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Note

Determination of chemical composition distribution of styrene–methyl methacrylate copolymers by reversed-phase high-performance liquid chromatography

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Analysis of polymeric compounds by high-performance liquid chromatography (HPLC) is predominantly carried out using the gel permeation mode (GPC), where the interaction between the sample and the stationary phase is negligible. However, with this mode only information concerning molecular volume can be obtained. Recently, normal-phase HPLC, in which the stationary phase is more polar than the eluent, using a polar gel such as silica gel or silica gel modified with cyano groups as the stationary phase, was applied to the determination of the chemical composition distribution (CCD) of copolymers[1–7]. We have also demonstrated that CCDs of styrene–butadiene[8] and styrene–methyl methacrylate (St–MMA) copolymers[9] can be determined by normal-phase HPLC using cross-linked acrylonitrile gel and a non-polar eluent. In normal-phase HPLC, the separation mechanism was found to be adsorption or partition, rather than fractional dissolution (phase separation).

Glöckner and Van den Berg[6,7] used a reversed-phase gel, *e.g.*, a non-polar gel such as octadecylsilica gel, and a non-polar eluent for the separation of copolymers according to composition. They found that in this system the separation was governed by fractional dissolution and that St–MMA copolymer was not well resolved, although St–acrylonitrile copolymer showed good resolution. Recently, Glöckner[10] reported that copolymers can be separated by reversed-phase HPLC on octadecylsilica with methanol–tetrahydrofuran as the eluent. Poor resolution of St–MMA copolymer was observed using cross-linked polystyrene gel and a non-polar eluent[9].

In this paper we report the possibility of determining the CCD of St–MMA copolymer by reversed-phase HPLC using cross-linked polystyrene gel as the stationary phase and a polar eluent consisting of dichloromethane–acetonitrile. The effect of molecular weight on the separation was also examined.

EXPERIMENTAL

St–MMA copolymers (1–5) having different compositions were prepared in bulk using benzoyl peroxide as an initiator. Copolymer samples with different molecular weights (6–8) were prepared by copolymerization with the same monomer in the presence of different amounts of *n*-butyl mercaptan. The copolymers were separated by GPC to obtain samples with narrow molecular weight distributions. The

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TABLE I

POLYMERIZATION CONDITIONS AND MOLECULAR CHARACTERISTICS OF STYRENE–METHYL METHACRYLATE COPOLYMERS

Sample	*Polymerization conditions**		*Properties of copolymer*		
	Styrene in feed, mol-%	*Yield, wt.-%*	*Styrene in polymer, mol-%*	M_n** $\times 10^4$	M_w** $\times 10^4$
1	84.1	5.0	78.3	9.5	13.9
2	70.0	6.9	67.9	8.7	12.4
3	54.9	6.1	53.7	8.8	11.9
4	27.6	7.6	35.4	10.4	13.5
5	14.6	7.6	24.0	13.7	24.3
6	50.0	2.8	49.1	11.0	16.2
7***	50.0	2.2	48.8	2.2	4.3
8***	50.0	1.2	49.1	0.5	1.0
Fraction of 6–8:					
6–1			48.8	18.1	24.7
6-2			48.5	7.1	8.1
7-2			48.3	4.8	5.4
8-2			48.7	2.1	2.6
7-3			48.8	1.1	1.3

* Bulk copolymerization at 60°C using benzoyl peroxide as initiator with a concentration of 0.25 mol-% of monomer.

** M_n = number-average and M_w = weight-average molecular weight. Measured by GPC using calibration graphs for standard polystyrene and poly(methyl methacrylate).

*** Polymerized in the presence of *n*-butyl mercaptan; 0.1 mol-% (sample 7) and 1.0 mol-% (sample 8) of the monomer.

conversions were adjusted to less than 10% in order to obtain samples with narrow CCDs (Table I). The composition was determined from the ^{1}H NMR spectra using the intensity ratio of the phenyl proton in the styrene unit and the α-methyl proton in the methyl methacrylate unit. The molecular weight was determined by GPC using standard polystyrene and poly(methyl methacrylate) as calibration standards.

Styrene (20 ml) and divinylbenzene (49 ml) (containing 45% of ethylvinylbenzene) were copolymerized by conventional suspension copolymerization in the presence of toluene (71 ml) and polystyrene (1.9 g) as diluents and using poly(vinyl alcohol) as a suspension reagent. The resulting copolymer was washed successively with hot water, acetone and chloroform three or four times. The copolymer beads, having diameters of 5–10 μm, were collected by decantation in acetone and packed in a stainless-steel column (25 cm $\times$ 4.5 mm I.D.) by the usual slurry method. This column had an exclusion limit of *ca.* $6 \cdot 10^5$ for polystyrene when chloroform was used as the eluent.

HPLC was conducted at ambient temperature (*ca.* 20°C) using two Jasco 880-PU high-pressure pumps, one for providing dichloromethane and the other acetonitrile. The two solvents were mixed after the pump and were delivered to the injector through a filter, which reduced the noise produced by mixing. The flow-rate was set at 0.5 ml/min and the proportion of dichloromethane was increased linearly

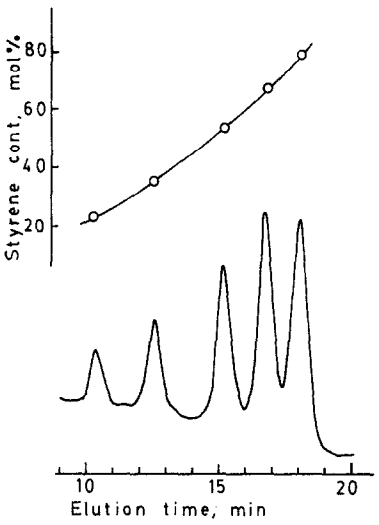
from 20 to 80 vol.-% in 25 min. A 10-μl portion of a dichloromethane solution of the sample (10 mg/ml) was injected through a Reodyne 7125 injector. The column effluent was monitored with a Jasco Uvidec 254 (254 nm) UV detector.

