Chem. Mater. **1999,** *11,* 1533−1540 1533

ROMP-Based, Highly Hydrophilic Poly(7-oxanorborn-2-ene-5,6-dicarboxylic acid)-Coated Silica for Analytical and Preparative Scale High-Performance Ion Chromatography

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Received December 2, 1998. Revised Manuscript Received February 4, 1999

Homopolymers of 7-oxanorborn-2-ene-5,6-dicarboxylic anhydride (ONDCA) and norborn-2-ene (NBE), respectively, as well as copolymers of ONDCA and NBE with well-defined block sizes and molecular weights have been prepared by ring-opening metathesis polymerization (ROMP) using initiators of the type $Cl_2Ru(PR_3)_2(CHAr')$ (R = phenyl, cyclohexyl, Ar′ = C_6H_5, *p*-F−C_6H_5). Despite the fact that ONDCA is not initiated stoichiometrically by the initiators employed, the block-copolymers are well-defined in the case where the polymerization is started with NBE. The linear polymers and copolymers were coated onto various vinyl-silanized silica materials and subsequently cross-linked employing azobis(isobutyronitrile) (AIBN). The influence of particle size, pore diameter and volume, the specific surface of the inorganic carrier, the influence of the block sizes, and the amounts of coating on the chemical stability of the resulting materials as well as on the separation efficiency and selectivity have been studied. The high hydrophilicity of any ONDCA-containing polymer or copolymer ensures a strong interaction of the mobile phase with the material even in the case of a low organic solvent content (<2%). The high selectivity of the stationary phases is demonstrated by fast baseline separations (6−10 min) of various isomeric anilines and lutidines as well as hydroxyquinolines. The complementary use of apolar, NBE-based coatings and highly polar, pure ONDCA-based coatings allows an in depth discussion of the separation mechanism. Tests designed to detect underivatized, accessible surface silanol groups (Engelhardt test) confirmed the quantitative coating of the surface, which also accounts for the significantly elevated pH stability compared to standard silica materials.

Introduction

Coating procedures, e.g., the dynamic coating of *n*-alkyl-derivatized stationary phases with alkyl sulfonates and alkylammonium salts, respectively, for ion chromatography have been known for a long time.[1] In 1987, Schomburg et al. reported on the preparation of poly(butadiene-*block*-maleic acid)-coated silica columns for ion chromatography.[2] Kurganov et al.[3] demonstrated that, in particular, micro- and mesoporous materials show a significant loss in pore volume and specific surface after coating with a polystyrene−diethoxysilane copolymer which was attributed to pore narrowing owing to the polymer immobilization. Nevertheless, the performance of the silica materials in terms of plate height and plate number was reported constant. Finally, the use of surface immobilized vinyl, acryl, or methacryl groups for cross-linking has been investigated intensively. In combination with hydrosilylation reactions, this approach has also been used successfully for the preparation of ultrathin silicon films.[4] Since then, the concept of polymer-coated inorganic or organic carriers has been further developed and improved. Organic coatings may now be characterized in a very profound way[5] and have gained interest in separation science[6−8] as well as chemical sensing. Optimum deposition conditions[9] have been developed both for the hydrophobic coating of silica,[3,10−14] alumina, titania,[15] or zirconia[16−20]

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10.1021/cm980772i CCC: $18.00

using poly(butadiene) or poly(styrene) and for the hydrophilic coating[21−26] of these materials including ligands for ion exchange and simple chiral separations. Recently, Läubli et al. reported on poly(maleic acid)-based columns with improved durability.[27,28] At the same time, the copolymerization of maleic acid, adsorbed onto alumina, with 1-octadecene and subsequent cross-linking with 1,4-divinylbenzene was described.[29]

So far, there have been no reports on the incorporation of designed ligands or more complex molecules into a polymeric matrix for coating purposes by well-defined polymerization processes. In case of radical polymerization, even simple molecules such as maleic acid lose some of their special properties, e.g., the cis-configuration of the two carboxylic acid groups in the course of the polymerization.[30] This entails consequences in the case where such polymers are used for chromatographic separations. While *cis*-1,2-dicarboxylic acids have chelating properties and are expected to show synergistic effects for the two carboxylates in any separation, poly(maleic acid)-based polymers lose these capabilities, as the two carboxylic acid groups are preferably located in a trans-position along the polymer chain. Additionally, copolymers are difficult to prepare, their block sizes are hard to control, and the capacity of the resulting stationary phase is instead based on empirical knowledge rather than on stoichiometry. In this contribution, we describe the use of a designed functional monomer, 7-oxanorborn-2-ene-5,6-dicarboxylic anhydride, and its controlled, living polymerization as well as copolymerization with norborn-2-ene (NBE). By variation of the block sizes, synergistic effects on the separation of the hydrophilic poly(ONDCA) part and the hydrophobic poly(NBE) part can be studied, and the optimum copolymer compostion for particular HPIC separations may be determined.

Experimental Section

I. Synthetic Part. All experiments were performed in a nitrogen-mediated drybox (BRAUN, Garching, Germany) or by standard Schlenk techniques unless stated otherwise. Reagent grade pentane, diethyl ether, THF (tetrahydrofuran), and toluene were distilled from sodium benzophenone ketyl under argon. Reagent grade dichloromethane was distilled from CaH_2 under argon.

