector model Uvidec-100VI. The column used for l.a.c. was 50 mm in length and 4.6 mm i.d. and was packed with silica gel of 30 Å pore size and 5 μm particle diameter. This column was thermostated at a specified temperature in a column oven model TU-300. S.e.c. columns were two Shodex KF 80M HPSEC columns (30 cm × 8 mm i.d.) (Showa Denko Co., Minato-ku, Tokyo 105, Japan) packed with PS gels for polymer analysis.

The mobile phase for l.a.c. was a mixture of DCE and ethanol. Three mobile phases of different compositions were prepared: A, a mixture of DCE/ethanol (99:1, v/v); B, DCE/ethanol (95:5, v/v); and C, DCE/ethanol (90:10, v/v). The composition of the mobile phase was regulated by linear gradient elution. The other gradient elution conditions are given in the next section. The flow rate was 0.5 ml min^{-1}. The gradient elution was started 1 min after the injection of a sample solution. The mobile phase for s.e.c. was DCE and the flow rate was 1 ml min^{-1}.

P(S–MMA), P(S–EMA) and P(S–BMA) copolymers were prepared by solution polymerization at a low degree of conversion[8,14]. The composition of the copolymers was measured by u.v. spectrophotometry. A P(EMA–BMA) copolymer with a 1:1 monomer ratio was also prepared by the same method. The composition of this copolymer was not determined and expressed as the monomer feed ratio. Samples were dissolved in DCE at a concentration of 0.01–0.02% for l.a.c. and 0.2% for s.e.c. Injection volume was 0.1 ml for l.a.c. and 0.2 ml for s.e.c.

RESULTS AND DISCUSSION

PS and PMMA were dissolved in DCE and the u.v. spectra of the polymer solutions were measured with DCE as a reference solvent. The u.v. absorption coefficients for the polymers were calculated at 1 nm intervals and compared with each other. The u.v. absorption coefficient at wavelength 233 nm for PS was nearly equal to that for PMMA: 5.97 compared to 5.79 respectively per unit concentration (w/v) in a 1 cm cell, a difference of only 3%. The wavelength of 233 nm was selected as the keyband to monitor the sample concentration in the effluent.

When DCE was used in place of chloroform as one component in the mobile phase, a large amount of ethanol in the mobile phase and/or lower column temperature were required to elute the styrene copolymers from a column. Similar elution and resolution of peaks have been obtained in the following pairs for the separation of the copolymer mixtures: column temperature 30°C (chloroform)[10] *versus* 10°C (DCE); 80°C (chloroform)[10] *versus* 50°C (DCE); final ethanol content 7% (chloroform)[14] *versus* 10% (DCE). However, the separation mechanism and the elution behaviour of the copolymers in the system of silica gel/DCE–ethanol were assumed to be similar to the system of silica gel/chloroform–ethanol: the increase of the ethanol content in the mobile phase and/or the decrease of the column temperature were effective to elute the copolymers retained in the column. The hydrogen bonding between the carbonyl groups in the copolymers and the silanol groups on the silica surface was the major interaction for the separation of the copolymers.

An l.a.c. chromatogram for P(S–MMA), with a narrow CCD, in addition to PMMA is shown in *Figure 1*. The gradient elution condition was as follows: the initial mobile phase of 100% DCE was altered linearly to 100% mobile phase B in 30 min and to 100% mobile phase C in another 5 min. Column temperature was 70°C. A PMMA peak can be seen at retention volume 20.6 ml (peak i). Another distinctive feature of this system is that samples of similar concentrations have similar peak intensities in spite of their composition difference. Peak intensities proportional to the composition for copolymers of similar concentrations have been obtained previously (e.g. Figure 2 in ref. 10 and Figure 5 in ref.

