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Polymer-coated cation exchangers in high-performance ion chromatography: preparation and application

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ABSTRACT

Low-capacity cation-exchange stationary phases for ion chromatography were prepared by coating a vinyl-modified silica gel with polystyrene or poly(glycidyl methacrylate). Strong acid ion-exchange groups were formed by sulphonation with concentrated sulphuric acid or by ring opening of the polymer-coated silica gels with sulphite solution. Carbon–sulphur elemental analyses of the polymer-coated cation exchangers (PCCEs) were applied to determine the average polymer film thickness. The pH stability depended on the polymer film thickness. The PCCEs were stable in the pH range 0.5–9. The low-capacity PCCEs (capacities 18–91 μmol/g) were applied to determine alkali and alkaline earth metal ions in tap and mineral waters.

INTRODUCTION

Most stationary phases used in ion chromatography are based on polymer or silica gel materials [1–3]. Silica particles possess favourable properties, such as a homogeneous matrix, good porosity and excellent stability to solvents and pressure. The advantage of polymer-based stationary phases is their stability over en broad pH range, commonly from 0 to 12. Silica gel phases are stable only from pH 2 to 8. Polymer-coated silica gel phases should combine good pH stability with the good chromatographic properties of silica gel carriers.

The preparation of a sulphonated polystyrene-coated cation exchanger (PS-PCCE) and its application to heavy metal separations have been described [4]. The preparation of poly(glycidyl methacrylate)-coated cation exchangers (PGMA-PCCEs) and separations of alkali and alkaline earth metal ions by using PS- and PGMA-PCCE columns have been reported previously [5]. This paper describes the preparation, properties and applications of PCCE columns in high-performance ion chromatography (HPIC), together with aspects such as the polymer film thickness, pH stability and examples of rapid separations of alkali and alkaline earth metal ions.

EXPERIMENTAL

Preparation of stationary phases

The synthesis of the PCCEs is a three-step procedure (see Fig. 1):

(1) The silica gel surface was modified with triethoxyvinylsilane.

(2) The thermal decomposition of an incorporated peroxide started the polymerization of styrene or glycidyl methacrylate and divinylbenzene to form a cross-linked polymer network.

(3a) The polystyrene-coated silica gels were sulphonated with concentrated sulphuric acid.

(3b) The PGMA-coated silica gels were sulphonated with 1 mol/l sodium sulphite solution in the presence of tetrabutylammonium bromide as catalyst.