II. Analytical Part. NMR data were obtained in the indicated solvent at 25 °C on a Bruker Spectrospin 300 unless stated otherwise and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in hertz. IR spectra were recorded on a Midac FTIR and a Nicolet 510 FT-IR, respectively. Values for the specific surface were determined by the BET method (multipoint measurement), using a Quantachrome/NOVA 2000. Sample preparation: 2 h at 60 °C; measurement with nitrogen 5.0. Titrations were performed on a Metrohm 686 Titroprocessor. Molecular weights and polydispersities were determined by means of GPC in THF using a 717 Autosampler, a column heater (35 °C), a 510 HPLC pump, a 490E UV-detector, a 410 RI detector, and a Millenium work package (all Waters). GPC columns (Ultrastyragel 10^5, 10^4, and 10^3 Å; all 7.8 × 300 mm; Waters) were calibrated vs polystyrene (PS). Column packing was carried out at $p = 400$ bar using a Knaur high-pressure HPLC packing pump. HPLC experiments were carried out on a Waters LC-1 module (UV detection) and on a Waters 600 S controller system (484 UV-detector), using a Baseline work package (Waters), respectively.

Monomers, Polymers, and Catalysts. Silica materials were all purchased from Merck (Darmstadt, Germany). Micra beads were a generous gift from Bischof, Leonberg, Germany. Trisoperl glass beads were purchased from Schuller, Wertheim, Germany. 7-Oxanorborn-2-ene-5,6-dicarboxylic anhydride[31,32] and the initiators, $Cl_2Ru(PPh_3)_2CHC_6H_5$, $Cl_2Ru(PCy_3)_2CH{-}p{-}F{-}C_6H_4$ and $Cl_2Ru(PCy_3)_2CHC_6H_5$,[33,34] (Ph = phenyl, Cy = cyclohexyl) as well as other educts or reagents were prepared according to literature procedures and checked for purity by means of NMR. Purchased starting materials, HPLC solvents, and azobis(isobutyronitrile) (AIBN) as well as the investigated amines were used without any further purification.

Poly(norborn-2-ene) (Poly(NBE). Norborn-2-ene (5.0 g, 53.2 mmol) was dissolved in methylene chloride (50 mL), and $Cl_2Ru(PPh_3)_2CHC_6H_5$ (70 mg, 89.7 μmol) was added. The solution was stirred at room temperature for 2 h. Methanol (150 mL) was added, and the precipitate of poly(norborn-2-ene) was collected by filtration. Recrystallization from methylene chloride/methanol (containing 1% of thiourea) yielded the polymer as an off-white powder. Yield: 4.9 g (98%). Polymer data: $M_w = 91\,000$; PDI 1.21. IR and NMR data were identical with those reported in the literature.[34]

Poly(7-oxanorborn-2-ene-5,6-dicarboxylic anhydride) (Poly(ONDCA)). 7-Oxanorborn-2-ene-5,6-dicarboxylic anhydride (5.0 g, 29.8 mmol) was dissolved in methylene chloride, and $Cl_2Ru(PCy_3)_2CHC_6H_5$ (60 mg, 73.5 μmol) was added. Within 10 min, the color of the solution changed from red to yellow. The mixture was stirred for 12 h at 50 °C, resulting in a cloudy solution of the polymer. The product was precipitated from solution using a 1:1 mixture of diethyl ether and *n*-pentane. Workup was identical as for poly(NBE). Yield: 4.75 g (95%). Polymer data: $M_w = 129\,500$; PDI = 1.22. IR (KBr): 1871 m, 1782 vs (CO), 1732 vs (CO), 1630 m, sh (C=C), 1223 b,vs (C−O), 1078 m (C−O−C), 1016 m, 970 m, 689 b,w cm^{-1}.

Poly(7-oxanorborn-2-ene-5,6-dicarboxylic anhydride)-*block*-poly(norborn-2-ene) (Poly(NBE-*block*-ONDCA)). The following procedure is typical. 7-Oxanorborn-2-ene-5,6-dicarboxylic anhydride (17.6 g, 104.8 mmol) was dissolved in methylene chloride, and $Cl_2Ru(PCy_3)_2CHC_6H_5$ (436 mg, 0.53 mmol) was added. Within 10 min, the color of the solution changed from red to yellow. The mixture was stirred for 4 h resulting in a cloudy solution of the polymer. Norborn-2-ene (10.0 g, 106.4 mmol) was added, and the mixture was stirred for another 2 h. Workup was identical as for poly(NBE). In all cases, the consumption of norborn-2-ene proved to be quantitative. Yields were in the range of 82−94%, depending on the

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Table 1. Properties of Homo- and Copolymers

	material	M_w	PDI	concn (g/L)[c]
A[a]	NBE_{600}-*block*-$ONDCA_{500}$	140 000	1.13	2.0
B[a]	NBE_{600}-*block*-$ONDCA_{200}$	88 000	1.31	1.4
C[b]	poly$(NBE)_{970}$	91 000	1.21	2.0
D[a]	poly$(ONDCA)_{770}$	129 500	1.22	2.0
E[a]	NBE_{330}-*block*-$ONDCA_{170}$	60 000	1.48	2.0

[a] Catalyst. [b] $Cl_2Ru(PCy_3)_2(CHPh)$. [c] $Cl_2Ru(PPh_3)_2(CHPh)$ in THF.

