Ring-Opening-Metathesis Polymerization for the Preparation of Carboxylic-Acid-Functionalized, High-Capacity Polymers for Use in Separation Techniques

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Abstract: Ring-opening-metathesis polymerization (ROMP) was used for the modular, molecular design of stationary phases. New materials for solid-phase extraction (SPE) as well as for air and water clean-up have been prepared by ring-opening-metathesis suspension polymerization of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo,endo*-dimethanonaphthalene (**I**) and its copolymerization with the functional monomer *endo,endo*[2.2.1]bicyclohept-2-ene-5,6-dicarboxylic anhydride (**II**), using the well-defined Schrock catalyst Mo(*N*-2,6-*i*-Pr_2-C_6H_3)$CHCMe_2Ph(OCMe(CF_3)_2)_2$ (**III**). The resulting cross-linked polymers have been investigated in terms of influence of the polymerization sequence as well as of the stoichiometries **I/II** and **II/III** on swelling behavior, surface area, capacity, accessability of the functional groups, and their possible use in SPE, respectively. In order to obtain further information about the new resins, the microstructure of poly(**II**) was determined by NMR techniques. Investigations revealed that it represents an all cis, atactic polymer. Due to the polymerization technique employed, capacities of the different weak cation exchangers are entirely predeterminable and may be varied over many orders of magnitudes (up to 10 mequiv/g). The materials have been used successfully for solid-phase extraction of 15 different substituted anilines and lutidines from water as well as for the sampling of volatile, airborne aliphatic amines. The unambigous advances of the new SPE materials are discussed in detail.

Introduction

Modern separation techniques require designed, high-performance materials with regard to functionalities, capacity, particle size, and porosity, respectively. Among these techniques, solid-phase extraction (SPE) has become an important tool for sample clean-up and analyte preconcentration in analytical chemistry. As a consequence, a large variety of different SPE materials is available and has been applied successfully to different problems.[1−4] Except for a few sulfonated resins, most of the materials carrying functional groups are based on silica because of their low price and the simplicity and straightforwardness of the synthetic route, after which various functionalities may be introduced. Nevertheless, these materials are very often subject to hydrolysis under acidic or basic pH conditions, limiting significantly their applications. In addition, due to the surface-modified character of the material, capacities are quite low. Organic polymers, which are usually based on styrene, may overcome the problem of pH stability, yet they do not meet the requirement of functional variety and high capacity. Furthermore, in most cases a tedious and poorly controllable derivatization of preformed polymer supports is necessary. In the course of our search for new polymers and applicable polymerization techniques, we developed a completely new approach toward SPE materials, applying the technique of ring-opening-metathesis polymerization (ROMP). The new concept entails the polymerization of well-defined, prefunctionalized monomers by a rigid and selective mechanism, leading to stationary phases of entirely predeterminable, predictable, and reproducible properties with regard to particle size, porosity, functionality, and capacity. Finally, due to the organic backbone, the materials are stable over the entire pH range.

Mainly on the basis of the work of Schrock et al.[5−8] and Grubbs et al.,[9−12] ROMP represents now a well-understood polymerization technique. Well-defined transition metal alkylidene complexes are used for the polymerization of strained olefines. While the molybdenum- or tungsten-based systems represent highly active initiators in combination with electronegatively substituted alkoxides, they are generally not capable of polymerizing monomers containing protic hydrogens such as alcohols, carboxylic acids, and thiols. However, a broad range of functional monomers based on substituted norborn-2-enes and norbornadienes bearing anhydrides, esters, or amides may be polymerized.[13−15] The ruthenium-based systems developed by Grubbs et al.[16,17] exhibit a higher stability toward