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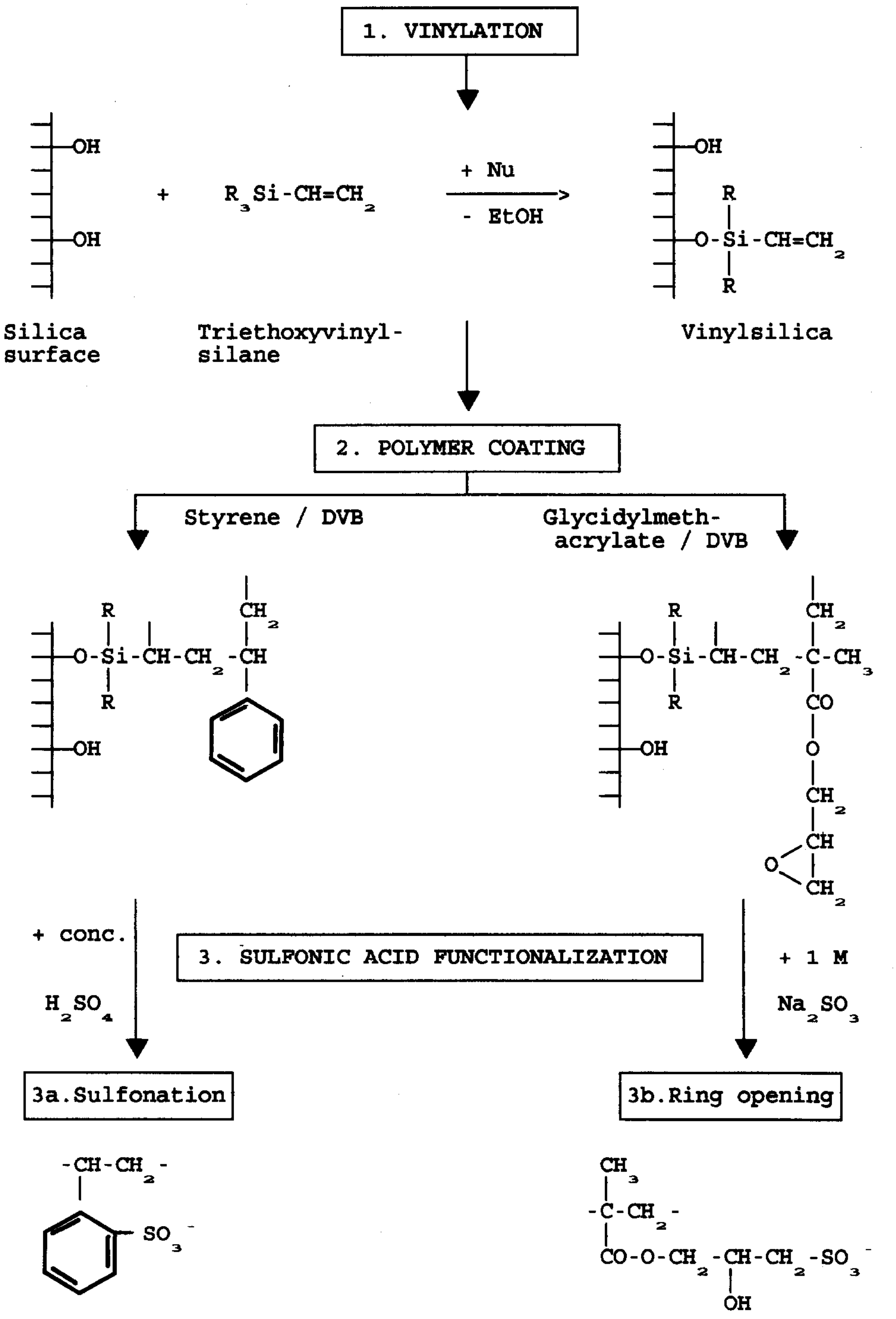

Fig. 1. Preparation of polymer-coated cation exchangers (PCCE). Nucleophil (Nu): triethylamine, pyridine, imidazole.

TABLE I

CHARACTERIZATION OF UNMODIFIED SILICA GELS

A_s = specific surface area by the BET method; D_{part} = average particle diameter; d_p = average pore diameter; V_p = pore volume.

Silica gel[a]	PCCE No.	A_s (m^2/g)	D_{part} (μm)	V_p (ml/g)	d_p (nm)
LI 60-5	VI	650	5	0.95	6
ES 360-4	VII	120	4.5	1.09	13
ES 210-7	VIII	177	7	0.93	21

[a] LI = LiChrospher (Merck); ES = ES-gel (Leuna).

The columns were slurry packed with a mixture of cyclohexanol and toluene as dispergent. The capacities of the filled columns were determined by a breakthrough experiment with conductivity detection of the effluent as described previously [5].

Instrumentation

IC analyses were performed on a modular HPLC system (Knauer, Berlin, Germany) consisting of an analytical pump (Model 64 HPLC pump), an injection valve, a conductivity detector and a recorder. The sample volumes injected were 20 μl.

For carbon–sulphur elemental analyses, a C–N–S 932 Analyser (LECO, St. Joseph, MI, USA) was used.

Materials and reagents

The mobile phases for the separation of alkaline earth metal ions were prepared by mixing analytical-reagent grade ethylenediamine and oxalic acid solutions. For pH adjustment, nitric acid was used. The mobile phases for the separation of alkali metal ions was dilute nitric acid. The mobile phases were filtered and degassed.

Stock solutions of 1 g/l of alkali and alkaline earth metals were prepared from potassium nitrate, sodium chloride, calcium chloride and magnesium sulphate and diluted to the desired concentrations with deionized water. All reagents were of analytical reagent-grade quality.

Table I shows some characteristics of the silica gel supports used. ES-Gels were obtained from Leuna (Leuna, Germany) and LiChrospher from Merck (Darmstadt, Germany).