ONDCA block size. For polymer data, refer to Table 1. IR (KBr): 2960 s, 1700, bvs, 1180 bs, 967m, 733 m cm^{-1}.

Preparation of the Polymer Solutions. Distilled THF was used throughout. After workup, polymers were stirred in THF for 2−3 days in order to be dissolved completely. In case of ONDCA-based polymers, any hydrolysis of the anhydride during workup has to be prevented, as this significantly aggrevates or even impedes their subsequent dissolution in THF.

Vinylation of Silica. The corresponding silica was refluxed for 12 h in toluene using a Dean−Stark apparatus in order to remove all water. Toluene was removed, and silanization (10.0 g silica) was carried out under reflux in methylene chloride (200 mL) using vinyltrimethoxysilane (10 mL, 65.5 mmol). A reaction time of 2 h was found to be suitable. Finally, the solvent and excess silyl reagent were removed by distillation, and the material was subsequently washed with dry toluene and acetone and finally dried in vacuo. An overview on the actual amount of vinyl groups is given in Table 2.

Coating Procedure. Vinylated silica was placed in a round-necked flask and a solution of the corresponding polymer in THF (1−2 g/L) as well as AIBN (25% with respect to polymer) was added. The mixture was stirred vigorously for 1 h and subsequently sonicated for 1 h to remove all air bubbles. Finally the solvent was slowly evaporated (approximately 50 mL/h). Thermal cross-linking was carried out at $T = 90$ °C under vacuum within 12 h. The resulting coated materials were characterized by elemental analysis and BET measurements prior to and after use (see Table 3).

Determination of Actual Amount of Vinyl Groups. Quantitative analyses were carried out according to the literature.[35] Complementarily, the brominated silica supports were analyzed by elemental analysis. The total amounts of vinyl groups calculated from these experiments are summarized in Table 2.

Determination of the Capacity. A 200 mg sample of the corresponding coated material (anhydride form) was stirred in 10 mL of a mixture of 0.05 M NaOH for 6 h. The resin was filtered off and washed with deionized water, and the combined washings were titrated with 0.05 M hydrochloric acid using potentiometric end point indication.

Results and Discussion

Recently, we described the use of ring-opening metathesis polymerization (ROMP) for the preparation of beaded, functionalized polymers[36,37] for applications in SPE of organic compounds[38−40] as well as for the selective extraction of lanthanides[41,42] and transition metals.[43,44] The fact that functional polymers may be prepared which are additionally well-defined in terms of molecular weight, polydispersity, and even backbone structure prompted us to extend our investigations onto the synthesis of soluble functional polymers and block copolymers and the preparation of coated stationary phases therefrom.

Selection and Polymerization of the Monomer. In contrast to standard polymerization techniques, ROMP allows the synthesis of tailor-made polymers and copolymers in terms of structure, molecular weight, and block size by a controlled, stoichiometric polymerization mechanism.[45] For ion chromatography, monomers bearing either sulfonic or carboxylic acid groups are of general interest. In this context, 7-oxanorborn-2-ene-5,6-dicarboxylic acid (ONDCA) represents an interesting molecule for various reasons. In case this monomer is polymerized by ROMP techniques, the resulting polymer backbones consist of a vinylene-spaced poly(tetrahydrofuran) (poly(THF)) with each unit bearing two *vic,cis*-configured carboxylic acids (Figure 1). These vinylene groups in the linear polymer may further be used for subsequent cross-linking reactions. The oxygen in the resulting five-membered ring significantly elevates the hydrophilicity of this ligand compared to the parent poly(norborn-2-ene-5,6-dicarboxylic acid). Furthermore, the *cis*-configuration of the carboxylic acid leads us to expect some synergistic effects. In contrast to norbornene derivatives, which are preferably polymerized with molybdenum-based initiators,[46] ONDCA is best polymerized with either $Cl_2Ru(PCy_3)_2CHC_6H_5$ or $Cl_2Ru(PCy_3)_2CH-p\text{-}F-C_6H_4$47. Despite the fact that the initiation is not stoichiometrically with both initiators, a living polymerization within the limits of the classical definitions (no chain termination, no chain transfer)[48,49] may be performed. In case polymerizations are started with NBE, well-defined block copolymers with regard to block size and molecular weight, one block consisting of poly(ONDCA) and another of poly(NBE), may be prepared. Table 1 gives an overview over the polymers prepared.

Coating Procedure. The coating of soluble prepolymers onto various surfaces represents a well-established procedure,[50] and some materials prepared from soluble silicon precursors may even be characterized by means of solid-state NMR as well as electron microscopy.[51,52]

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Table 2. Carbon Contents of Vinylated Silica Supports

material	% C	% H	% vinyl[a]	vinyl/g (μmol)[a]	vinyl/g (μmol)[b]	vinyl/m^2 (μmol)[b]
Micra	0.56	0.86	2.4	230	20	0.7
LiChrosorb 60-7	3.74	0.83	16.1	1580	280	0.4
Polygosil 300-7	0.56	0.14	2.4	230	100	0.8
Polygosil 100-7	2.23	0.62	9.6	940	230	1.0
Nucleosil 50-7	2.52	0.78	10.8	1060	270	0.9
Kieselgel 60 (silica 60)	5.16	1.06	22.2	2180	200	0.6
Trisoperl (glass beads)	1.36	0.39	5.8	540	180	0.6

[a] Calculated from elemental analysis on the basis of $CH_2{=}CHSi(O-)_3$. [b] Determined by titration[35] and confirmed by elemental (bromine) analysis.