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protic functionalities compared to the molybdenum and tungsten analogues. This permits the polymerization of functionalized norborn-2-enes and 7-oxanorborn-2-enes even in aqueous media.[18−21] Unfortunately, they quite often do not exhibit the same high activity toward substituted norborn-2-enes as the Schrock systems. Additionally, strong donor ligands such as nitriles or pyridines basically inhibit any polymerization by the Grubbs system.[22] It is yet worth mentioning that the stability of both systems versus functionalities still exceeds by far any other polymerization technique. Except for their tuneable activity, additional advantages can be stated for both systems. As a consequence of their rigid polymerization mechanism, they often permit living polymerizations. "Living" in this context means that a controlled and stoichiometric initiation takes place. Furthermore, chain-transfer as well as chain-terminating reactions are absent during propagation. Finally, the active end of the polymer remains unaffected until a controlled termination is performed. This does not only result in polymers with a low polydispersity (PDI) but also allows their stoichiometric design, such as controlled chain length and the buildup of block-copolymers. Finally, the formation of a certain backbone structure (the relative orientation of one monomer unit to another) may be predetermined by the choice of a certain initiator. In order to rely on these potential advantages, a careful investigation of the polymerization system is necessary. After a suitable monomer−initiator system has been found which fulfills all requirements of a living polymerization,[23−25] it may be used in suspension poymerization, allowing the preparation of beaded particles. Consequently, the influence of different solvents on the macroscopic properties of the resulting particles with regard to porosity and specific surface area have to be studied carefully.

Results and Discussion

Choice of the Initiator. It is well-known that molybdenum-based initiators are capable of the polymerization of **I**.[26,27] According to available literature, only one brief attempt[28] to polymerize **II** has been performed. This procedure was not pursued consequently due to the significant insolubility of the resulting oligomers. A more intense investigation of the present polymerization system suggests that the polymerization of **II** using Mo(*N*-2,6-*i*-Pr_2-C_6H_3)$CHCMe_2Ph(OCMe(CF_3)_2)_2$ **III** proceeds in a living way at least for shorter, still-soluble polymer chains with less than 15 monomer units. This assumption is underlined by several facts. First of all, these oligomers exhibit a fairly low polydispersity (1.73 for a 10-mer) and theoretical (1862 g mol^{-1}) and experimental (2163 g mol^{-1}) values for M_n (all for the 10-mer) are in good accordance. Secondly, ^{1}H NMR investigations reveal a highly ordered polymer backbone structure, indicating a rigid polymerization mechanism. Finally, polymer yields for poly(**II**) are always quantitative. The conclusions that can be drawn from these findings are the following: (i) the initiation proceeds stoichiometrically and (ii) no chain termination reactions occur. Due to the lack of analytical data for higher molecular weight polymers, a living character for the polymerization system is still not unambiguously proven yet is strongly suggested. Other molybdenum- and ruthenium-based initiators were found to be unsuitable. Compound **II** is not initiated stoichiometrically by Mo(*N*-2,6-Me_2-C_6H_3)$(CHCMe_2Ph)(OCMe(CF_3)_2)_2$, a finding which is surprising, since the reactivity of a molybdenum-based initiator is usually controlled by the electronic and steric nature of the alkoxide. Less-active initiators such as Mo(*N*-2,6-*i*-Pr_2-C_6H_3)$(CHCMe_2Ph)(OCMe_3)_2$ as well as ruthenium-based systems ($Ru(PCy_3)_2Cl_2CH$-*p*-F-C_6H_4; Cy = cyclohexyl) do not polymerize **II** in a satisfactory way.

Stationary Phases. Depending on the desired application, the basic requirements for stationary phases used for chromatography are a suitable particle size distribution, an acceptable swelling behavior, and a certain, easily accessible amount of functional groups, usually expressed as capacity (mequiv/g).[29] For solid-phase extraction (SPE), a maximum of capacity and a minimum of swelling are desired. Despite the fact that particle size and particle size distribution are less important for this method,[3,30−35] a minimum particle diameter must be achieved in order to facilitate column loading and to minimize back-pressure. In principle, the synthesis of functionalized polymer particles with narrow particle size distribution may be performed by many routes, although only one leading to high-performance materials was found to be applicable to the present polymerization system so far.

Underivatized Polymers. Suspension polymerization of the pure cross-linker **I**, which has been used by Schrock et al. for the preparation of star-block-copolymers,[26,27] was chosen for various reasons. First of all, it represents the simpliest system for the optimization of polymerization parameters such as monomer−initiator−solvent ratio, reaction time, and stirring velocity. Furthermore, the influence of different solvents on porosity as well as on the specific surface area may be investigated. Finally, the resulting materials represent ideal complementary stationary phases to any functionalized materials, as the interaction of the analyte with the bare backbone in absence of any functional group may be documented.

