Characterization of covalently bonded and adsorbed polymer coatings on silica, alumina and zirconia by means of physico-chemical and chromatographic methods

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ABSTRACT

Polymer coatings on porous silica, alumina and zirconia were prepared by covalent bonding of a copolymer of styrene and vinylsilane on the oxidic surface with or without subsequent cross-linking of the immobilized polymeric layer. Polybutadiene and polychloromethylstyrene were adsorbed on the surface of porous alumina without covalent bonding and were cross-linked after deposition. Analysis of the pore structure of coated oxides by means of nitrogen adsorption, mercury porosimetry and inverse size-exclusion chromatography revealed different polymer distributions across the modified surface and different changes of the porosity of the initial oxides depending on the method of polymer immobilization. By covalent bonding of the copolymer of styrene and vinylsilane to alumina and zirconia with subsequent cross-linking the modifying polymeric layer, highly hydrolytic stable packings were synthesized and their applications in separations with aggressive eluents were demonstrated.

INTRODUCTION

Modified silica packings are the most commonly used stationary phases in HPLC [1]. Depending on the HPLC mode being applied, they differ in the chemical nature of the modifying layer. Among these, polymer-coated packings have attracted considerable interest over the last decade. Their synthesis [2,3], chromatographic properties [4] and application to the separation of biologically active compounds [5] have been reviewed.

One of the essential features in the coating process is the spreading of the modifying polymer across the modified surface and the change in the porosity of the initial packing after modification. Figge *et al.* [6] investigated the porosity of silicas coated with poly(*n*-octadecylmethylsiloxane) and polybutadiene by means of nitrogen adsorption and inverse size-exclusion chromatography and reported retaining the pore size distribution of the initial matrix even at high polymer loadings. The pore structural and chromatographic properties of silicas modified with copolymers of styrene and vinylsilane have been examined [7] and marked changes in the pore

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structure of the materials with pore sizes smaller than 10 nm were observed. Later Hanson and co-workers investigated the distribution of adsorbed polybutadiene on the surface of non-porous [8] and porous silicas [9,10] and detected a non-homogeneous distribution of the polymer across the modified surface.

In this work, the primary focus was on the comparison of the porosities of polymer-coated packings obtained by covalent bonding or by adsorption of the polymers. The second aspect of interest was to elucidate the effect of cross-linking of the polymeric layer on the porosity of the final packing. From polymer chemistry it is well known that cross-linking can generate non-porous (gel-like) or porous products depending on the method used. The third aspect was to examine the influence of the chemical nature of the surface to be modified on the polymer distribution and on the structure of the cross-linked polymer layer. As supports silica, alumina and zirconia were used.

EXPERIMENTAL

Chemicals and materials

LiChrospher Si 100, LiChrospher Si 300, Alox T and Aluspher 100, all of particle diameter $d_p = 5$ or 10 μm, were obtained from Merck (Darmstadt, Germany). Experimental silica was a gift from MZ Analysentechnik (Mainz, Germany). Alusorb N 200 was obtained from Lachema (Prague, Czech Republic). Alumina A5Y was obtained from Phase Separations (Deeside, UK). Zirconia was a gift from Thermoxide (Jekaterinburg, Russian Federation).

Polystyrene standards with molecular mass ranging from 182 to 3 340 000 were purchased from Polymer Laboratories (Church Stretton, UK), Polymer Standards Service (Mainz, Germany) and Merck.

All solvents employed for the synthesis were of analytical-reagent grade and were used without additional purification. HPLC-grade solvents for chromatographic measurements were obtained from Merck.

3-Chloromethylstyrene and polybutadiene of average molecular mass 5000 containing 20% vinyl fragments and 80% cis- and trans-1,4-frag-ments were purchased from Aldrich-Chemie (Steinheim, Germany).

Synthesis of polymers

A copolymer of styrene and vinyl-methyldiethoxysilane (copolymer I) was synthesized by radical copolymerization. Both monomers were subjected to reaction at a ratio 1:1. Dicumyl peroxide was added to the reaction mixture as an initiator at a concentration of 1% (w/w) of monomers. Polymerization was carried out at 120°C under a nitrogen atmosphere for 6 h. The reaction mixture was then diluted with toluene and the copolymer formed was precipitated in dry methanol. The precipitation was repeated twice after dissolving the polymer in toluene and dropping the solution into methanol under agitation. The polymer was then filtered off through a glass frit and dried under vacuum at 40°C. The ratio of styrene to silane units was found to be 8:1 from elemental analysis. The mean molecular mass of the copolymer was determined to be 5500 using size-exclusion chromatography (SEC) with polystyrene standards.

The radical polymerization of 3-chloromethylstyrene was performed in toluene solution at 110°C for 6 h. Dicumyl peroxide was used as an initiator at a concentration of 2.5% (w/w) of monomers. After the polymerization, poly-chloromethylstyrene was precipitated in methanol and purified as described above. The mean molecular mass was 4500 as determined by SEC.

Preparation of coated oxides by covalent bonding and by adsorption of polymers

Deposition of copolymer 1 on the oxidic surface was carried out by the following procedure. A weighed amount of the oxide was placed in a three-necked flask equipped with a stirrer and Dean–Stark separator and 100 ml of toluene per 10 g of oxide were added. The suspension was heated under reflux until no further water was liberated, then a solution of copolymer in toluene was added (ca. 0.2 mg of the copolymer 1 per square metre of specific surface area of silica). The suspension was heated under reflux for 5 h and the hot suspension was filtered off, washed twice with hot

toluene and dried under vacuum at 60°C. The amount of bonded copolymer was assessed by means of elemental analysis and from thermogravimetric measurements (Tables I and III).

The chloromethylation of the immobilized polystyrene was performed according to the conventional procedure by reaction of the coated packing with a mixture of thionyl chloride, dimethoxymethane and zinc chloride in dichloroethane at room temperature. Cross-linking of the chloromethylated polymer was then carried out by boiling the suspension of the corresponding material in dichloroethane or toluene in the presence of zinc chloride as a catalyst. With dichloroethane as a solvent cross-linking occurred, whereas in toluene the cross-linking was additionally accompanied by arylation of the polymeric layer. In the latter instance the degree of cross-linking was lower, but the resulting carbon content was higher compared with the procedure using dichloroethane.

Adsorption of polybutadiene was performed according to Schomburg et al. [11]. A 10-g amount of oxide was weighed into a chamfered flask. A solution of 0.8 g of polybutadiene and 40 mg of dicumyl peroxide in 50 ml of n-pentane was added to the oxide and the solvent was evaporated by means of a Rotavapor. The subsequent cross-linking was performed at 120°C. The modified oxide was suspended in hot toluene by means of ultrasonic treatment and then filtered off. This procedure was repeated three times. The filtered oxide was then dried under vacuum at 60°C. The same procedure was used for immobilization of polychloromethylstyrene. No cross-linking initiator was used in this instance because cross-linking of polychloromethylstyrene took place due to the self-condenzation of chloromethyl phenyl groups by heating the material up to 150°C.