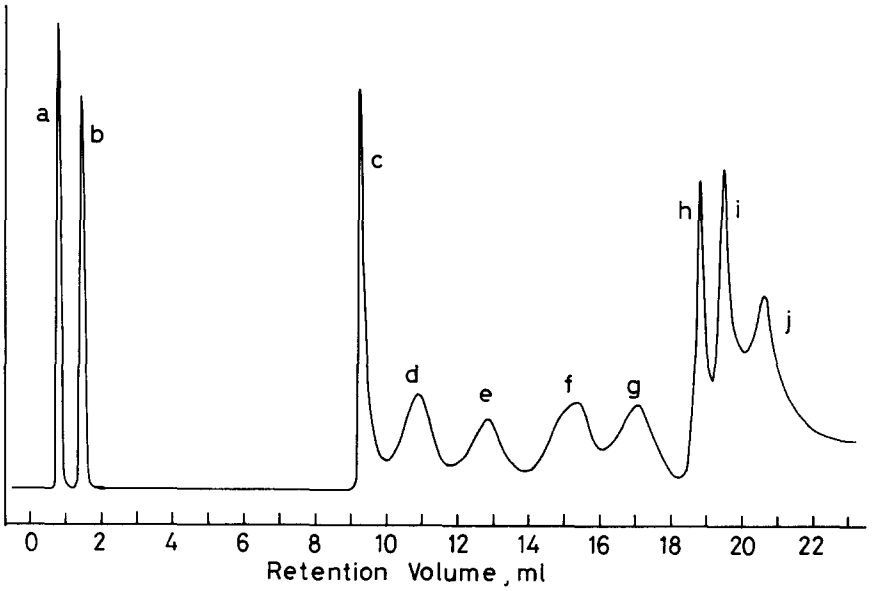

Figure 1 L.a.c. chromatogram for P(S–MMA), with a narrow CCD, and PMMA. Peaks a and c–i, P(S–MMA) with styrene content (mol%) in the copolymers: a, 85.5; c, 73.4; d, 66.3; e, 57.4; f, 48.7; g, 42.1; h, 26.5; i, 15.2. Peak b, solvent related materials; peak j, PMMA. Column temperature, 70°C; u.v. detector, 233 nm; 0.32 AUFS; sample concentration ≈0.01% each

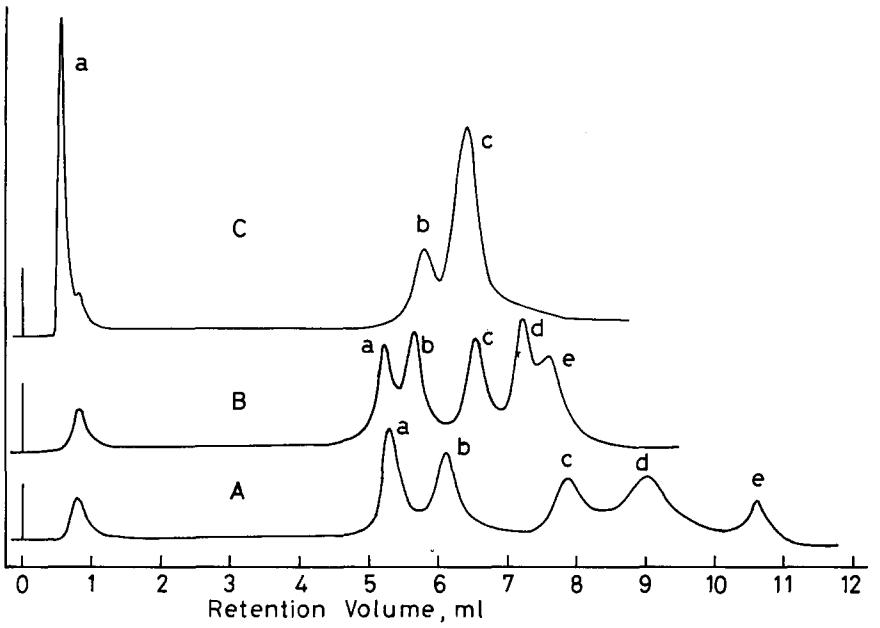

Figure 2 L.a.c. chromatograms for styrene–methacrylate copolymers and methacrylate homopolymers: curve A, P(S–MMA) and PMMA; curve B, P(S–EMA) and PEMA; curve C, P(S–BMA) and PBMA. Styrene content (mol%) in the copolymers: curve A, a, 64.5; b, 47.3; c, 28.7; d, 14.7; e, PMMA; curve B, a, 69.1; b, 50.2; c, 30.4; d, 15.5; e, PEMA; curve C, a, 69.6; b, 50.3; c, an overlapping peak with two copolymers (styrene content, 30.7 and 14.5 mol%) and PBMA. Column temperature, 60°C

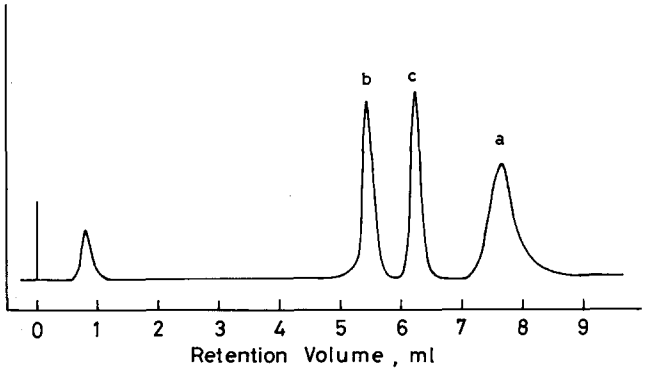

Figure 3 L.a.c. chromatogram for a mixture of (a) PEMA, (b) PBMA and (c) P(EMA–BMA) copolymer (1:1). Column temperature, 60°C

12) where a chloroform–ethanol/u.v. at 254 nm system was utilized.