Species **I** was polymerized using **III** as an initiator in two different noncoordinating solvents (Scheme 1). Figure 1a shows a REM (reflection electron microscopy) picture of poly(**I**) prepared in methylene chloride. The material consists of irregularly shaped particles with a mean diameter of 50 ± 10 μm after removal of the solvent. The specific surface area was found to be in the range of 25−30 m^2/g, indicating a microporous structure. The REM picture of this material (Figure 1a) confirms this proposed microporosity, yet shows some few

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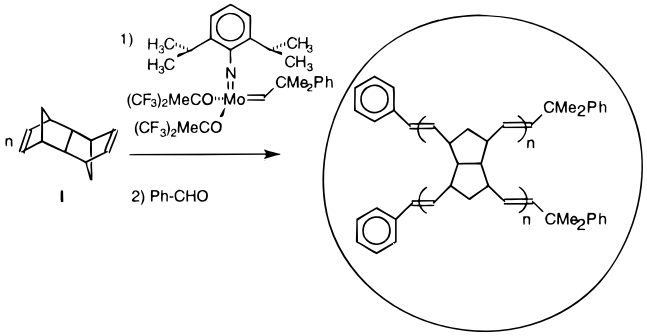
Scheme 1. Preparation of Underivatized Polymer (poly(**I**))



additional macrochannels. As a consequence of the rather large particle diameter, the resulting back-pressure of columns filled with this material is quite low, making this type of resin suitable for SPE. On the contrary, poly(**I**) prepared in toluene is obtained as a solvent swollen gel without any distinctive particles. It needs to be ground up after drying, exhibits a significantly increased specific surface area (150 m^2/g), generates a considerable back-pressure due to its poorly defined particle diameter, and is therefore not a suitable material for SPE. Figure 1b shows the ground material, where the smaller particles which are formed during the process of grinding can be clearly seen. These small particles (<0.5 μm) are responsible for the clogging of the frits and, as a consequence, for the resulting high column back-pressure. Due to the fact that poly(**I**) prepared in methylene chloride is suitable for SPE, no further experiments using toluene as a solvent were performed. SPE experiments carried out with poly(**I**) prepared in methylene chloride are discussed in detail below.

Carboxylic-Acid-Derivatized Polymers. Suspension polymerization of **II** in dichloromethane using **III** as an initiator yields linear polymer chains of poly(**II**), still bearing the active initiator on its end. The solubility of poly(**II**) strongly depends on the chain length. Oligomers containing up to approximately 10−15 monomer units are soluble; longer chains are entirely insoluble. Addition of **I** to the living polymers covalently binds them during course of the copolymerization into the consecutively formed, highly cross-linked matrix. The same resulting polymer may be expected if the polymerization sequence is started with **I**, followed by the copolymerization of **II**. A random copolymerization by adding **I** and **II** to the initiator at the same time was found to result in the same polymer as formed when **I** and **II** were added consecutively to **III**, indicating that the overall rate constant (initiation and propagation) of the polymerization of **I** using **III** is significantly higher than the overall rate constant of **II** with the same initiator.

Despite the high reactivity of **I** and **II** toward **III**, a reaction time of 6 h for the preparation of poly(**II**) and a further 6 h for subsequent cross-linking is necessary. This is due to the formation of insoluble products which are formed at the very beginning of the reaction. In order to meet the requirements of the concept for a stoichiometrical buildup of the materials, a quantitative consumption of the functional monomer and of the cross-linker was strongly desired. The living polymer end is believed to be sufficiently solubilized during polymerization at its active site. For shorter reaction times, unreacted functional monomer **II** was recovered from the combined methylene chloride washings. In no case was unreacted cross-linker **I** observed.

The macroscopic behavior and the physical constants of the resulting cross-linked resins strongly depend on the polymerization sequence, as well as on the ratio **I**/**II** and **II**/**III**. When these parameters are varied, different resins are prepared. An overview over these polymers and of some of their physical properties is given in Table 1.