Thermal analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted with a Model 2100 TGA-Analyser (DuPont, Wilmington, DE, USA). The temperature was increased to 1000°C at a rate of 20°C/min under a dry nitrogen or air atmosphere.

Electron spectroscopy for chemical analysis (ESCA)

ESCA measurements were performed with a Contron (Munich, Germany) ESCA analyser at the Institute of Organo-Element Compounds, Moscow, according to the standard procedure.

Mercury porosimetry

Mercury porosimetry was conducted on a Carlo Erba (Milan, Italy) porosimeter with a maximum pressure of about 2500 bar. The pore size distribution was calculated on the basis of the Washburn equation using the standard software supplied by Carlo Erba.

Low-temperature nitrogen adsorption

The nitrogen adsorption isotherms of native and polymer-coated oxides were measured at 77 K with an ASAP 2400 system from Micromeritics (Norcross, GA, USA). The BET specific surface area, the specific pore volume and pore size distribution were calculated by means of the standard software implemented in the ASAP 2400 system.

Chromatographic experiments

The coated oxides were packed into columns of 250 × 4 mm I.D. or 125 × 4 mm I.D. (Merck) using a 5% (w/w) suspension of cyclohexanol–toluene (1:1, v/v). Methanol was used as a displacing solvent. Chromatographic experiments were performed using an HPLC system consisting of an L-6200 pump, an L-4250 variable-wavelength detector and a D-2500 integrator (all from Merck).

RESULTS

Modified silica packings

The coating of porous silicas by covalent bonding of the copolymer of styrene and vinylmethyldiethoxysilane led to packings with coating densities ranging from 2.8 to 12 μmol of monomer units per square metre of specific surface area (Table I). The coating density increased with increase in the pore diameter of the parent silica. The observed changes in the coating density reflect the better accessibility of large pores for the polymer coils bonded to the

TABLE I

CHARACTERISTIC PARAMETERS: SPECIFIC SURFACE AREA (a_s), SPECIFIC PORE VOLUME (V_p) AND MEAN PORE DIAMETER (d_p) FOR NATIVE AND COATED SILICA PACKINGS[a]

No.	Silica	Type of modification	Polymer content (mg/g)	Coating density (μmol/m²)	Coating thickness (Å)	Low-temperature nitrogen adsorption			Mercury porosimetry			Inverse size-exclusion chromatography		
						a_s (m²/g)	V_p (ml/g)	d_p (Å)	d_p (Å)	V_p (ml/g)	a_s^b (m²/g)	V_p (ml/g)	d_p (Å)	a_s (m²/g)
1	LiChrospher Si 100	Native	–	–	–	352	1.23	140[b] 140[c]	–	–	–	1.31	150	349
2		Coated with PS[d]	96	2.8	3.0	282	0.95	135	–	–	–	1.20	86	558
3		Cross-linked[e]	137	2.8	4.5	470	1.01	110[b] 130[c]	–	–	–	1.06	44	963
4	LiChrospher Si 300	Native	–	–	–	59	0.56	383[b] 300[c]	350	0.75	86	1.05	474	162
5		Coated with PS	70[g] 83[h]	12.1	12.7	65	0.51	319[b] 250[c]	300	0.62	83	0.79	134	313
6		Cross-linked[f]	77[g] 84[h]	12.1	14.3	123	0.58	189[b] 200[c]	300	0.61	81	0.96	268	143
7	LiChrospher Si 300	Native	–	–	–	80	0.68	341[b] 320[c]	330	0.80	97	1.25	434	115
8		Coated with PS	85[g] 84[h]	11.1	11.6	79	0.61	309[b] 316[c]	300	0.55	73	1.25	126	396
9		Cross-linked[f]	100[g] 99[h]	11.8	14.0	173	0.59	137[b] 290[c]	300	0.54	72	0.86	252	136
10		Cross-linked[e]	134[g]	–	19.4	159	0.56	141[b] 300[c]	300	0.55	73	0.80	260	123
11	Experimental silica	Native	–	–	–	58	0.67	462[b] 400[c]	350	0.82	94	1.15	480	94
12		Coated with PS	47	8.9	8.5	59	0.61	413[b] 370[c]	300	0.63	84	0.87	174	200
13		Cross-linked[f]	52	8.1	9.4	97	0.62	258[b] 350[c]	300	0.61	81	0.88	282	125

[a] All values are normalized for 1 g of modified silica.
[b] Calculated according to Wheeler, $d_p = 4V_p/a_s$.
[c] Maximum of d_p from pore size distribution curve.
[d] PS = polystyrene.
[e] Cross-linked in toluene (see Experimental).
[f] Cross-linked in dichlorethane (see Experimental).
[g] Calculated from elemental analysis.
[h] Derived from TGA experiments.

surface. These observations agreed with our previous results [7] and those of other workers [12,13] who also used the same method for polymer immobilization.

The distribution of elements at the surface of LiChrospher Si 300 determined by means of ESCA shows that the content of silicon atoms at the surface layer decreased from 35% for native silica to 20% for the cross-linked packing after the modification (see Table II). Complete shielding of the silica surface was not reported for either a conventional "brush-type" RP packing (26.9%) or a highly polymer-loaded non-porous

packing, Monospher (7.9%) [8]. Taking the amount of silicon in the polymer chain into account, one can assume the same degree of shielding of the surface by the copolymer as found by ESCA for common RP packings.

The polymer content of composites calculated from elemental analysis agreed fairly well with the polymer content assessed from thermal analysis (TGA) (Table I). The thermal decomposition of the immobilized and cross-linked polymer layer occurred to equal extents (Fig. 1A), but the thermal decomposition curve for the packing with non-cross-linked layer (curve 1 in Fig. 1A)

TABLE II

DISTRIBUTION OF CARBON, OXYGEN AND SILICON ATOMS IN THE SURFACE LAYER OF LICHROSPHER SI 300 COATED WITH COPOLYMER OF STYRENE AND VINYLMETHYLDIETHOXYSILANE