Table 3. Coated Materials: NBE = Poly(norborn-2-ene) and ONDCA = Poly(7-oxanorborn-2-ene-5,6-dicarboxylic anhydride)

polymer	material[b]	particles (μm)	pore volume (mL/g)	pore size (Å)	σ_1[c] (m^2/g)	σ_2[c] (m^2/g)	coating (mg/g)	coating (μg/m^2)	d[g] (nm)	mequiv H$^+$ theor/found
I[c] A	Polygosil 60-10	10	0.75	60	450	180	118	260	0.23	0.77/0.21
II[c] A	LiChrosorb Si 60-7	7	0.75	60	500	250	118	240	0.21	0.77/0.25
III[c] A	LiChrosorb Si 60-7	7	0.75	60	500	270	24	50	0.03	0.16/0.13
IV[c] A	LiChrosorb Si 60-7	7	0.75	60	500	287	88	180	0.12	0.6/0.49
V[c] B	LiChrosorb Si 60-7	7	0.75	60	500	244	117	230	0.13	0.42/0.39
VI[c] C	LiChrosorb Si 60-7	7	0.75	60	500	160	121	240	0.23	0.00/−
VII[c] A	Polygosil 100-7	7	1.0	100	300	233	113	380	0.27	0.74/0.38
VIII[c] A	Polygosil 300-7	7	0.8	300	100	79	117	1170	0.75	0.76/0.09
IX[c] A	Nucleosil 50-7	7	0.8	50	450	274	106	240	0.21	0.69/0.56
X[d] A	Micra	1.5	nonporous		4	1.5	10	2500	249	0.07/−
XI[c] D	Nucleosil 50-7	7	0.8	50	450	232	100	220	0.17	1.3/0.93
XII[e] E	silica 60 (Merck)	40−63	0.71−0.78	60	490	288	58	120	0.15	0.3/0.3

[a] Catalyst: $RuCl_2(PCy_3)_2(CHPh)$ in CH_2Cl_2. [b] Silanized with vinyltrimethoxysilane. [c] Specific surface prior to (σ_1) and after (σ_2) coating. [d] Column dimensions: 150 × 4 mm. [e] Column dimensions: 60 × 4 mm. [f] Column dimensions: 230 × 26 mm. [g] d = thickness of polymer layer, calculated from $S = (R/T) \times 1000/(1 - (R/T)\sigma_1\rho)$.[25] R = % C of coated material, T = carbon content of polymers A−E, and ρ = polymer density (≡1 g/mL for simplicity).

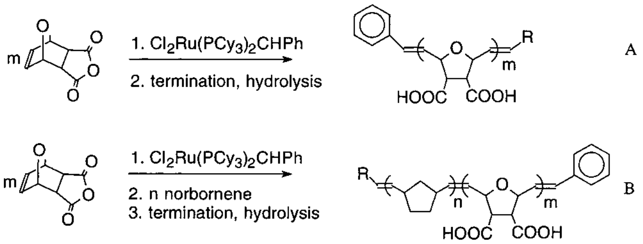

Figure 1. Preparation and polymer structure of poly(7-oxanorborn-2-ene-5,6-dicarboxylic acid) (A) and poly(7-oxanorborn-2-ene-5,6-dicarboxylic acid)-*block*-poly(norborn-2-ene) (B).

In general, the nature of the polymer is not considered critical,[10] as it is placed onto the surface by evaporation. Standard modification procedures are performed either by polymerizing and depositing monomer from solution or from the gas phase (restricted to volatile monomers) without any additional cross-linking or, in a few cases, by attaching silicon-based polymers onto the surface.[2,10,25,53]

The coating procedure presented in this contribution leads, in combination with the use of well-defined polymers and copolymers, to more reproducible materials, as the amount of polymer and consequently the capacity (expressed in mmol/g) of the material is simply determined by weight. Nevertheless, coating conditions definitely strongly depend on the nature of the prepolymer used, and special care must be taken in the case of polymers bearing functional groups in order to prevent them from degrading or having any kind of change. In general, optimum coatings are achieved in the case of coating or cross-linking temperatures which lie above the glass-transition temperature of the prepolymer. This ensures a perfect coverage of the surface and reduces the clogging of smaller pores. Unfortunately, polymers with protic functionalities (e.g., COOH, NH_2), in particular, very often do not show any glass transitions due to strong hydrogen bondings and/or high crystallinity. Consequently, we were not able to determine any glass transitions for the ONDCA-based homo- and copolymers. Therefore, to contribute to a maximum cross-linking temperature ($T_{1/2}$ of AIBN at T = 70 °C is 6 h) and to avoid any polymer degradation (decarboxylation), the final cross-linking was carried out at T = 90 °C.