RESULTS AND DISCUSSION

The composition and concentration of the mobile phases depend on the chemical properties and ion-exchange capacities of the stationary phases used. Table II shows the measured column capacities and the calculated mass capacities (column capacity divided by the mass of stationary phase per column). The ion-exchange capacities are influenced by the

TABLE II

CAPACITIES OF THE POLYMER-COATED CATION EXCHANGERS

Column	Dimensions (mm)[a]	Li^+ capacity[b] (μmol per column)	Mass capacity[c] (μmol/g)
PCCE VI	30 × 4	11	50
PCCE VII	30 × 4	8	36
PCCE VIII	30 × 4	17	91

[a] Stainless-steel columns, length × I.D.

[b] Determined by recording the effluent conductivity change.

[c] Column capacity divided by dry mass of stationary phase per column.

TABLE III

ELEMENTAL ANALYSIS OF THE POLYMER-COATED SILICA GELS

Column	Polymer coating[a]	Elemental analysis		Average polymer film thickness[b] (nm)	C/S ratio
		C (%)	S (%)		
PCCE VI	PS	3.9	1.4	0.12	2.8
PCCE VII	PGMA	2.2	0.15	0.33	15
PCCE VIII	PGMA	2.5	0.42	0.27	5.9

[a] PS = polystyrene; PGMA = poly(glycidyl methacrylate).

[b] Average polymer film thickness = $[(x/y) \cdot 1000]/[(1 - x/y)\, A_s\, d]$, where x = carbon content (%) of the PCCE stationary phase, y = average carbon content (%) of the monomer mixture (styrene–divinylbenzene), A_s = specific surface area (m^2/g) and d = polymer film density (1 g/cm^3 was assumed).

amount of the bonded-polymer coating and the degree of sulphonation of anion-exchange syntheses (third step in Fig. 1: sulphonation with sulphuric acid or ring opening with sodium sulphite solution).

The sulphonation of the PS-coated silica gels gave nearly completely monosulphonated PS-PCCEs, as calculated from the results of carbon–sulphur elemental analyses. The C/S ratio (Table III) gave a value close to the theoretical value (3 for styrene monosulphonic acid). This degree of sulphonation was obtained by using concentrated sulphuric acid with short reaction times (10–15 min) and temperatures of 80–90°C. The duration and the temperature of sulphonation must be limited in order to avoid PS networks on the silica gel surface as much as possible. The opening of the epoxy rings showed lower degrees of sulphonation (theoretical C/S ratio = 3). In this instance, longer reaction times were necessary to obtain higher degrees of sulphonation and higher ion-exchange capacities.

TABLE IV

COMPARISON OF THE AVERAGE POLYMER FILM THICKNESS AFTER POLYMER COATING AND AFTER SULPHONIC ACID FUNCTIONALIZATION

Column	Average polymer film thickness (nm)[a]		*B*/*A* (%)
	A	*B*	
PCCE VI	0.24	0.12	50
PCCE VII	0.49	0.34	69
PCCE VIII	0.39	0.28	71

[a] *A* = Average polymer film thickness after polymer coating; *B* = average polymer film thickness after sulphonic acid functionalization.

The average polymer film thickness [6], calculated from the results of elemental analyses (Table III) was used as a practical value for the characterization of the polymer coating bonded to the silica gel surface. After polymer coating, the average polymer film thickness was 0.25–0.5 nm (Table IV). Comparison of the polymer film thickness of the PCCEs after polymer coating and after ion-exchange syntheses (sulphonation) showed that the degradation of the PS-PCCE was greater than that of the PGMA-PCCE. It can be assumed that part of the PS coating decomposed during the sulphonation. The polymer network was partly oxidized, or the covalent Si–C bond linking the polymer network to the silica substrate was partly broken. By this means, the PGMA-PCCE showed a higher polymer film thickness and therefore higher pH stability (Fig. 2).