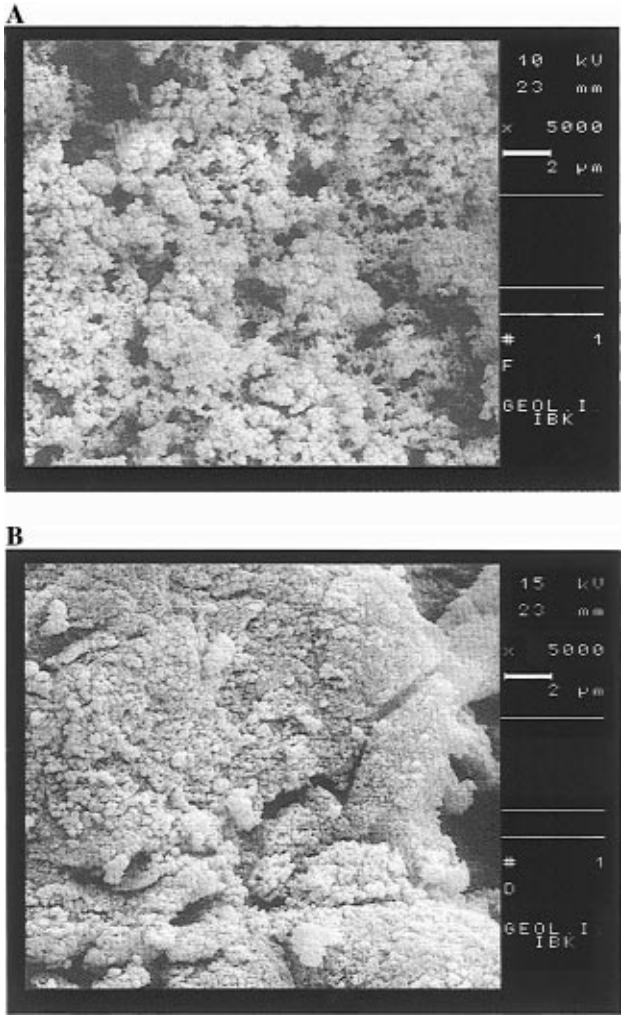


Figure 1. (a) REM picture of poly(**I**) prepared in methylene chloride. Particle size: 50 ± 10 μm. Specific surface area: 30 m^2/g. The scale bar represents 2 μm. (b) REM picture of poly(**I**) prepared in toluene. Specific surface area: 150 m^2/g. The scale bar represents 2 μm.

Polymerization Sequence. Resins (resin type 1) prepared by the reaction of **II** with **III** followed by cross-linking using **I** were formed in quantitative yield (Scheme 2). All polymerizations were end-capped using benzaldehyde in order to ensure a clean removal of the molybdenum core from the polymer. Prior to use, all resins were transformed into the corresponding dicarboxylic acid by treatment with aqueous sodium hydroxide, followed by addition of an excess of aqueous hydrochloric acid. As expected, the conversion of the polyanhydride into the corresponding polydicarboxylic acid was found to be fast. When the stirred suspension was treated with a mixture of 2 N NaOH in methanol:water (1:4), the resin reacted exothermally. No significant change in capacity was observed by varying the reaction time between 2 and 6 h for the conversion from the anhydride to the dicarboxylic acid. In order to ensure a complete removal of the molybdenum, the resin was stirred with NaOH for 6 h. Determination of the actual molybdenum content of the resin by means of ICP-AES (inductively coupled plasma-atomic emission spectroscopy) confirmed the almost complete extraction of the metal. The actual molybdenum content of the resin was found to be less than 40 ppm for all resins. This corresponds to a removal of more than 99.6%.

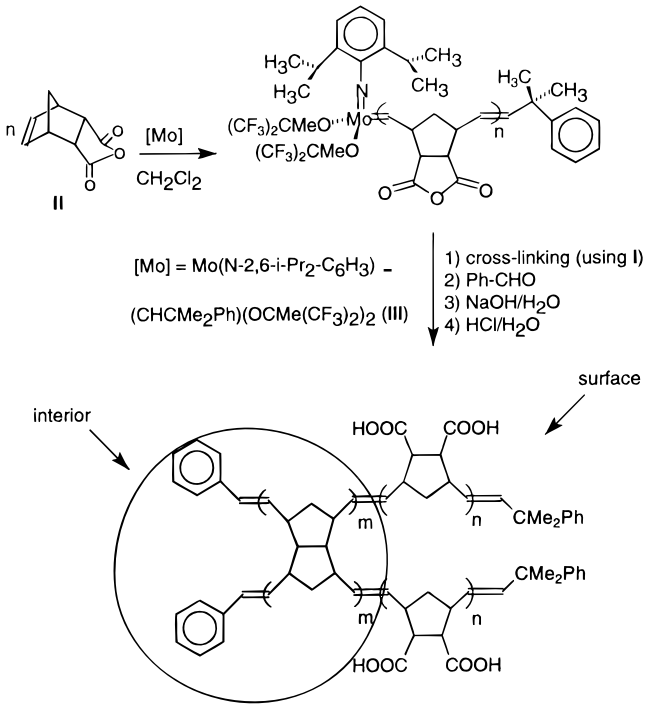
Typical polymer beads are shown in Figure 2. They consist of spherical particles with a diameter of approximately 2 μm