In a first step, silica was dried[11] and reacted with vinyltrimethoxysilane in order to obtain polymerizable groups at the surface and to convert as many surface silanol groups as possible to silyl ethers. Table 2 shows the actual carbon loadings of the different silica supports. The carbon content determined by elemental analysis was found to be in the expected range for porous and nonporous silica. Nevertheless, some general problems encountered with the chemistry of surface silanizations have to be addressed. Generally, surface silanizations have been shown to be strongly dependent on reaction time, solvent, and silane reagent as well as on the type and surface area of silica.[54] Additional effects are encountered with the water content of the silica surface. Evidence for the formation of differently bound silanes and the additional formation of alkoxy groups directly bound to the silica surface was obtained by ^{29}Si CP−MAS experiments.[54,55] While an exact identification of the actual species bound to the surface

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may be achieved by solid-state NMR, the exact amount of vinyl groups may easily be determined by titration methods. Volumetric microanalyses based on the addition of mercury(II) acetate,[56,57] iodine,[58] and bromine[35] have been reported. Nevertheless, due to the inactive character of the vinylsilane group, only the addition of bromine under catalytic conditions[35] leads to reproducible results. A comparison of the data for the total amounts of vinyl groups based on the assumption that $H_2C{=}CHSiO_3$ is the predominant group with those obtained by titration clearly underlines the importance of such investigations (Table 2). In this context it is also worth noting that Micra materials with a specific surface area of 4 m^2/g may still be silanized effectively, still giving raise to vinyl loadings of 20 μmol of vinyl/m^2 (Table 2). These comparably high loadings may partially be attributed to the formation of oligosiloxanes at the surface. Furthermore, Dubois et al.[59] described the reaction of methyltrimethoxysilane with highly dehydroxylated silica surfaces and postulated a reaction with surface-located, highly strained disiloxane rings. This reaction entails the formation of surface methylsiloxanes and may be another reason for the high carbon loadings in the case of the Micra materials, whose preparation involves a final high-temperature calcination step.

Different amounts of prepolymer were deposited at the surface and finally cross-linked using thermal initiation. Parts a and b of Figure 2 show ELMI pictures of coated Silica 60 and Nucleosil 50−7 materials, respectively. Table 3 gives an overview over the materials investigated. The general quality of the coating method was checked using a standard Engelhardt test,[60−62] which is based on the retention characteristics of a certain mixture of compounds in order to detect unwanted silanol-analyte interactions. For that purpose, a simple poly(NBE)-coated material was prepared (column VI) and checked for its retention behavior for various basic and polar analytes. Using this test, we were not able to detect any polar interactions of the analytes with the stationary phase, indicating that no more free silanol groups were present. Figure 3 shows the proposed surface structures of the coated silicas.

Influence of Coating on Stability, Specific Surface Area, and Accessibilty of Functional Groups. Especially in the case of silica-based materials, certain stability criteria have to be addressed and fulfillled. On one hand, any coating must be thick enough to prevent chemical degradation of the carrier. On the other hand, the coating may not be too thick, as this significantly further reduces the chromatographic surface and consequently leads to significantly diminuished separation efficiencies. To obtain stable and efficient materials, different amounts of polymer (10−120 mg/g) were deposited onto the surface of various silica materials, resulting in 0.03−250 nm polymer layers. Due to the high average molecular weights of the polymers, a loss of pore volume and specific surface area was expected to occur in the case of microporous materials. In fact, the observed loss in specific surface area was higher in the case of materials with smaller pores compared to those with larger pore diameters. While the specific surface of silica (σ) with a 60 Å pore diameter was reduced by a factor of 2, 100 or 300 Å materials showed only a loss in σ of approximately 20%. This clogging of the pores also results in a diminuished accessibility of carboxylic acid groups (vide infra). Nevertheless, separation materials based on silica with 60 Å pores were still found to be highly selective separation media. In this context, the influence of the coating thickness on any separation is best illustrated by comparing the results for columns I−III. While a thickness of 240−260 μg/m^2 allows a baseline separation of the analytes of both test mixtures (Figures4 and 5), a thickness of 50 μg/m^2 results in a material with insufficient separation efficiencies (Table 4), which give rise to a number of unresolved peaks in the chromatogram.