In Fig. 2, the square root of the number of theoretical plates per column is plotted against the volume of alkaline buffer solution as the number of column volumes. The number of theoretical plates per column was calculated with a 10 mg/l Mg standard sample by using the same chromatographic conditions for each measurement. The pH stabilities of PCCE VI and PCCE VIII were determined by pumping buffer solutions of pH 9.5 and 11, re-

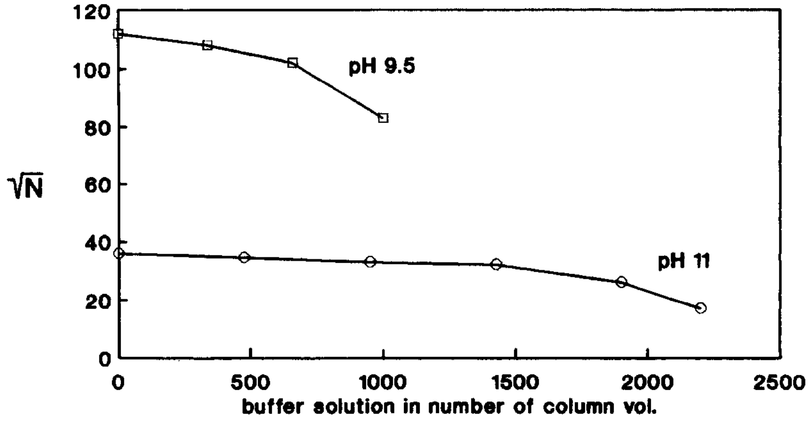

Fig. 2. pH stability of the PCCE. Plots of the square root of the number of theoretical plates against the alkaline buffer solution as number of column volumes. ○ = PCCE VIII; □ = PCCE VI.

spectively, through the columns. With degradation of the silica core, the column bed decreased, producing a dead volume on the head of the column and the efficiencies of the columns decreased. The PCCE VIII material, with the greater polymer film thickness, was much more stable, indicating that pH stability is strongly dependent on the thickness of the polymer coating.

On the other hand, a thin layer (partly) surrounding the impervious silica core gives rise to a rapid radial mass transfer of the solute in the polymer network (c parameter of the Knox equation [7]). The best comparative measure of the kinetic performance of a column packing material is a plot of the reduced plate height (h) against the reduced velocity (v) along with a measure of the column resistance parameter (φ) [7]. An efficient column must have both a low reduced plate height and a low resistance factor. In practice, φ is found to lie within the range 500–800 for silica phases, depending on the method of packing the column and the porosity of the packing material. The values of φ (Table V) fall in the upper part of the acceptable range, indicating that the materials showed good flow properties.

A summary of the additionally reduced column parameters (v and h) of the PCCE columns used is given in Table V. All parameters lie in the region that are typical for silica-based materials with the

TABLE V

REDUCED COLUMN PARAMETERS OF THE POLYMER-COATED CATION EXCHANGERS

D_{part} = mean particle diameter; φ = column resistance parameter = $\Delta p D_{part}^2/u\eta L$, where u = eluent linear velocity, η = eluent viscosity, L = column length, and Δp = pressure drop across column; h = reduced plate height = H/D_{part}, where H = plate height; v = reduced velocity = uD_{part}/D_m, where D_m = diffusion coefficient of solute in eluent.

Column[a]	D_{part} (μm)	φ	v	h			
				Mg	Ca	Na	K
PCCE VI	5	790	16	10	8.5	16	61
PCCE VII	4	890	25	9.5	7.8	8.5	9.8
PCCE VIII	7	850	30	7.5	5.8	5	5.5

[a] For dimensions, see Table I.

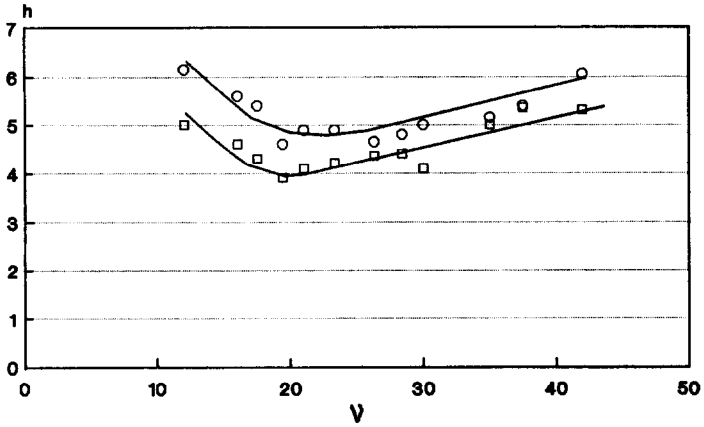

Fig. 3. *h versus v* plots for the PCCE VIII. Injection of 20 μl of standard (□) 6 mg/l Na^+ and (○) 8 mg/l K^+ samples. Column, 30 mm × 4 mm I.D.; eluent, 3 m*M* nitric acid.