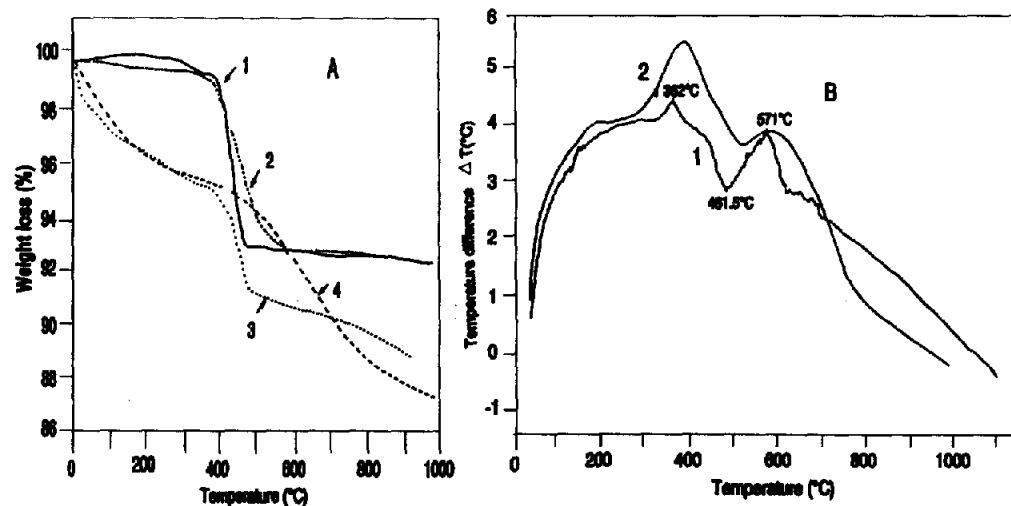| LiChrospher Si 300	Amount of copolymer (mg/g)	C (atom%)	O (atom%)	Si (atom%)
Native	–	14.6	50.4	35.1
Coated with copolymer	92	32.3	37.5	30.2
Coated with chloromethylated copolymer	109	47.5	28.4	22.4
Coated with cross-linked copolymer	109	50.5	27.7	21.0

Fig. 1. (A) Thermogravimetric and (B) differential thermogravimetric analysis of silica LiChrospher Si 300 (1, 2) and alumina Aluspher 100 (3, 4) coated with covalent bonded copolymer of styrene and vinylsilane (1, 3) and subjected to additional cross-linking (2, 4).

was steeper than that for the packing with the cross-linked layer (curve 2 in Fig. 1A). The mass loss was in all instances independent of the probe type and the atmosphere in which the decomposition was carried out.

DTA indicated a difference between the packings bearing the non-cross-linked and the cross-linked polymeric film (Fig. 1B). The DTA curve under a nitrogen atmosphere for the non-cross-linked packing showed a less pronounced endothermic peak at 362°C and two other exo- and endothermic peaks at 481 and 571°C, respectively. For the cross-linked packing the same was observed, but the first peak at 362°C was much more pronounced. It is highly probable that the first endothermic effect is connected with the destruction of the polymeric network and bonds at the oxidic surface, which is in agreement with the small mass loss of 1% (w/w) up to 400°C (Fig. 1A).

The specific surface area of the 100 Å pore size silica decreased by about 20% after coating with the copolymer I (see Table I). The decrease for the wide-pore supports was only 5%. In all instances the cross-linking of the polymeric layer caused an increase in the specific surface area by a factor of about two. This increase was probably

due to the formation of small pores in the polymer layer, as described earlier by Davankov and Tsyurupa [14] for bulk polystyrene which was intensively cross-linked in the dissolved state.

The specific pore volume of the native 100 Å pore size silica decreased by about 26% after the modification. The changes in V_p for wide-pore silicas were within the accuracy of the measurement. Cross-linking of the polymer layer did not cause any significant changes in the specific pore volume of the packings.

The mean pore diameter of silicas determined by the nitrogen adsorption technique diminished only slightly after the coating with the copolymer, but dropped sharply after the cross-linking (Table I). The mean pore diameter according to Wheeler and the maximum of the pore size distribution coincided well for native and coated non-cross-linked packings. For the cross-linked packings the deviation of these values was up to 50%.

As a representative example, the pore size distributions of LiChrospher Si 300 (sample No. 7 in Table I) and its polymer-coated derivatives are shown in Fig. 2. The position of the peak maximum of the pore size distribution curve did
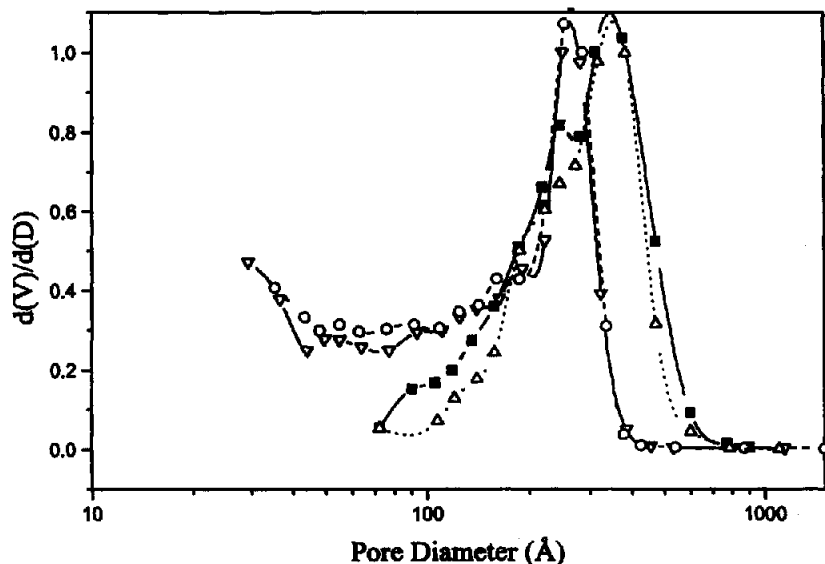

Fig. 2. Pore size distribution of silica LiChrospher Si 300, (■) native, (△) modified with covalent bonded copolymer I and (○, ▽) modified with cross-linked covalently bonded copolymer I determined from nitrogen adsorption isotherm.

not change after the coating with the copolymer and moved slightly to lower values after the cross-linking, independently of the method used (compare curves 3 and 4 in Fig. 2).

The parameters determined by means of mercury porosimetry coincided fairly well with those obtained from nitrogen adsorption measurements for native silicas or packings coated with non-cross-linked polymer (Table I). However, the mean pore diameter and the specific surface area of the cross-linked packings derived from mercury porosimetry differed significantly from the corresponding values obtained from nitrogen adsorption measurements.

The third method used for the evaluation of the pore structure parameters was inverse size-exclusion chromatography (ISEC). The specific pore volume assessed by this method is related to the volume of packing in the column. To recalculate this value per gram of packing in the column, it was assumed that the specific density of the pore walls of all silicas is equal to the true density of quartz (2.2 g/ml). This assumption seems to be reasonable. Stegeman et al. [15] determined the specific density of walls for one sample of silica and found an identical value. The density of polymer-coated packings was assumed to be a linear function of their composition. The calculated values are given in Table I. The specific pore volume of the 100 Å pore size silica determined by ISEC coincided reasonably well with those determined by nitrogen adsorption. The specific pore volume of wide-pore packings markedly exceeded the values calculated from nitrogen adsorption. This difference is probably caused by uncertainties in the determination of V_p for wide-pore packings, as pointed by Stegeman et al. [15]. In this case one cannot clearly discriminate between the size-exclusion and hydrodynamic mechanism of separation. Within a series of silicas and their coated derivatives a decrease in the specific pore volume is observed (Table I). The subsequent cross-linking slightly increased the specific pore volume or did not change it at all.