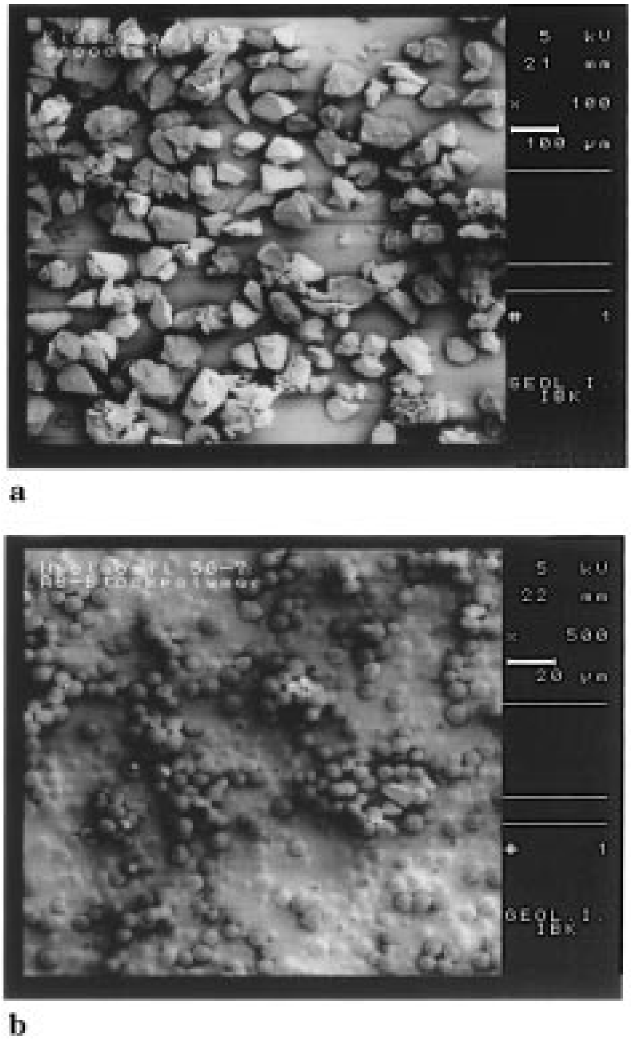

Figure 2. ELMI pictures of coated silica 60 (a) and Nucleosil 50-7 (b).

Another major point of interest was the determination of the optimum coating thickness with regard to the accessibilty of the carboxylic acid groups. For this purpose, different materials were prepared and sub-

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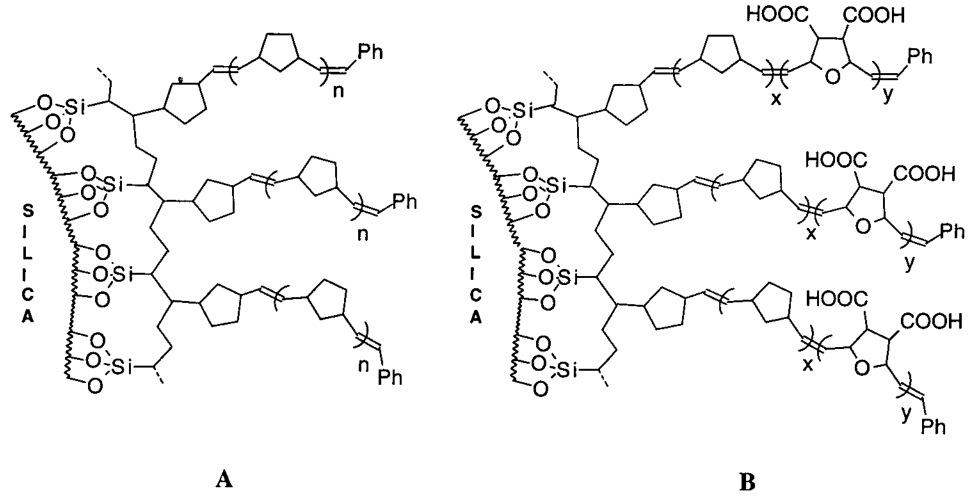

Figure 3. Proposed structures of coatings: (A) poly(norborn-2-ene) coating; (B) poly(7-oxanorborn-2-ene-5,6-dicarboxylic acid)-*block*-poly(norborn-2-ene) coating.

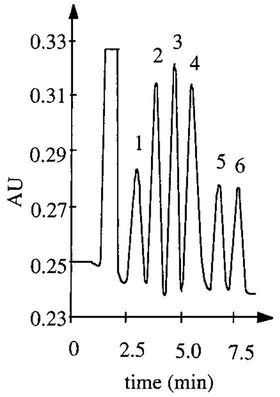

Figure 4. Separation of compounds **1**−**6** on column I. Conditions: Polygosil 60/10, mobile phase water−acetonitrile 98:2, 10 mM acetic acid, 7 mM triethylamine, flow 1.0 mL, and injection volume 5 μL (20 ppm each). UV (254 nm).

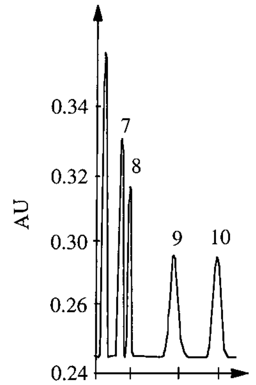

Figure 5. Separation of compounds **7**−**10** on column II. Conditions: Lichrosorb 60/7, mobile phase water−acetonitrile (95:5), and 2 mM tartaric acid. Flow: 1.8 mL. Injection volume: 5 μL. UV (254 nm).

jected to titration experiments. The amount of coating, expressed in μg of polymer/m^2 was found to be a suitable measure. Thus, polymer coatings in the range of 50−120 μg/m^2 were found to be thin enough to allow an almost quantitative interaction (80−100%) of the carboxylic acid groups with the mobile phase without diminishing the chemical stability of the support.