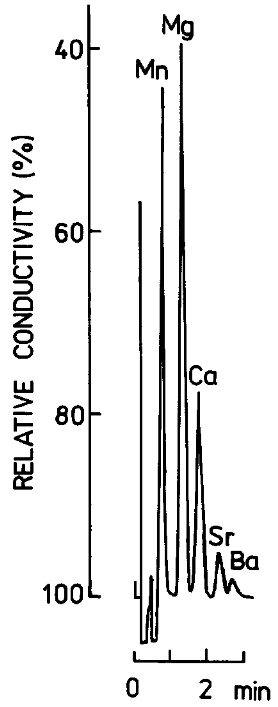

Fig. 4. IC analysis of a standard sample on PS-PCCE VI. Eluent, 0.85 m*M* ethylenediamine–1.2 m*M* oxalic acid–5 vol.% acetone; pH, 4.0; flow-rate, 1.5 ml/min; concentration of each metal ion, 10 mg/l.

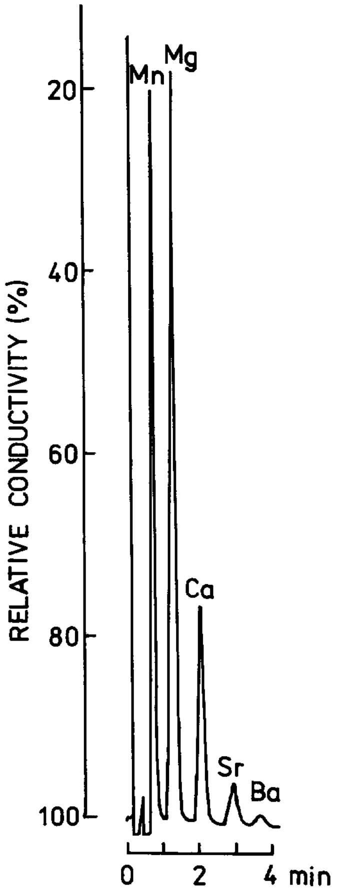

Fig. 5. IC analysis of a standard sample on PGMA-PCCE VIII. Eluent, 1.2 m*M* ethylenediamine–1.7 m*M* oxalic acid–5 vol.% acetone; pH, 4.0; flow-rate, 1.5 ml/min; concentration of each metal ion 10 mg/l.

exception of alkali metals on the PCCE VI column (PS coated). The number of theoretical plates (N) calculated for the short columns (30 mm length) was 600–850. These good N values were due to the excellent chromatographic efficiencies of the silica gels, which had small particle size and pore-size diameter distributions.

These results can also be seen in Fig. 3, which shows a plot of the reduced plate height against reduced velocity for sodium and potassium on the PCCE III column. The minimum values of h were 4 for sodium and 5 for potassium, and indicated good efficiencies of the polymer-coated silica gel columns. Of greatest interest are the shapes of the plots above the minimum values, which correspond to the c-values of the Van Deemter equation and reflect the resistance to mass transfer within the particles. The h *versus* v plots rise gradually with increasing velocity above the minimum values, showing good resistance to mass transfer within the thin polymer-coated particles, which is an advantage of the PCCE columns over the polymer phases. These characterized polymer-coated cation exchangers were tested for rapid separations of alkali and alkaline earth metal ions by using short columns. Other applications have been published previously [4,5]. As the capacity is low, rapid separations can be achieved with relatively weak eluents, which is favourable in single-column IC, particularly when conductivity detection is applied.

