

High-Performance Adsorption Chromatography of Polymers: Separation of Styrene-Acrylonitrile Copolymers on CN Silica

INTRODUCTION

As a result of continuing progress in modern liquid chromatography instrumentation, high-performance column adsorption chromatography with gradient elution begins to find application also in the analysis and fractionation of synthetic high polymers and copolymers. Klein and Leidigkeit¹ separated narrow polystyrene standards (molecular weight between 2.10^3 and 2.10^6) by adsorption chromatography on macroporous silica. Andrews and Vatvars² showed that telechelic methacrylates can be separated according to the number of hydroxyl groups in their molecule. The possibility of characterizing chemical heterogeneity of random copolymers by means of high-performance liquid column chromatography on columns packed by silica with gradient elution has been explored.^{3,4} The method separates copolymers according to their chemical composition and surpasses the often used thin-layer chromatography (TLC) of polymers^{5,6} in separation efficiency, reproducibility, speed of analysis, and ease of quantitation.

Chemical heterogeneity of random copolymers styrene-acrylonitrile (ST-AN copolymers) is particularly difficult to characterize because of their poor solubility in common solvents. Cross fractionation^{7,8} has been attempted but it is known to be very tedious and time-consuming. Tera-machi and Esaki⁹ found conditions for separation of ST-AN copolymers by TLC on silica, but their attempt to transfer these results to column chromatography was less successful.

In this note we report the separation of ST-AN random copolymers by adsorption column chromatography on silica with chemically bonded cyanoethyl groups (CN silica). This bonded phase is known to be compatible with both polar and nonpolar mobile phases, and the presence of CN groups on the chemically modified surface could enhance the selectivity of separation of acrylonitrile-styrene copolymers according to their composition: the retention is expected to increase with increasing content of the acrylonitrile moiety.

EXPERIMENTAL

Random copolymers styrene-acrylonitrile were prepared by radical polymerization under conditions that ensured a low chemical heterogeneity; their basic characteristics are summarized in Table I. Spherical silica (Separon SI VSK, Laboratory Instruments Works, Prague; particle size $10\ \mu\text{m}$, specific surface area $450\ \text{m}^2/\text{g}$) was reacted with cyanoethyltriethoxysilane in dry toluene; the details can be found elsewhere.¹⁰

TABLE I
Retention Volumes of Random Copolymers Styrene-Acrylonitrile
on a Column (50 mm Long) Packed with CN Silica^a

Sample	Mole fraction		$M_n \times 10^{-5}$ ^b	V_r (mL)
	AN			
PS	0 ^c		3.9	3.8
ST-AN I	0.08		2.4	4.75
ST-AN III	0.27		3.24	6.92
ST-AN IV	0.30		2.89	7.13
ST-AN V	0.36		2.07	7.89
ST-AN VI	0.51		2.49	9.14
ST-AN VII	0.59		3.40	10.19
SR-AN VIII	0.70		3.18	11.23

^a Linear gradient from 3% B in A to 100% B, 13 min.

^b Membrane osmometry.

^c Styrene homopolymer.

Tetrahydrofuran (THF) and dichloroethane (DCE) were purified similarly, as reported in our previous paper.⁴ Heptane (analytical grade, Loba Chemie, Vienna, Austria) was distilled and dried over molecular sieve. Acetonitrile (Avondale Laboratories, Oxon, England) and dimethylformamide (DMF; Lachema Brno, Czechoslovakia) were used as received.

All chromatograms were obtained with a Type 1084 B Liquid Chromatograph Hewlett-Packard (Palo Alto, CA) with UV detector (254 nm); short (50 mm, 4 mm I.D.) stainless steel columns of our own design were slurry-packed with CN silica, as described elsewhere.¹⁰

RESULTS AND DISCUSSION

In order to detect the presence of the styrene homopolymer in the analyzed samples, it was deemed necessary to select the initial mobile phase composition such that not only copolymers with the lowest content of acrylonitrile but polystyrene itself would be retained. Preliminary experiments showed that this is fulfilled in the mixture DCE:heptane (30:70 by volume—designated as solvent A). On the other hand, in the mixture CH₃CN:DCE (40:60 by volume—solvent B) all copolymers were displaced and appeared at the retention volume corresponding to that of polystyrene standards totally excluded on this packing in THF. Because of poor solubility of samples (particularly those with a high AN content) in the mobile phase, the copolymers were injected dissolved in the mixture THF:DMF (1:1); it was verified experimentally that these solutions did not precipitate upon injection into the mobile phase.