The pore size distribution from ISEC data was calculated according to the Knox method [16]. For non-modified silicas the calculated pore diameter was in good agreement with the value determined from nitrogen adsorption. In all instances coating with the polymer caused a marked decrease in the mean pore diameter (Table I). The pore diameter of coated silica packings determined by ISEC did not coincide with those calculated from nitrogen adsorption and from mercury porosimetry. Inspection of the SEC calibration graph reveals that the plot for the packing with a cross-linked polymeric layer lies between those for the native and coated non-cross-linked silica (Fig. 3A). Another interesting feature of Fig. 3A is that the calibration graphs are of almost the same shape. Similar changes were observed for the silica with 100 Å pore diameter, with the only difference that the calibration graphs for the packings coated with a non-cross-linked and with a cross-linked polymeric layer were very close to each other (Fig. 3B). This seems to be an indication that native and modified packings have approximately the same width of the pore size distribution, which is shifted for coated packings to smaller mean pore diameters. The latter is evidenced by the diminution of the size exclusion limit.

Modified alumina and zirconia packings

The coating procedure for aluminas and zirconia was essentially the same as that applied to the silicas. The results are given in Table III. The coating density of the packings based on Aluspher 100, Alumina A5Y and Alox T was comparable to the value obtained for LiChrospher Si 100. Alusorb N 200 gave a lower coating density, probably owing to its broader pore size distribution (not shown). The latter extended to the lower pore size and the main part of these small pores remained unmodified in the coating procedure.

The modification of alumina by means of covalent bonding of copolymer I caused the same changes in the pore structure as discussed for silicas. The cross-linking of the adsorbed polymer layer generated a bimodal pore size distribution (Fig. 4). The nitrogen adsorption isotherm exhibited two distinct steps in the desorption branch in the range of the capillary condensation ($0.4 < p/p_0 < 0.9$). Correspondingly, the pore size distribution curve showed two maxima (Fig. 4). One was identical with the
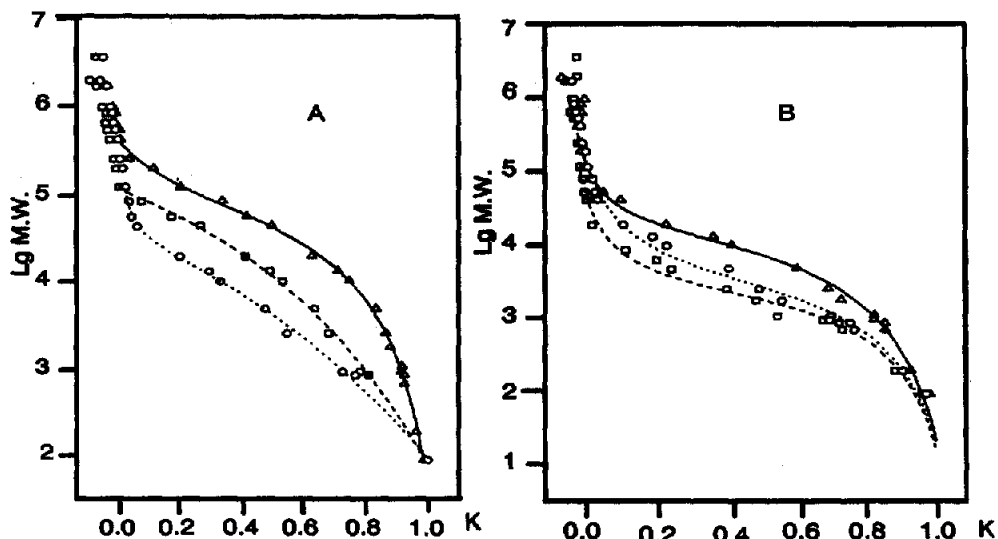
Fig. 3. SEC calibration graphs for (A) silica LiChrospher Si 300 and (B) silica LiChrospher Si 100: □ = coated with cross-linked covalently bonded copolymer I; O = coated with covalently bonded copolymer I; △ = native. M.W. = Molecular mass.

maximum of the pore size distribution curve of the unmodified alumina. The second maximum occurred at slightly lower values of about 40–60 Å.

The SEC calibration graphs for polymer-modified aluminas are shown in Fig. 5A. In accordance with the decrease in d_p, the exclusion limit of the polymer-modified aluminas also decreased as compared with the native oxide. However, in the low-molecular-mass range there was a slight difference in fractionation ability as compared with the parent material. The calibration graphs for native alumina and for the polymer-coated packing are very close to each other in this molecular mass range (Fig. 5).

Cross-linking of the polymeric layer decreased the exclusion limit much further and the calibration graph exhibited an extremely small slope in the range of the size-exclusion distribution coefficient, K, between 0 and 0.6. However, the pore size distribution from such a type of calibration graph cannot be calculated by ISEC owing to the lack of an appropriate fitting function.

The TGA experiments revealed that there is no significant difference in the thermal stability of the polymer layer deposited on the alumina surface compared with silicas. Unexpectedly, an enhanced thermal stability was observed for aluminas with a cross-linked polymer layer in a nitrogen atmosphere (Fig. 1A, curve 4). As is seen from the slightly sloping curve, the mass loss was minor up to 800°C for this packing (Fig. 1A, curve 3).

Contrary to the method of covalent bonding, the polymer load for Aluspher 100 modified by the adsorption of polybutadiene and polychloromethylstyrene is not limited. It is simply adjusted by the amount of the polymer employed for modification (Table III). The progressive increase in the polymer content was accompanied by a strong decrease in the specific surface area and the specific pore volume determined by nitrogen adsorption (Table III). The mean pore diameter and the pore size distribution of the modified packings were exactly the same as for the starting alumina (Fig. 6).

The ISEC method demonstrated distinct changes in the pore size distribution after modification. The SEC calibration graph for the polybutadiene-coated packing was different to that for the native alumina and major alterations were observed in the low-molecular mass range (Fig. 5). The exclusion limit of alumina was only slightly changed after the modification. Hence SEC clearly proved the appearance of small pores in the structure of coated packing.