Figs. 4–7 shows alkali and alkaline earth metal ion separations on PS- and PGMA-coated silica gels. For alkali metal ion separations nitric acid was used and for alkaline earth metal ion separations

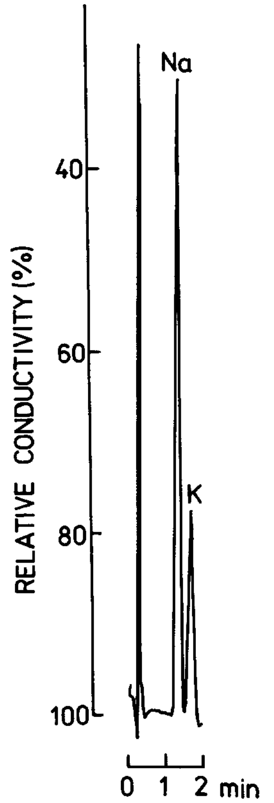

Fig. 6. Determination of alkali metal ions in drinking water (Kemberg) on PGMA-PCCE VIII. Eluent, 3 mM nitric acid; flow-rate, 1.5 ml/min; sample, 1:10 dilution, Na^+ 83 mg/l, K^+ 71 mg/l.

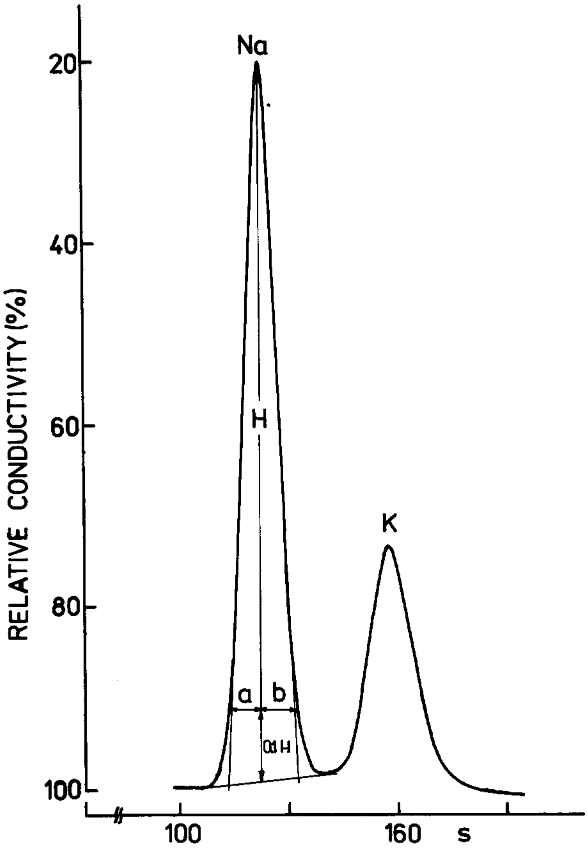

Fig. 7. IC analysis of a standard sample on PGMA-PCCE VIII. Eluent, 3 mM nitric acid; sample, Na^+ 6 mg/l, K^+ 8 mg/l. Peak symmetry factors (b/a): Na^+ = 1.18; K^+ = 1.13.

mixtures of ethylenediamine and oxalic acid were used as the eluent.

With the PCCE columns tested, all alkaline earth metals (Mg, Ca, Sr and Ba) and manganese were separated in at least 4 min. Sodium and potassium were separated in only 2–3 min using the PGMA phases (Figs. 5 and 6). The good chromatographic and flow properties of the PCCE columns produced very symmetrical signals (Fig. 6). The peak symmetry factor (b/a) [8] is 1.0 for an ideal symmetrical signal.

The columns were used to determine alkali and alkaline earth metal ions in mineral, drinking and tap waters. The results were in agreement with those obtained by flame atomic absorption spectrometry and EDTA titration.

The disadvantage of the short columns is the small loading capacity. Especially for alkali metal ion separations, the analyses had to be stopped when the retention times became too short. Under the conditions used for alkali metal ion separations, the alkaline earth metal ions were accumulated on the stationary phase and therefore had to be eluted by injection of 0.1 M nitric acid from time to time.

CONCLUSIONS

Polymer-coated cation exchangers with a silica core are very suitable for ion chromatography. The described procedure provides a reproducible means of preparing low-capacity polymer-coated cation exchangers. The average polymer film thickness was 0.12–0.33 nm. The ion-exchange capacities (30–90 μmol/g) and the pH stabilities (0.5–9.5) were limited. The pH stability of pure polymer phase were not achieved with polymer-coated materials based on silica gels. Good mass transfer properties were advantageous and were discernible from the h *versus* v plots. The PCCE columns showed good chromatographic and flow properties and were applicable to rapid separations of alkali and alkaline earth metals by using short columns.

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