For the separation of copolymers with an AN content varying within these broad limits (Table I) a linear gradient of solvent composition proved to be useful: polystyrene and all copolymers (except III and IV of nearly identical composition) were completely resolved within 13 min in a linear gradient from 3% B in A to 100% B (see Table I). The resolving power of the short column was excellent, and a mere 6% difference in the AN content was sufficient for a nearly baseline separation (Fig. 1). Similarly to the styrene/methyl methacrylate copolymers previously studied,⁴ the retention volumes were the same when the samples were injected individually or in a mixture.

With the commercial instrument employed it was not possible to follow the composition of the mobile phase leaving the column by means of a refractometer coupled in series with the UV detector, as in our previous paper,⁴ and the composition of the mobile phase was therefore calculated from retention volumes and from the shape and duration of the gradient; in view of the perfect reproducibility of retention volumes this was considered satisfactory. The calibration line plotted in Figure 2 has been obtained in this manner and shows the relationship between the composition of the mobile phase capable of displacing a given copolymer from the column and the molar fraction of AN units. Copolymers with a higher AN content are more strongly retained, and the calibration dependence in these coordinates is approximately linear.

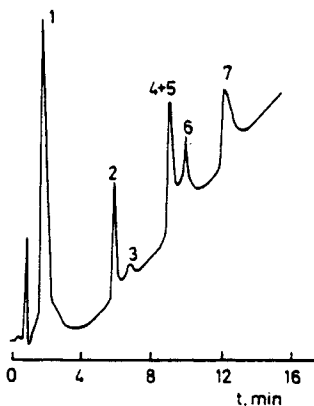


Fig. 1. Separation of styrene-acrylonitrile copolymers on a column packed with CN silica: (1) solvent peak; (2) polystyrene; (3) ST-AN I; (4) ST-AN III; (5) ST-AN IV; (6) ST-AN V; (7) ST-AN VII.

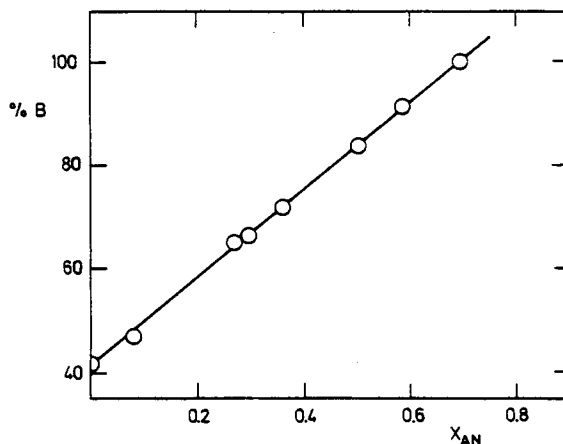


Fig. 2. Composition of mobile phase (% B in A) able to displace ST-AN copolymer with molar fraction X_{AN} of acrylonitrile units from the column packed with CN silica: Mixture A: DCE:heptane (30:70 by volume); Mixture B: CH_3CN :DCE (40:60 by volume).

CONCLUSION

Adsorption chromatography on silica containing chemically bonded cyanoethyl groups and with a gradient of mobile phase composition using organic nitrile as the displacer is a convenient method for determining chemical composition and/or chemical heterogeneity of random styrene/acrylonitrile copolymers. Very short columns can be used, resulting in negligible spreading and a reasonable analysis time. Retention volumes are reproducible and for a given copolymer are unequivocally related to the composition of the mobile phase.

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