

# High-Performance Column Adsorption Chromatography of Random Copolymers Styrene-Acrylics

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## Synopsis

Random copolymers of styrene with acrylics can be separated according to their chemical composition by gradient column adsorption chromatography on silica. The composition of the mobile phase that can displace a given copolymer from the silica surface is independent of the shape of the solvent strength gradient and also above the sample molecular weight of ca.  $M = 100,000$ .

## INTRODUCTION

Random copolymers, unless prepared by polymerization to a low conversion or at the azeotropic monomer composition, are chemically heterogeneous<sup>1</sup> (in addition to being polymolecular). As they are important from both the theoretical and practical points of view, it is desirable to develop reliable methods for determining their chemical heterogeneity. Some basic integral characteristics can be obtained by the method of light scattering.<sup>2</sup> The classical approach to the simultaneous determination of molecular weight distribution and chemical heterogeneity, i.e., precipitation fractionation in suitably selected solvent-precipitant systems<sup>3-5</sup> is very time consuming, and it can be shown theoretically<sup>6</sup> that systems which would separate exclusively according to chemical composition do not exist—the selection of a system separating only according to molecular weight is hardly attainable in practice. Gel permeation chromatography (GPC) with two detectors in series has been used,<sup>7-9</sup> but the hydrodynamic volume of a copolymer (the factor controlling separation in GPC) depends both on molecular weight and on chemical composition; the shape of these dependencies is unknown. One of the promising new approaches is thin layer chromatography (TLC). Inagaki, Matsuda, and Kamyama<sup>10</sup> and Belenkii and Gankina<sup>11</sup> independently made use of the previously known fact<sup>12</sup> that the adsorption of macromolecules on solid surfaces is essentially independent of molecular weight but depends strongly on chemical composition. More recent reviews<sup>13,14</sup> indicate that TLC can give useful, if mostly qualitative, information about the chemical heterogeneity of copolymers; quantitative analysis is hampered by the low reproducibility and accuracy of TLC.

The excellent separation efficiency, reproducibility, and easy quantitation, characteristic of modern high-performance liquid column chromatography, prompted us to investigate the potential of this method for the separation of copolymers according to their chemical composition.

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TABLE I  
Molar Fraction of Styrene Units ( $x_{ST}$ ) and Molecular Weight (from Light Scattering) of Random Copolymers

Sample	$x_{ST}$	$M_w \times 10^{-5}$
Poly(styrene-co-methyl methacrylate)		
I	0.111	2.20
II	0.231	2.20
III	0.351	2.35
IV	0.495	1.85
V	0.621	1.50
Poly(styrene-co-ethyl methacrylate) fractions		
1-v	0.531	2.58
1-n		1.58
2		1.32
3		0.83
4	0.509	0.37
N <sup>a</sup>	0.529	0.97

<sup>a</sup> Original, nonfractionated sample.

## EXPERIMENTAL

Random copolymers styrene-methyl methacrylate (ST-MMA) with different molar fraction of styrene units,  $x_{ST}$ , and styrene-ethyl methacrylate (ST-EMA) with practically the same  $x_{ST}$  but differing in molecular weight were prepared by radical polymerization under conditions that ensured very low chemical heterogeneity.<sup>15</sup> Basic characteristics of the copolymer samples employed are summarized in Table I.

Three types of silica were used as sorbents (see Table II). The original silica, A, was a commercial product (Separon SI VSK, Laboratory Instruments Works, Prague); two additional silicas (B and C) were prepared from it by hydrothermal treatment as described elsewhere.<sup>16</sup>

1,2-dichloroethane (DCE, Staart Enterprises, England) was distilled before use. Tetrahydrofuran (THF, Laborchemie, GDR) was freed from peroxides by standing with CuCl and then distilled from CuCl on a column. Both solvents were dried and stored over a molecular sieve.

The chromatograph was assembled from a positive displacement pump of our own design, a homemade mixing device for creating an exponential gradient of mobile phase composition with a stainless-steel cylindrical chamber (total volume 28.6 ml) provided with a PTFE-coated magnetic stirrer, a stop-flow sample injector (Laboratory Instruments Works, Prague), a UV detector from ALC 101 Liquid Chromatograph (Waters Associates, Framingham, MA), connected in series with a refractometric monitor (RD 1, Developmental Workshop, Czechoslovak Academy of Sciences) for simultaneous recording of peaks and of the