The available sample of zirconia exhibited an

TABLE III

CHARACTERISTIC PARAMETERS: SPECIFIC SURFACE AREA (a_s), SPECIFIC PORE VOLUME (V_p) AND PORE DIAMETER (d_p) FOR DIFFERENT OXIDES COATED WITH POLYMERS[a]

No.	Oxide	Type of coating procedure	Polymer content (mg/g)	Coating density (μmol/m^2)	Low-temperature nitrogen adsorption			Inverse size-exclusion chromatography		
					a_s (m^2/g)	V_p (ml/g)	d_p[b] (Å)	V_p ml/g	d_p (Å)	a_s[b] m^2/g
1	Alumina	Native	–	–	155	0.50	130	0.55	146	151
2	Aluspher 100	PS[c]	43[g] 98[h]	2.8	140	0.43	122	0.37	64	231
3		Cross-linked PS[d]	61[g] 93[h]	3.0	175	0.43	99	0.31	–	–
4		Cross-linked PS[e]	54[g]	3.1	184	0.46	100	0.40	–	–
5		Polybutadiene[f]	80[g]	12.3	108	0.35	128	0.37	48	308
6		Chloromethyl-PS	70[g]	3.0	135	0.41	122	–	–	–
7		Chloromethyl-PS	162[g]	8.3	86	0.27	124	–	–	–
8	Alumina	Native	–	–	75	0.24	131	–	–	–
9	Alox T	Coated with PS	52[g]	7.0	102	0.29	114	–	–	–
10	Alumina	Native	–	–	226	0.29	52	–	–	–
11	Alusorb N 200	Coated with PS	40[g]	1.7	214	0.26	47	–	–	–
12	Alumina A5Y	Coated with PS[d]	66[g]	4.0	172	0.28	65	–	–	–
13	Zirconia	Native	–	–	17	0.07	157			
14		Coated with PS	7.7	4.1	9	0.02	89			

[a] All values are normalized for 1 g of modified oxide.
[b] Calculated according to Wheeler, $d_p = 4V_p/a_s$.
[c] PS = polystyrene.
[d] Cross-linked in dichloroethane (see Experimental).
[e] Cross-linked in toluene (see Experimental).
[f] Coated according to Figge et al. [6].
[g] Calculated from elemental analysis.
[h] Derived from TGA experiments.

extremely low specific pore volume. The specific surface area of zirconia of 17 m^2/g clearly indicated that the sample was porous. Coating of zirconia with the polymer affected only slightly the shape of its pore size distribution. However, the values of a_s, V_p and d_p of the modified packing were reduced to half the initial values.

Chromatographic characterization

SEC was performed to evaluate the changes in pore structure parameters after the coating of the oxides with polymers. The results of these investigations are presented in Tables I and III and have already been discussed in context with the results of low-temperature nitrogen adsorption and mercury porosimetry. From the chromatographic point of view, the modification by means of covalent bonding diminished the exclusion limit and did not significantly change the molecular mass of the solutes enabling them to penetrate the pores of the packing. The selectivity [i.e., the derivative d(log M_r)/dV] of the packing remained nearly unaffected, while the calibration graphs of the modified and the native silicas are almost parallel to each other (Fig. 3). The cross-linking of the polymeric layer moved the calibration graph of the packing closer to those of native silica, thus increasing the exclusion limit.

The modification of oxides by means of adsorption of polybutadiene decreased only slightly the exclusion limit, but diminished strongly the
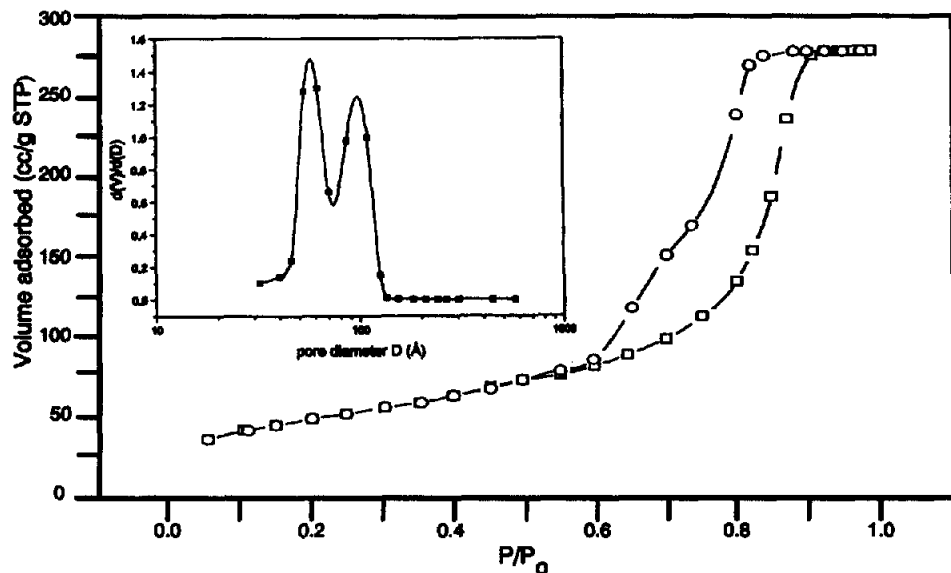
Fig. 4. Low-temperature nitrogen adsorption isotherm and calculated pore size distribution of alumina Aluspher 100 coated with cross-linked covalent bonded copolymer I: □ = adsorption; O = desorption. cc = ml.
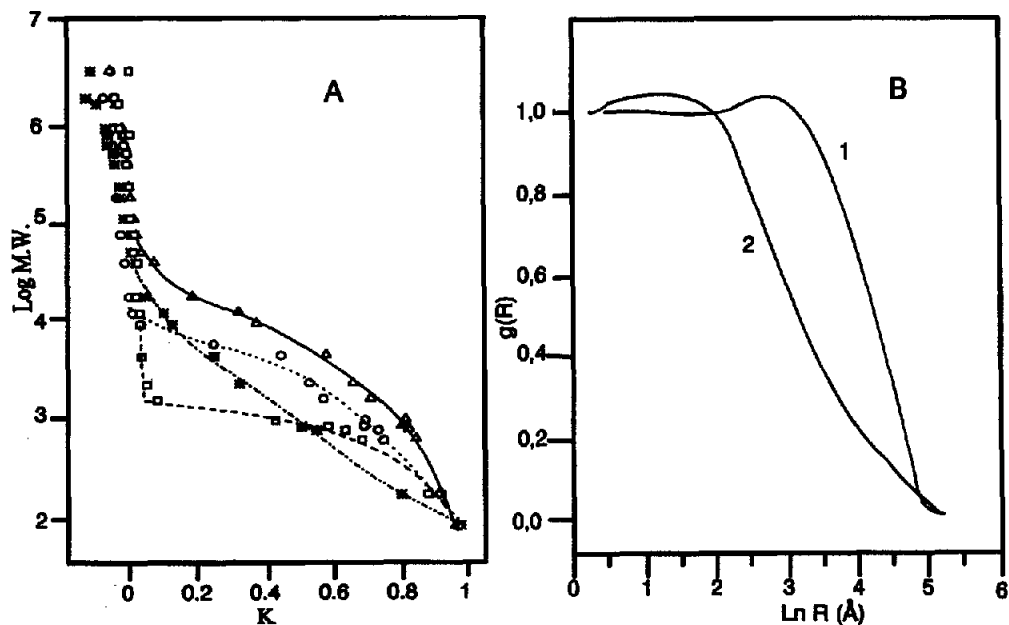