Peak shapes for peaks c, h, i and j in *Figure 1* may be changed by changing the gradient elution conditions. These peaks are much sharper than the others, but this does not indicate a narrower CCD for these copolymers than for the others. In order to determine the CCD for the copolymers from the peak shape, a calibration curve of retention volume *versus* composition must be constructed. The sharp peak of c resulted from the fact that weakly adsorbed copolymers started to elute at this point, and in consequence the slope of the calibration curve in the vicinity of the elution point was steep compared to other positions and separation by composition was not as good[10]. Unadsorbed copolymers appeared at the exclusion limit as peak a and the peak width was only the measure of the band broadening effect of the column system. The difference of the peak shape of peaks h to j from peaks d to g resulted from the difference of the gradient elution conditions. Similarly, peak a can be retained in the column and the elution of peak a will be retarded by increasing column temperature.

Figure 2 shows l.a.c. chromatograms for copolymers of P(S–MMA), P(S–EMA) and P(S–BMA), including their respective homopolymers. Column temperature was 60°C and the gradient elution conditions were as follows: the initial mobile phase of 100% A was altered linearly to 100% mobile phase C in 20 min for P(S–MMA) and P(S–EMA) copolymers and 40 min for P(S–BMA) copolymers. When the gradient elution time was 20 min for a mixture of P(S–BMA) and PBMA, peaks b and c in *Figure 2* were combined and appeared at around retention volume, $V_R = 5.5$ ml. The combined peak was split into two peaks by the increase of the gradient elution time to 40 min. An increase in column temperature or a change from mobile phase C to B may improve the resolution of peak c in *Figure 2*, curve C into two or three peaks, and moreover, the elution of peak a in *Figure 2*, curve C may be retarded and eluted at around $V_R = 5.5$ ml. It can be seen that the elution of methacrylate homopolymers was in the order of PBMA, PEMA and PMMA, and that the copolymers of P(S–EMA) eluted earlier than those of P(S–MMA) having the same styrene contents (e.g. peaks b (or c or d) in *Figure 2*, curves A and B).

The major advantage of the use of DCE is the possibility of detecting methacrylate and acrylate components. Methacrylate and acrylate homopolymers and their copolymers can also be detected with the use of a u.v. detector. Examples are shown in *Figures 1* and *2*, in addition to *Figure 3* which is a chromatogram of a mixture of PEMA, PBMA and their 1:1 copolymer separated by this l.a.c. system. Column temperature was 60°C and the gradient elution condition was: initial mobile phase A was altered linearly to mobile phase B

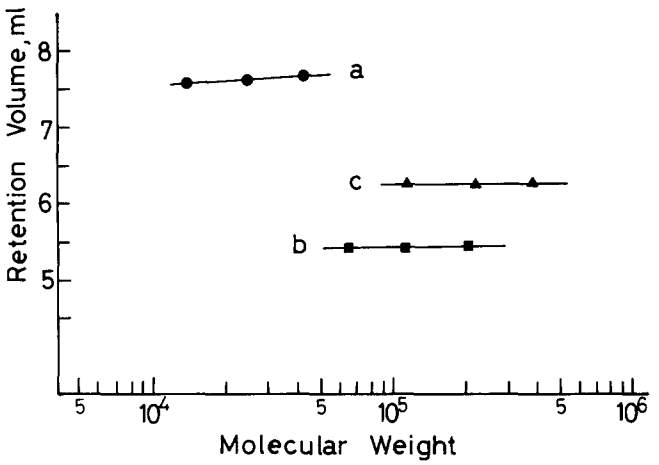

Figure 4 Relationship between retention volume and molecular weight of (a) PEMA, (b) PBMA and (c) P(EMA–BMA) copolymer (1:1)

in 20 min. PBMA eluted first at about $V_R = 5.4$ ml, the copolymer second at 6.25 ml, and PEMA last at about 7.6 ml. The difference in peak shapes between peaks a and c in *Figure 3* may be decreased by changing the gradient elution conditions. There has been only one report in the literature on the separation of methacrylate and acrylate homopolymers and copolymers[17]. A solvent evaporative light scattering detector was used, which required the evaporation of the mobile phase.

In order to determine the molecular weight dependence of retention volume, PEMA, PBMA and P(EMA–BMA) copolymer (50/50) were fractionated by s.e.c. into three fractions. The l.a.c. chromatograms of these fractions were measured and the relationship between retention volume and PS equivalent weight average molecular weight of these fractions is shown in *Figure 4*. No difference in retention volume is observed except for PEMA which showed a little difference in retention volume. This might be because of low molecular weights for PEMA fractions. PS equivalent weight average molecular weight for non-fractionated PEMA was 4.7×10^4, that for PBMA was 2.1×10^5 and that for the copolymer was 4.2×10^5.

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