Table 1. Carboxylic-Acid-Functionalized Resins

resin	**I/II**	**II/III**	capacity found (*X*) [mmol/g]	capacity calculated (Y) [mmol/g]	accessibility (%) (X/Y)	bed volume [mL/g]	swelling (%)[c]	specific surface (m^2/g)	yield (%)[d,e]
A[a]	0.52	77	7.30	7.60	96.0	6.4	144	30	100
B[b]	1.15	28	3.55	5.78	61.4	4.2	212	31	90
C[a]	0.84	35	3.75	3.95	95.0	4.7	136	14	98
D[b]	17.3	7	0.50	0.69	72.5	7.6	221	10	90
E[a]	2.42	22	3.13	3.32	94.3	5.6	164	24	100

[a] A-B-block-copolymer (A = functional monomer (**II**), B = cross-linker (**I**). [b] B-A-block-copolymer. [c] In water. [d] Based on recovered monomer. [e] All polymers prepared by suspension polymerization at 350 rpm.

Scheme 2. Preparation of Carboxylic-Acid-Functionalized Resin Type-1



aggregated to larger units of 30−50 μm (320−530 MESH) diameter. No distinct channels or pores are visible which is in accordance with the low specific surface area that has been determined experimentally (Table 1). Theoretical and experimental values for the capacity, which is usually expressed in millimoles COOH/gram resin, are in good accordance. Theoretical values were calculated from the molar ratio of **I/II** and experimentally confirmed by acid base titration. The swelling of the resins in polar solvents such as water and methanol is within acceptable limits (<165%). It is remarkable that these materials are wetted by water alone. This unique property is characteristic and necessary for all applications. As a consequence, no organic modifier is required in order to mediate between the apolar, organic resin and the highly polar solvent. This is only possible if a major part of the carboxylic acid functionalities is present at the surface of the particle. These properties do not change significantly within a limited range of capacity (2−8 mequiv/g). We therefore propose that this type of resin consists of an inner, cross-linked part and an outer part bearing the chains of functional monomers like a molecular fur.

A polymerization sequence consisting of the reaction of **III** with **I** followed by the reaction with **II** (resin type 2, Scheme 3) causes the yields of cross-linked polymer to be significantly lower. Furthermore, theoretical and experimental values for the capacity are no longer in accordance. A significantly enhanced swelling behavior of this type of resin in polar solvents is also observed. Due to the inverse polymerization sequence and the observed macroscopic properties, a structure with a major part of the carboxylic acid functionalities, being located in the interior of the resin, is proposed. It can therefore be concluded that only a polymerization sequence in which **II** is initiated and polymerized by **III** and finally cross-linked by **I** leads to polymer particles suitable for further use in separation techniques.