TABLE II  
Characteristics of Silica Sorbents

Sorbent	Specific surface area, m <sup>2</sup> /g	Particle size, $\mu$ m	Exclusion limit (PS in THF)
Silica A	830	9	3.10 <sup>4</sup>
Silica B	575	7	1.10 <sup>5</sup>
Silica C	~5	7	~1.10 <sup>7</sup>

shape of the mobile phase gradient on a double-pen potentiometric recorder Servogor (Goerz Electro, Wien, Austria). Stainless-steel columns (Laboratory Instruments Works, 250 mm long, 6 mm i.d.) and short columns (stainless steel, 50 mm long, 4 mm i.d., homemade) were slurry-packed at 30 MPa using a methanol-dioxane mixture (50:50, v/v) as the dispersing liquid. The columns were flushed by at least 10 column volumes of pure THF before each run, and then equilibrated in the binary solvent of the initial composition (usually 3 vol % THF in DCE).

## RESULTS AND DISCUSSION

Columns packed with the three types of silica were first calibrated in the GPC mode with narrow polystyrene standards using THF as the mobile phase. The molecular weight exclusion limits are given in Table II. When the copolymer samples were run with THF alone, they were totally excluded both on silica A and silica B, whereas on silica C their retention volume was always close to that of totally permeating, low-molecular-weight solutes. On the other hand, from pure DCE all copolymers were irreversibly retained on all three sorbents. Experiments with the short columns revealed that each copolymer can be eluted at a suitable composition of the binary solvent THF-DCE within the range of about 3–20 vol % THF, a higher content of THF being necessary for copolymers containing less styrene. This indicates that a suitable gradient of mobile phase composition can be used for separating copolymers of styrene with acrylics according to their chemical composition.

In order to ascertain whether separation according to molecular weight is not superimposed on the expected separation according to chemical composition, fractions of the ST-EMA copolymer having essentially the same content of styrene (see Table I) were first injected into a column (250 × 6 mm) packed with silica A, and then eluted using an exponential gradient of 3–20 vol % of THF in DCE. The eluent composition at the respective peak maxima was found from the simultaneously recorded signal of the refractometric monitor. The results

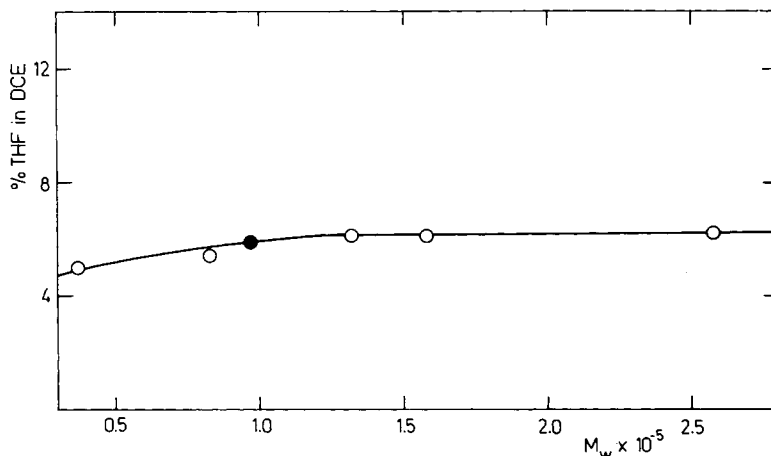


Fig. 1. Molecular weight dependence of critical solvent composition. ST-EMA copolymers on silica A; full point corresponds to nonfractionated sample N.

TABLE III  
Composition of Binary Solvent (Vol % THF in DCE) at Peak Maxima of ST-MMA Copolymers

Sample	Sorbent					
	Silica A		Silica B		Silica C	
	1 ml/min	2 ml/min	1 ml/min	2 ml/min	1 ml/min	2 ml/min
I	16.0	16.15				
II	11.7	12.0				
III	10.5 (10.2) <sup>a</sup>	(10.5)	(10.4)	(10.6)	(9.5)	(9.7)
IV	7.6 (7.2)	(7.35)	(7.0)	(7.6)	(6.45)	(6.5)
V	5.0 (4.75)	(4.8)	(4.45)	(5.0)	(4.2)	(4.0)

<sup>a</sup> Numbers in brackets were obtained by injecting samples III-V simultaneously.

are shown in Figure 1; the eluent composition at the peak maximum was independent of molecular weight down to about  $1 \cdot 10^5$ , in agreement with TLC results reported by Inagaki, Matsuda, and Kamiyama<sup>10</sup> and Belenkii and Gankina.<sup>11</sup>