The cloud point of the sample was determined at 20°C. Acetonitrile was gradually added to a dichloromethane solution of the sample (10 mg/ml) and the cloud point was observed visually.

RESULTS AND DISCUSSION

An mixture of equal weights of five St–MMA copolymers containing 24–87 mol-% of styrene units (samples 1–5 in Table I) was separated using acetonitrile–dichloromethane as the eluent in which the proportion of dichloromethane, which is a good solvent for the copolymer, was gradually increased from 20 to 80 vol.-%. These samples were eluted in order of decreasing styrene content and exhibited five peaks, as shown in Fig. 1. This elution order is opposite to that in normal-phase HPLC[9]. It is noteworthy that cross-linked polystyrene gel showed a good resolution of St-MMA copolymer with the use of a polar eluent, although it did not provide a good resolution when a non-polar eluent was used[9].

In order to examine the separation mechanism, the proportion of the good solvent (dichloromethane) in the eluent was plotted against the styrene content of the sample, together with the cloud point (Fig. 2). It was found that the proportion of the good solvent is almost equal to the cloud point for a fractional dissolution mechanism, whereas the former is higher than the latter in an adsorption or partition mechanism[9]. The proportion of the good solvent in the eluent is 20–30% higher than



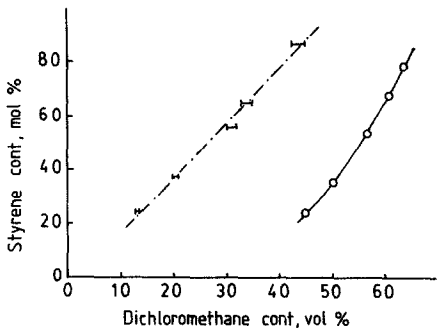


Fig. 1. HPLC trace of a mixture of five styrene–methyl methacrylate copolymers. The dichloromethane content was increased linearity from 20 to 80 vol.-% in 25 min.

Fig. 2. Dichloromethane concentration in the eluent and the cloud point of the styrene–methyl methacrylate copolymer.

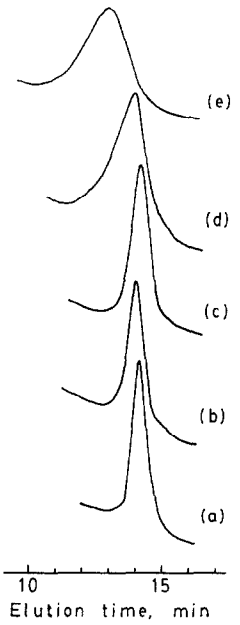


Fig. 3. HPLC traces of styrene–methyl methacrylate copolymers having number-average molecular weights of (a) $18 \cdot 10^4$, (b) $7.1 \cdot 10^4$, (c) $4.8 \cdot 10^4$, (d) $2.1 \cdot 10^4$ and (e) $1.1 \cdot 10^4$.

the cloud point. For comparison, when cross-linked acryronitrile gel was used as the stationary phase, the proportion of the good solvent was almost equal to the cloud point, although the sample concentration was much higher in the cloud point experiment. The relationship between the cloud point and elution behaviour indicates that with a combination of a non-polar gel and a polar eluent the separation was governed by an adsorption or partition mechanism, whereas the sample was eluted by a fractional dissolution mechanism when a polar gel and a polar eluent were used.

Usually the separation of copolymers by HPLC is influenced by the molecular weight of the sample in addition to the composition. Samples with almost the same styrene content and different molecular weights (samples 6–8) were prepared with the same monomer feed and different amounts of chain-transfer reagent (*n*-butyl mercaptan). The samples obtained were fractionated by GPC, giving five fractions having styrene contents of 49–50 mol-% and number-average molecular weights of $1.1 \cdot 10^4$–$18 \cdot 10^4$. Fig. 3 shows the HPLC traces of the five fractions. Samples with number average molecular weights higher than $4.8 \cdot 10^4$ showed a peak at almost the same elution time of 14.1 ± 0.1 min, whereas the samples with molecular weights lower than this critical value displayed peaks at earlier elution times as the molecular weight decreased. The effect of molecular weight on the elution volume is slightly greater in normal-phase than reversed-phase HPLC[9]. The peak width at half-height increased as the molecular weight decreased, as expected from Stockmayer's equation[11]. The abrupt increase in the peak width for samples with number-average molecular weights lower than $2.1 \cdot 10^4$ may be parently attributed to the effect of molecular weight on the elution volume.

The retention volume and peak area for each sample were perfectly reproducible, as in normal-phase HPLC using cross-linked acrylonitrile gel[9]. In addition to the good reproducibility, a long lifetime of the column (more than 1 year) was confirmed. This may be ascribed to the high degree of cross-linking of the gel, which reduced the swelling and shrinkage during the experiments with a solvent gradient. It is concluded that the CCD can also be analysed by reversed-phase HPLC. A detailed comparison of reversed-phase and normal-phase HPLC will be presented in a subsequent paper.

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