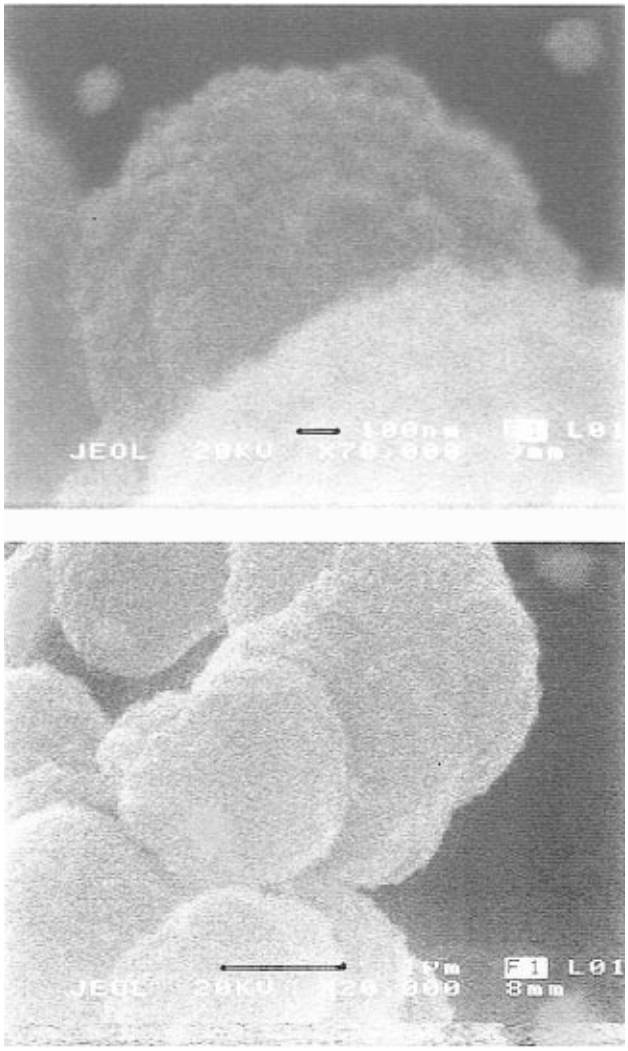
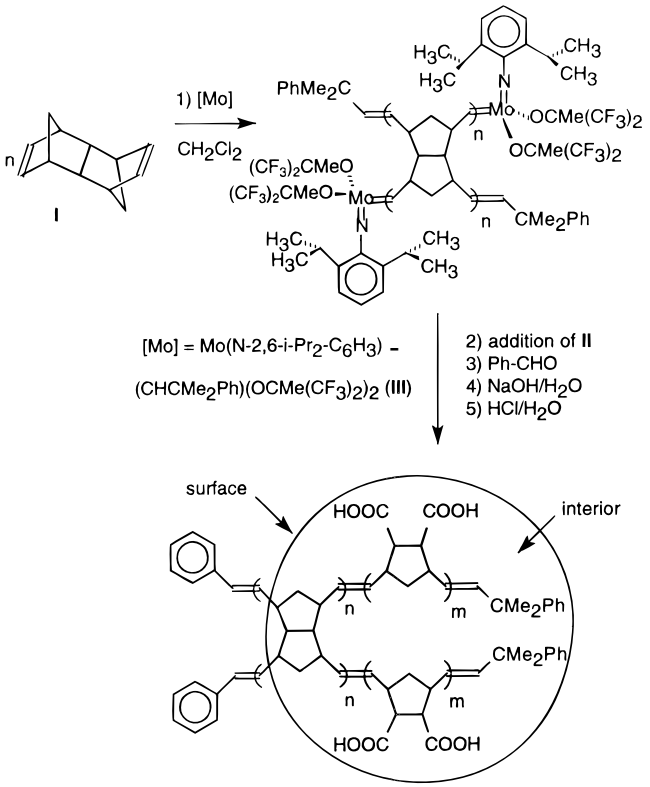


Figure 2. REM pictures of carboxylic-acid-functionalized resin (resin C, 3.9 mequiv/g). The scale bar represents 0.1 μm (top) and 1 μm (bottom), respectively.

Variation of the Molar Ratios of I/II and II/III in Resin Type 1. In addition to the polymerization sequence, the molar ratios of both **I/II** and **II/III** are important for the final properties of the resulting resins. On the one hand, the ratio of **I/II** is responsible for the capacity of the resin as well as for the degree of cross-linking [**I**/(**I** + **II**)], which in turn influences the porosity and, as a consequence, the swelling behavior. On the other

Scheme 3. Preparation of Carboxylic-Acid-Functionalized Resin Type-2



hand, the ratio of **II/III** is responsible for the chain length of poly(**II**) covalently bound to the cross-linked backbone, which again influences porosity and properties derived thereof.