Homo- versus Copolymer. From an economical point of view, one might expect that a suitable amount of poly(ONDCA) might present the optimum coating for any silica. Consequently, the use of ONDCA-based homopolymers and the chemical stability as well as chromatographical performance of the resulting stationary phases were investigated. Surprisingly, we found that homopolymers based on poly(ONDCA) did not show the desired pH stability, despite the fact that the polymer layer was subsequently cross-linked with the surface vinyl groups. This might be explained by the highly hydrophilic character of poly(ONDCA) polymers, where both H$^+$ and OH$^-$ groups are believed to reach the silica surface due to diffusion. This results in a permanent and time-delayed cleavage of the Si−O−Si groups. This finally leads to a slow, yet significant loss of polymer coating, especially under basic conditions. To circumvent this problem, we used copolymers of NBE and ONDCA with different total molecular weights and block sizes (Table 1). Besides being of a higher solubility, these copolymers have general advantage of entirely different chemical properties of the two polymer blocks. While the poly(NBE) block is highly hydrophobic, the poly(ONDCA) block is highly hydrophilic. In course of the coating, where the polymer starts to precipitate onto the surface, a self-assembly of the block copolymer is believed to occur, where major amounts of the apolar NBE part are deposited onto the apolar surface vinylsilyl groups and major amounts of the polar, THF-solubilized poly(ONDCA) part form the new support surface. This assumption may also explain the rather high accessibilty of carboxylic acid groups up to a film thickness of roughly 200 pm. Subsequent radical cross-linking involves the silica surface vinyl as well as the NBE block double bonds, leaving the poly(ONDCA) block rather unaffected. Consequently, the resultling material is believed to consist of a tentacle-type modified silica with an imperveous, apolar surface layer of cross-linked poly(NBE). These polymer layers were found to be extremely intert to acids and bases. Under acidic conditions, they may be treated repeatedly with even 15% nitric without any loss of polymer coating. In basic media (aqueous sodium hydroxide), we operated the stationary phases up to a pH of 12 for several days

Table 4. Number of Theoretical Plates (*N*/*m*) and Reduced Plate Heights (h_{red}) for Compounds 1–10 on Columns I–III, IX, and XI[a]

			II[b]		IX[c]		XI[d]		I[e]		III[f]	
		compound	*N*/*m*	h_{red}	*N*/*m*	h_{red}	*N*/*m*	h_{red}	*N*/*m*	h_{red}	*N*/*m*	h_{red}
1		2,6-dimethylaniline	6400	60	6900	75	3660	184	3800	183	4900	1200
2		*N*-methylaniline	10000	17	11500	35	5860	55	6000	55	6600	242
3	**mix-1**	pyridine	7600	19	7200	44	9400	28	6200	41	9000	64
4		*N*,*N*-dimethylaniline	14900	9	13600	20	9800	24	6000	35	*g*	*g*
5		2,6-lutidine	19200	6	15600	16	11800	17	8500	21	*g*	*g*
6		3,4-lutidine	16400	7	15500	14	15600	12	7600	22	*g*	*g*
7		2-hydroxyquinoline	5800	134	10600	81	9800	57	3400	433	*g*	*g*
8	**mix-2**	4-hydroxyquinoline	7300	62	14500	37	13000	25	4100	169	*g*	*g*
9		6-hydroxyquinoline	10000	19	15400	23	13900	18	5000	40	3600	130
10		8-hydroxyquinoline	12200	13	16100	19	10700	22	6000	28	5200	50

[a] Key: $N = 5.54(R_t/w_{1/2})^2$; $N_{eff} = 5.54(R_t - R_o/w_{1/2})^2$, H_{eff} (μm) $= L/N_{eff}$, $h_{red} = H_{eff}/d$, L = column length, $w_{1/2}$ = half-width of peak, R_0 = dead volume, R_t = retention time of analyte; d = particle diameter (μm). For all columns in this table, conditions are as follows: Flow = 1 mL, compounds **1**–**6**: 20 ppm. Compounds **7**–**8**: 5 ppm. Compounds **9**–**10**: 2 ppm. Injection volume: 5 μL λ (UV) = 254 nm. [b] **1**–**6**: H_2O:AcCN = 98:2, 2 mmol HOAc, 1.4 mmol NEt_3. **7**–**10**: H_2O:AcCN = 95:5, 2 mmol tartaric acid. [c] **1**–**6**: H_2O:AcCN = 92:8, 20 mmol HOAc, 14 mmol NEt_3. **7**–**10**: H_2O:AcCN = 85:15, 10 mmol tartaric acid. [d] **1**–**6**: H_2O:AcCN = 85:15, 40 mmol HOAc, 28 mmol NEt_3. **7**–**10**: H_2O:AcCN = 85:15, 20 mmol tartaric acid. [e] **1**–**6**: H_2O:AcCN = 98:2, 10 mmol HOAc, 7 mmol NEt_3, **7**–**10**. H_2O:AcCN = 95:5, 1 mmol tartaric acid. [f] **1**–**6**: H_2O:AcCN = 90:10, 2 mmol HOAc, 1.4 mmol NEt_3, **7**–**10**. H_2O:AcCN = 99:1, 0.5 mmol tartaric acid. [g] No baseline separation.

without any change in elution time, order or even peak shape and half-widths.