ST-MMA copolymers with different styrene content were then eluted from columns packed by the three silicas using the same exponential gradient of solvent strength as before. The results are summarized in Table III. The solvent composition at the peak maximum for individual samples does not depend on the flow rate and is the same, irrespective of whether the copolymers were injected individually or in a mixture, but depends strongly on copolymer composition, showing that the methacrylate segments are more strongly adsorbed on the silica surface. The mean values of critical solvent composition for each of the three sorbents are plotted against  $x_{ST}$  in Figure 2. These calibration lines are the same within the limits of experimental error for silica A and B, where the respective exclusion limits in GPC are smaller than the molecular weight of the copolymer samples: the calibration dependence for silica C is somewhat different, but this shift is relatively small considering the much wider pores of the latter sorbent

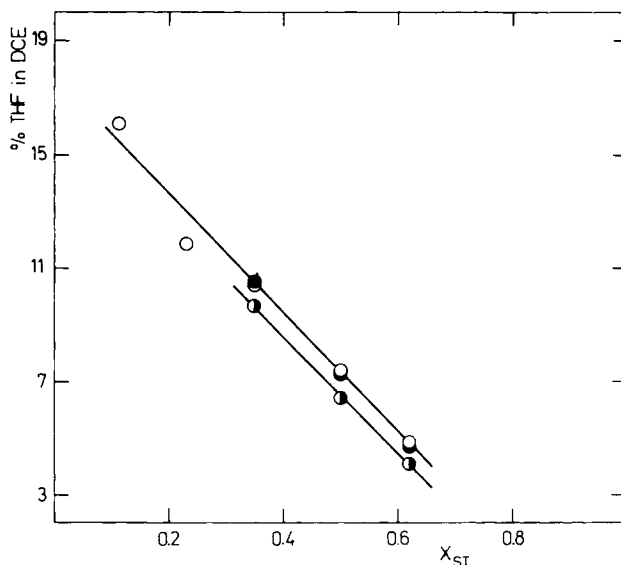


Fig. 2. Dependence of the critical-solvent composition on molar fraction of styrene units,  $x_{ST}$ . O, silica A, ●, silica B, ○, silica C.

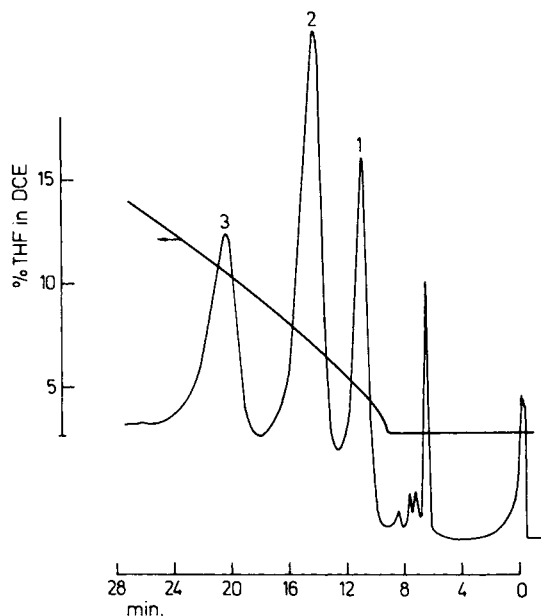


Fig. 3. Chromatogram showing separation of three ST-MMA copolymers: (1) copolymer V, (2) copolymer IV, (3) copolymer III. Scale at left gives solvent composition in vol % THF in DCE.

almost completely permeated by the copolymer molecules in the GPC mode. Under conditions of strong interaction between the polymeric chains and the silica surface (at THF content lower than critical), the macromolecules can obviously penetrate the pores, although they are completely excluded under conditions of GPC (both THF and DCE are thermodynamically good solvents for polystyrene and methyl methacrylate homopolymers).

In contrast to results of Teramachi et al.,<sup>17</sup> the retention characteristics of ST-MMA copolymers on all three sorbents tested were perfectly reproducible and no shift of the calibration dependences shown in Figure 2 was observed during a period of several months.

An example of the actual separation of three ST-MMA copolymers by gradient elution on a column packed with silica A is shown in Figure 3.

In conclusion, it can be said that an unequivocal correlation exists between copolymer composition and the strength of the solvent that can displace the copolymer from the silica surface. This dependence is not affected by the flow rate and, if the activity of the sorbent is controlled by flushing the column with pure THF prior to injecting the sample, the retention characteristics are reproducible. Columns packed by microparticulate silica in conjunction with gradient elution can thus be employed for determining the compositional heterogeneity of random copolymers. Work on an extension of these results to other copolymers is in progress.

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