Fig. 5. (A) SEC calibration graphs and (B) calculated pore size distribution for alumina Aluspher 100 and its derivatives. (A) △ = native; □ = coated with covalently bonded cross-linked copolymer I; O = coated with covalently bonded copolymer I; * = coated with adsorbed polybutadiene. (B) 1 = Native; 2 = coated with adsorbed polybutadiene. M.W. = Molecular mass.
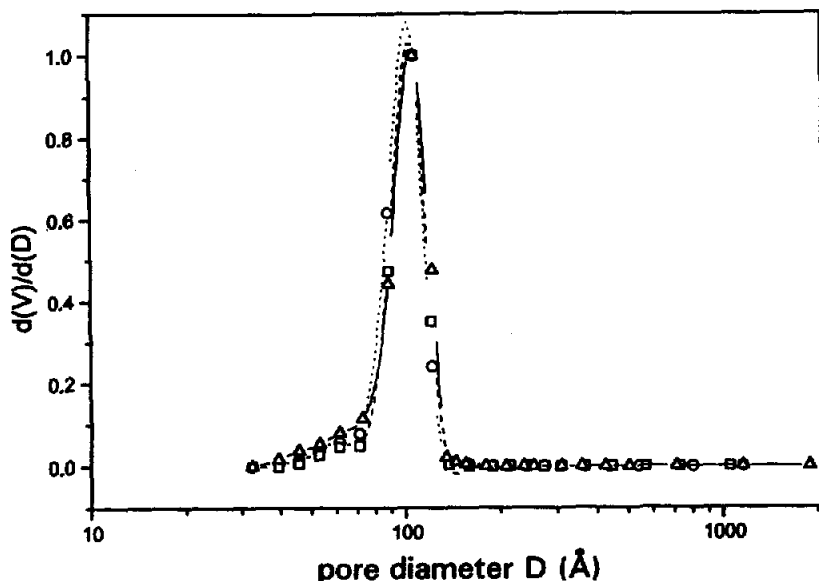
Fig. 6. Pore size distribution of alumina Aluspher 100 modified with adsorbed polychloromethylstyrene determined from low-temperature nitrogen adsorption: O = native; □ = 7% loading; △ = 16.2% loading.

molecular mass, enabling molecules to penetrate all pores of the packing. The calibration graph for the coated packing was therefore much steeper than that for the native material (Fig. 5). As a consequence, the selectivity of the modified packing was markedly decreased because its fractionation range became wider.

The impact of cross-linking of the polymeric layer of the packings on the selectivity of separation in the RP mode of chromatography is demonstrated in Fig. 7. There is actually no large difference between the two sorbents in the separation of basic compounds. Good efficiency and peak symmetry were observed for amines on both cross-linked and non-cross-linked coated silicas, reflecting the good shielding of the silica surface by the polymeric layer. It should be emphasized that no end-capping of the poly-styrene-modified silica was carried out and no addition of any other basic or salt compounds to the eluent was required. The separation were performed with a simple water–acetonitrile eluent.

Basic compounds were also eluted with symmetrical peaks on alumina and zirconia modified by covalent bonding of copolymer I, indicating no specific surface–solute interaction

(Fig. 8). As the chemical stability of alumina or zirconia towards strong alkali or strong acid eluents is much higher than that of silica, separations can be carried out with acidic and alkaline eluents which are not compatible with modified silicas (Fig. 9).

DISCUSSION

The modification of porous silicas and aluminas by means of adsorption of different types of cross-linkable polymers has been intensively investigated by Schomburg [3,4]. Coatings with covalently bonded pre-synthesized reactive copolymers have been studied in the chiral ligand-exchange chromatography of enantiomers [17] and in the reversed-phase [18] and ion-exchange chromatography [19] of proteins and peptides. Whereas the main focus of the previous investigations was on the assessment of the chromatographic performance, in this work we addressed the problem of the distribution of polymers in the pores of modified oxides.

The pore size distribution of alumina Aluspher 100 determined by means of low-temperature nitrogen adsorption was not changed after the coating with polychloromethylstyrene (Fig. 6) or
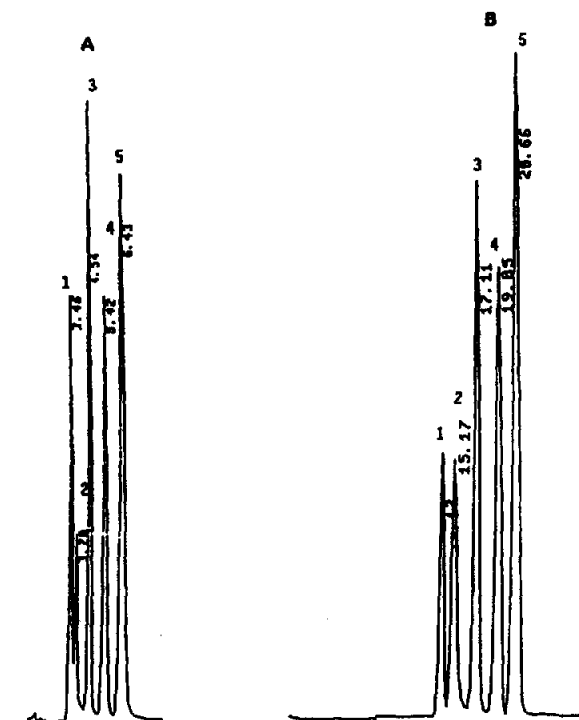
Fig. 7. Separation of a mixture of basic compounds on (A) silica LiChrospher Si 300 coated with covalently bonded copolymer and (B) silica LiChrospher Si 100 coated with cross-linked covalent bonded copolymer. (A) $d_p = 10$ μm; column, 125 × 4 mm I.D.; flow-rate, 0.5 ml/min; eluent, acetonitrile–water (1:1). (B) $d_p = 10$ μm; column, 125 × 4 mm I.D.; flow-rate, 0.25 ml/min; eluent, acetonitrile–water (6:4). Analytes; 1 = pyridine; 2 = o-toluidine; 3 = N-methylaniline; 4 = N,N-dimethylaniline; 5 = 2-ethylaniline. Retention times (min) indicated at the peaks.