Copolymer Block Sizes and Molecular Weights. The synthesis of various copolymers and the subsequent preparation of coated silicas therefrom revealed no significant dependence of selectivity on molecular weight. Roughly a 1:1 ratio of NBE and ONDCA was found to be suitable. For practical purposes, block sizes larger than 500 for ONDCA shall be avoided, as the resulting polymers are not soluble enough. Nevertheless, the total amount of carboxylic acid groups accessible in course of the separation has a significant impact on the final separation. The high accessible carboxylic acid content of columns IX and XI (0.6 and 0.9 mmol of H^+/g, respectively) generates the need for a higher acetonitrile content in the mobile phase. In contrast, lower values for H^+ as in column I, allow fast baseline separations with an organic fraction of less than 2%. Depending on the application, one may take advantage of both materials. Coatings used in columns IX and XI offer a larger variety in mobile phase, whereas those used for column I allow fast and low-cost separations.

Comparison of Materials, Separation Mechanism, and Examples of Application. As predicted by theory, separation efficiencies encrease with decreasing particle diameter of the material. Thus, polymer-coated 10 μm particles (column I) show significantly elevated numbers for the reduced plate heights (h_{eff}) than polymer-coated 7 μm particles (columns II, IX, XI; Table 4). In general, the use of microporous materials seems favorable, despite the fact that a significant percentage of the pore volume is lost in the course of the coating procedure.

Stationary phases derived from the copolymers allow the separation of isomeric anilines and lutidines. High selectivities may be achieved, as demonstrated by the fast (<8 min) baseline separation of six isomeric anilines und lutidines, which are similar with regard to pK_a values, size and chemical properties. Thus, an optimized separation of analytes **1**–**6** on column I was complete in less than 8 min (Figure 4). Separation efficiency is positively influenced by the presence of some apolar sites from the poly(NBE) block. The importance of such apolar sites suggests some additional reversed-phase interaction of the analytes with the material. Consequently, separations of these analytes on a poly(ONDCA) homopolymer-based column are poor.

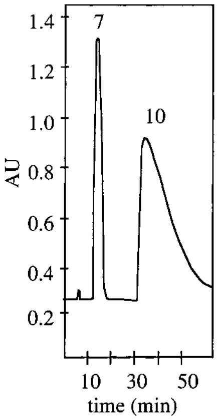

Figure 6. Preparative scale separation of compounds **7** and **10** on column XII. Conditions: silica 60, mobile phase water–acetonitrile (97:3), 0.5 mM tartaric acid, flow 30 mL/min, and injection volume 1 mL (0.25% each). UV (254 nm).

Materials based on NBE–ONDCA copolymers were also found to be suitable for the separation of isomeric hydroxyquinolines. Thus, compounds **7**–**10** may be baseline separated on column II within 6 min. It is yet worth mentioning that stationary phases based on ONDCA homopolymers (column XI) possess favorable properties for the separation of highly polar analytes such as these isomeric hydroxyquinolines, despite their reduced stability under strongly basic conditions. This may be explained by the chemical nature of these compounds. All four isomeric hydroxyquinolines exhibit a zwitterionic character at roughly neutral pH, while the conditions chosen for their separation (1–20 mM tartaric acid) generate a cationic species, leaving the phenolic functionality undissociated. For that reason, their separation under these conditions must be considered as almost exclusively based on ion exchange. Nevertheless, some additional hydrogen bonding between the phenolic and the carboxylic acid groups, which accounts for the rather strong retention compared to compounds **1**–**7**, are definitely present. Consequently, the use of columns with comparably high carboxylic acid contents (column XI) results in impressive values for the reduced plate height (N_{eff}) in ion chromatography between roughly 20 and 50 for these compopunds. The general applicability and straightforwardness of the preparation of these stationary phases are demonstrated by the manufacture of a coated material (column XII) suitable for the preparative scale separation of these isomeric hydroxyquinolines (Figure 6). Preparative scale liquid chromatography columns with dimensions of 230 × 26 mm were filled with large diameter coated silica (column XII, Table 3). As can be seen, milligramm quantities of 2-hydroxyquinoline and 8-hydroxyquinoline are easily separated in less than 1 h using a volume fraction of expensive and toxic acetonitrile of only 3%.

Conclusions

The broad applicability of ROMP-based homo and block copolymers in the preparation of chromatography supports has been demonstrated. Block copolymers with different block sizes and average molecular weights are easily prepared and have been used for the coating of silica supports. The optimum amount of coating is believed to be in the range of 200−400 μg/m^2. The new materials show high selectivities in ion chromatography as well as an extraordinary pH stability compared to standard silica materials. The optimum carrier material for analytical scale separations was found to consist of spherical 7 μm particles with 50−60 Å pore diameters, whereas preparative scale separations may conveniently be carried out using standard 40−60 μm silica supports with surface areas of approximately 500 m^2/g. Current investigations focus on their use as sorbents for transition metal ions. These results will be reported in due course.

Acknowledgment. The authors thank Dr. Richard Tessadri for carrying out the BET-measurements as well as Dr. I. Stingl (both Institute for Mineralogy and Petrography, University of Innsbruck) for the recording of the electron-microscope pictures. Financial support was provided by the Austrian National Science Foundation (FWF, Vienna, Austria; Project Numbers P-11740-GEN and P-12963-GEN) and the European Commission (Project Number F14 W-CT96-0019)).

CM980772I