All of the investigated type 1 resins have been prepared within a range of 0.5−2.5 for **I/II**, in which a sufficient degree of cross-linking was observed. As a consequence, the swelling was within an acceptable range. For this reason, the ratio of **I/II** must be regarded as an important, yet less dominant, variable in these polymerization systems. The most critical parameter in the preparation of these resins is represented by the ratio of **II/III**. While ratio values for **II/III** below 40 are suitable, the macroscopic behavior of these materials changes dramatically when ratio values above 40 (e.g., **II/III** = 77, resin A, Table 1) are chosen. Upon treatment with polar solvents such as methanol, water, and even diethyl ether, the material starts gelling. This is explained by the formation of strong hydrogen-bonding caused by the long dicarboxylic-acid-functionalized chains concentrated at the surface of the particles. In the case where the ratio of **II/III** > 50, they obviously become long enough to cause a strong interparticle interaction, leading to the formation of a gel-like, solvent swollen matrix. This behavior is considered to be another proof for the proposed fur-like structure of resin type 1.

Specific Surface Area and Polymer Backbone. The specific surface area of all type 1 resins was found to be within 10−30 m^2/g, which suggests a nonporous or microporous structure. Nevertheless, a nonpermanent porosity due to the increase in volume in the swollen state must be assumed. This assumption was confirmed for resin C by determining the characteristic parameters by means of GPC (gel permeation chromatography).[36−38] Thus, resin C was found to possess a specific pore volume of 750 μL/g and a specific surface area of ca. 80 m^2/g in the conditioned state.

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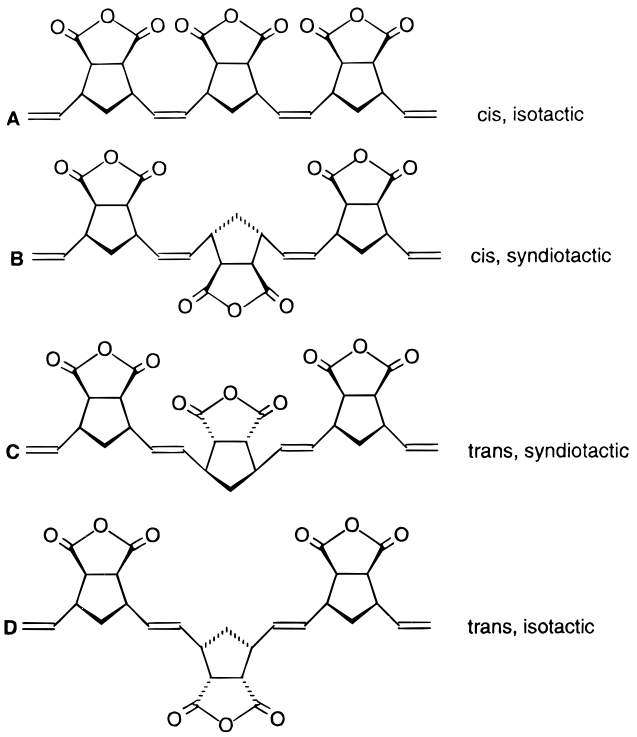

Figure 3. The four possible regular structures for poly(**II**).

In contrast to any change in solvent, none of the ratios of **I/II** and **II/III** significantly influence the specific surface; only for capacities higher than 5 mequiv/g is a slight increase (30 m^2/g) observed.

A characterization of the polymer backbone is possible for non-cross-linked poly(**II**). As a result of the stoichiometric initiation of the polymerization, short polymer chains of the functional monomer **II** with 10 monomer units may be prepared. These oligomers are still slightly soluble in benzene-d_6 and therefore allow the recording of a proton spectrum. In order to obtain ^{13}C NMR-based information about the oligomers, they may be dissolved in D_2O/LiOD (10%) resulting in a viscous solution of polylithium poly(norborn-2-ene-5,6-dicarboxylate). Information about the polymer structure, which may have either a cis or trans configuration at the olefinic double bonds and be either tactic or atactic, hardly allows some correlation with the polymer properties in the cross-linked state, yet is still important and useful in terms of polymer chemistry. The four possible structures for a regular backbone are shown in Figure 3. A detailed description of the stereochemical situation in mono-substituted poly(norbornenes) as well as 2,3-disubstituted poly(norbornadienes) has already been given by Schrock et al. and Feast et al.[39,40] Due to the analogous situation concerning elements of symmetry, the stereochemical situation for poly(**II**) will only be discussed briefly. In all four possible, regular structures, a plane of symmetry passes through the oxygen of the anhydride bond and the methylene carbon. All olefinic protons are chemically equivalent; therefore, only one signal for the olefinic proton may be expected. Additionally, symmetry elements, which lead to a situation where all olefinic protons are also equivalent in terms of their chemical environment (magnetically equivalent), may be found for either form of cis or trans tacticity. Consequently, ^{1}H NMR does not allow the distinction between cis or trans configuration. As shown in Figure 4a, the proton spectrum of poly(**II**) shows only one signal