Fig. 8. Chromatographic separations on alumina Aluspher 100 coated with covalent bonded cross-linked copolymer I. Column, 125 × 4 mm I.D.; $d_p = 10$ μm; flow-rate, 0.5 ml/min; eluent, acetonitrile–water (1:3). (A) Separation of a mixture of barbiturates: 1 = barbitole; 2 = allo-barbitole; 3 = luminale; 4 = prominale. (B) Separation of a mixture of (1) 2,6-dimethypyridine and (2) pyridine. (C) Separation of a mixture of basic compounds: 1 = N-methylaniline; 2 = pyridine; 3 = aniline; 4 = N,N-dimethylaniline; 5 = o-toluidine; 6 = 2-ethylaniline. Retention times (min) indicated at the peaks.

polybutadiene (not shown), in spite of a strong decrease in the specific pore volume and specific surface area (Table III). Since the same results have been observed earlier for other oxides coated with other polymers [6,9,10], it seems that the preservation of the pore size distribution of the native material after modification by the adsorption method is a fairly general phenomenon.

The preservation of the pore size distribution of the parent oxide after modification with a polymer cannot be expected assuming the common model of modification where the polymer is deposited on the surface of pores. Another model has been suggested [10] in which the pores are not coated, but simply filled with the poly-
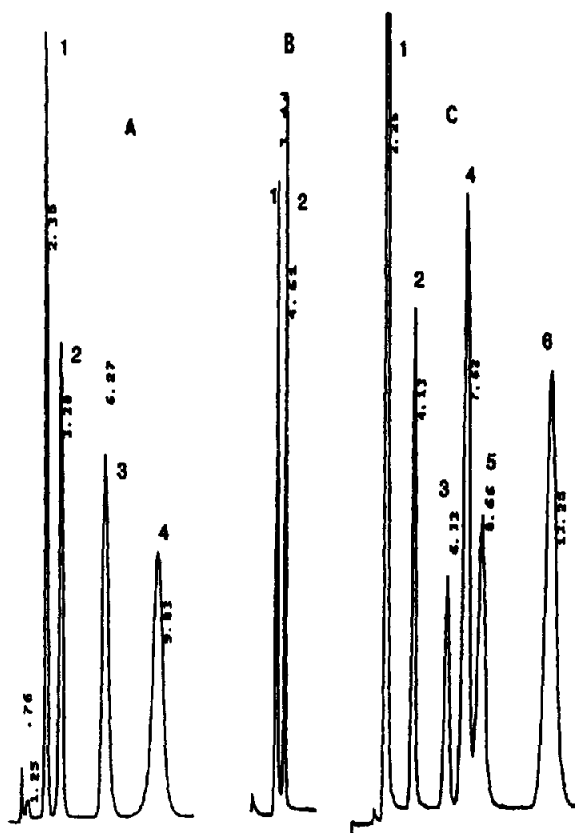
mer. However, this model is not yet able to explain the preservation of pore size distribution. This phenomenon can be explained by the model of Lecourtier et al. [20], in which the polymer is deposited mainly on the outer surface of the particles. This model is strongly supported by scanning electron micrographs of Aluspher 100 coated with polybutadiene, where the presence of polymer agglomerates on the other surface of particles was detected. The micrographs demonstrate the same picture as was reported earlier for polybutadiene-coated LiChrospher Si 300 [9].
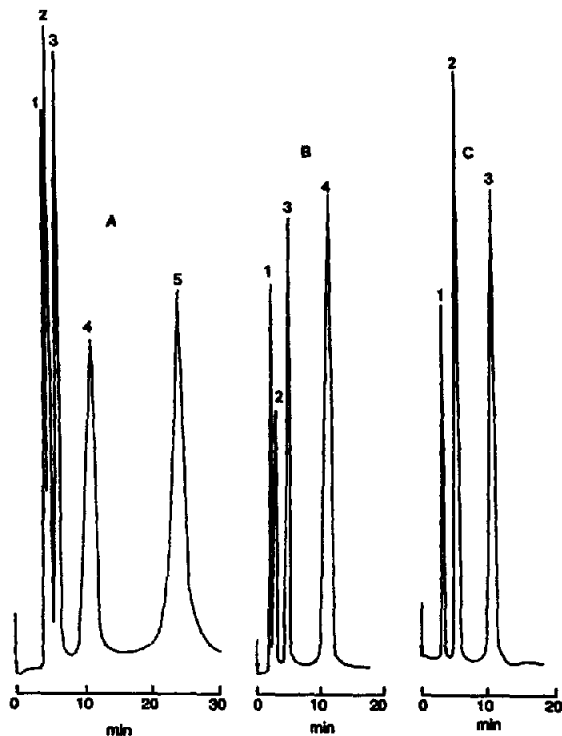
Fig. 9. Chromatographic separations on zirconia coated with cross-linked covalent bonded copolymer I. Column, 150 × 6 mm I.D.; d_p = 10–20 μm. (A) Eluent, acetonitrile–0.1 M HNO$_3$ (1:9); flow-rate, 0.5 ml/min. Analytes: 1 = pyridine; 2 = dipyridyl; 3 = 2,6-dimethylpyridine; 4 = phenanthroline; 5 = acridine. (B) Eluent, acetonitrile–water (1:5); flow-rate, 1.0 ml/min. Analytes: 1 = 2-aminopyridine; 2 = pyridine; 3 = aniline; 4 = p-nitroaniline. (C) Eluent, methanol–0.13 M NaOH (1:1); flow-rate, 1.0 ml/min. Analytes: 1 = 2-amino-pyridine; 2 = aniline; 3 = p-nitroaniline.

The pore size characteristics of packings modified by the adsorption method obtained by ISEC were in contradiction with the results from nitrogen adsorption measurements and provide evidence for the formation of small pores in the polymer layer. As a result, the pore size distribution of polybutadiene-coated Aluspher 100 calculated from SEC data shifted to smaller pore diameters (Fig. 5B). According to the method of synthesis applied, the polybutadiene layer should have a gel-like structure, which normally demonstrates no porosity when in the dry state [21]. The polymeric layer swells under SEC conditions and generates small pores, which shift the pore size distribution of composite packings to lower diameters compared with the native oxide.

The properties of the packings modified by means of covalent bonding of copolymer I supported the common model of modification assuming the deposition of modifier on the surface of pores. For silicas and aluminas with a mean pore diameter of 100 Å, an addition to the normal decrease in the specific pore volume and the specific surface area was observed owing to the blocking of small pores by the bounded polymer (Tables I and III). Wide-pore oxides of pore diameter ⩾300 Å modified by this method show little change in their porosity after the modification, and small pores were absent in the structure of these materials (Fig. 2). The decrease in the mean pore diameter for modified packings from SEC data was found to be more pronounced than was determined from nitrogen adsorption measurements (Tables I and III). This is strong evidence for the swelling of the polymeric layer under SEC conditions.

The cross-linking of the immobilized copolymer causes a strong increase in the specific surface area determined by nitrogen adsorption (Table I) whereas the specific pore volume was found to be changed only slightly. The pore size distribution determined from the nitrogen adsorption isotherm reveals the formation of small pores in the polymer film after the cross-linking and in the case of Aluspher 100 even a bimodal mesopore structure was found (Fig. 4).

The SEC measurements provided clear evidence that the cross-linking of the bonded copolymer I decreased the swelling ability of the polymeric layer because the exclusion limit of the modified wide-pore packings was increased after the cross-linking (Fig. 3A). For LiChrospher Si 100 the changes (Fig. 3B) were small and for Aluspher 100 even a progressive decrease in the molecular mass exclusion limit after cross-linking was detected (Fig. 5). The molecular mass fractionation range of Aluspher 100 coated with a cross-linked polymer layer was between 1000 and 300 only. Nevertheless, it was not decreased to the level of low-molecular mass compounds (e.g., benzene, toluene) as took place for Aluspher 100 modified with adsorbed polybutadiene (Fig. 5). The shape of the SEC curve observed for Aluspher 100 modified with a cross-linked polystyrene layer is a challenge for

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theoretical considerations in SEC because according to model used even for the packing having pores of a single size only the fractionation range should be at least 1.5 log M_r [22]. Nevertheless, SEC calibration graphs with a very narrow fractionation range have been reported for different types of packings [23,24] and elucidation of their pore structures needs additional investigations.

The modification of oxides other than silica by covalent bonding of copolymer I containing reactive silane groups leads to the formation of surface Si–O–E bonds, the hydrolytic stability of which decreases in the order E = Si > Al > Ti > Zr [25]. Because the hydrolytic stability even of Si–O–Si bonds is not sufficient in many applications, it is essential to cross-link the polymeric film as the ultimate step in the synthesis of coated oxides. The chromatographic separations with coated aluminas or zirconia clearly demonstrate that not only the oxide was stable against aggressive eluents, but also the polymer layer. The separation of basic compounds on these packings can be easily performed with neutral, basic or acid eluents, as the packings are stable towards hydrolysis (Fig. 9). It is interesting that alumina coated with polystyrene demonstrates a different selectivity towards amines compared with polystyrene-coated silica (Figs. 7 and 8), but there was no evidence for any decrease in column performance due to the kinetic hindrance in spite of the different pore structures of composites synthesized from silica or alumina.

CONCLUSIONS

Two different methods of polymer coating of oxides have been discussed, namely modification by adsorption of cross-linkable polymers and by covalent bonding of pre-synthesized reactive copolymers. Examination of the pore structure characteristics of the packings by means of low-temperature nitrogen adsorption, mercury porosimetry and inverse size-exclusion chromatography revealed two different modes of polymer distribution on the surface of the oxides. Cross-linking of the immobilized polymeric layer produced additional porosity which can be detected by means of SEC or nitrogen adsorption

measurements, but has little impact on the separations by means of adsorption chromatography. Good chromatographic analytical-scale separations can be achieved with both types of coated packings. Examples of separations on packings with covalent bonded polymeric layer have been presented.

Coating by means of covalent bonding with subsequent cross-linking of the immobilized polymeric layer can be applied to oxides other than silica. The changes in the porosity of the parent oxide after deposition of the polymer was found to be the same as observed for silica packings. The chemical nature of the surface to be modified strongly influenced the changes in the composite porosity in the cross-linking step and different pore structures were detected for alumina and silica modified with cross-linked polystyrene. The chromatographic separations on the coated aluminas and zirconia demonstrate excellent chemical stability of these packings towards aggressive eluents.

REFERENCES

1 K. Unger (Editor), Packings and Stationary Phases in Chromatographic Techniques, Marcel Decker, New York, 1990.
2 M. Hanson and K. Unger, Trends Anal. Chem., 11 (1992) 368.
3 G. Schomburg, Trends Anal. Chem., 10 (1991) 163.
4 G. Schomburg, LC · GC Mag., 6 (1988) 37.
5 A.E. Ivanov, V.V. Saburov and V.P. Zubov, Adv. Polym. Sci., 104 (1992) 136.
6 H. Figge, A. Deege, J. Köhler and G. Schomburg, J. Chromatogr., 351 (1986) 393.
7 A. Kurganov, O. Kuzmenko, V. Davankov, B. Eray, K. Unger and U. Trüdinger, J. Chromatogr., 506 (1990) 391.
8 M. Hanson, K. Unger and G. Schomburg, J. Chromatogr., 517 (1990) 269.
9 M. Hanson, Ph.D. Thesis, Johanes Gutenberg-Universität, Mainz, 1992.
10 M. Hanson, B. Eray, K. Unger, A. Neimark, J. Schmidt, K. Albert and E. Bayer, Chromatographia, 35 (1993) 403.
11 G. Schomburg, J. Köhler, H. Figge, A. Digge and U. Bien-Vogelsang, Chromatographia, 18 (1984) 265.
12 A. Alpert and F. Regnier, J. Chromatogr., 185 (1979) 340.
13 A. Ivanov, L. Zhigis, E. Chekhovskykh, P. Reshetov and V. Zubov, Bioorg. Khim., 11 (1985) 1527.
14 V.A. Davankov and M.P. Tsyurupa, React. Polym., 13 (1990) 27.

15 G. Stegeman, J. Kraak and H. Poppe, *J. Chromatogr.*, 550 (1991) 721.

16 J.H. Knox and H.P. Scott, *J. Chromatogr.*, 316 (1984) 333.

17 A. Kurganov, A. Tevlin and V. Davankov, *J. Chromatogr.*, 261 (1983) 479.

18 V. Davankov, A. Kurganov and K. Unger, *J. Chromatogr.*, 500 (1990) 519.

19 A. Kurganov, V. Davankov and K. Unger, *J Chromatogr.*, 548 (1991) 207.

20 J. Lecourtier, R. Audebert and C. Quivoron, *J. Liq. Chromatogr.*, 1 (1978) 479.

21 D.H. Freeman and S.B. Schram, *Anal. Chem.*, 53 (1981) 1235.

22 L. Hagen, in P.L. Dubin (Editor), *Aqueous Size-Exclusion Chromatography*, Elsevier, Amsterdam, 1988, p. 147.

23 K. Unger, N. Becker and E. Krämer, *Chromatographia*, 8 (1975) 283.

24 A. Maruska, A. Sérys, J. Liesiené, J. Urbonaviciené and A. Zygas, *J. Chromatogr.*, 596 (1992) 157.

25 U. Trüdinger, G. Müller and K. Unger, *J. Chromatogr.*, 535 (1990) 111.