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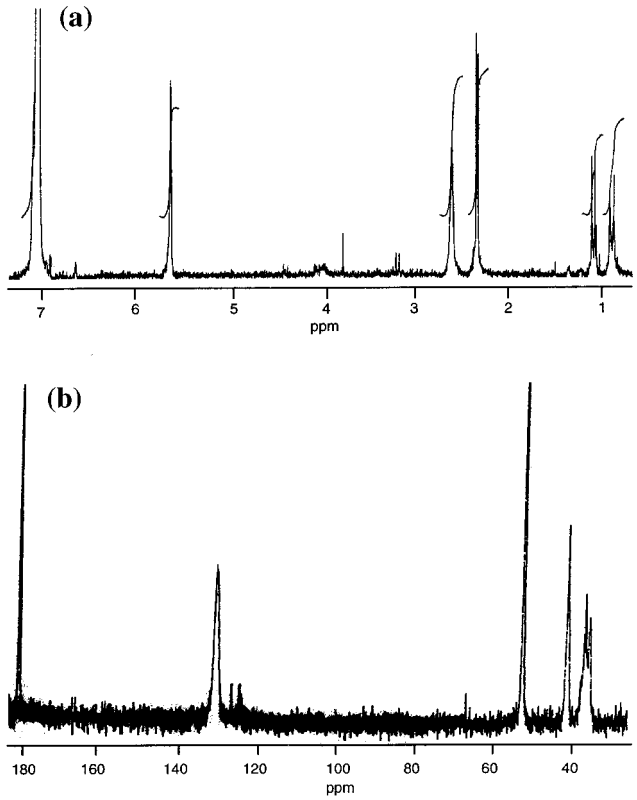

Figure 4. (a) ^{1}H NMR (C_6D_6) of poly(**II**). (b) ^{13}C NMR (LiOD, 10%) of poly(**II**).

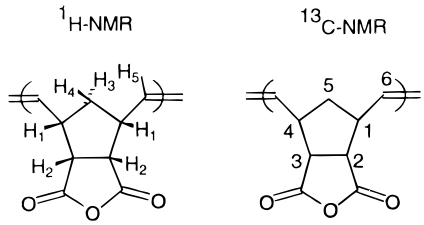

Figure 5. Notation used for the description of the polymer backbone (see also the Experimental Section).

at 5.70 ppm for the olefinic protons. It is split to a triplet (J = 1.6 Hz), which is believed to result from some second-order (allylic) coupling of the olefinic proton with H_1 (Figure 5). However, existing ^{13}C NMR data for disubstituted norbornenes allow the distinction between the two possible configurations at the carbon−carbon double bond by determining the chemical shift of C_1 and C_4, respectively (Figures 4b and 5). The chemical shift of 44.9 ppm for these carbons suggest a cis configuration. This is in accordance with the finding that **III** polymerizes 1,2-disubstituted norbornenes[8,39] and norbornadienes[41] in comparable systems with a high cis content. The fact that two different signals for C-5 are observed suggest a reduced tacticity of the polymer.

General Properties. The polymers prepared by the procedure described above show a mean particle diameter of 40 ± 10 μm. The particle shape itself is quite irregular. Resin type 1 polymers are wetable by water alone and represent entirely pH-stable and recyclable materials. No loss in performance has been observed after more than 20 cycles. When the polymer is exposed to air for at least 2 months, a change in color from bright white to yellow may be observed. This change in color does not influence the characteristic properties of these resins. Swelling is within acceptable borders (<160%) for water or methanol. THF or methylene chloride are absorbed readily, resulting in a swelling of the material of more than 300% and in a drastic increase in weight (up to 1000%). As a logical consequence, the latter ones are even in mixtures of less than 40% (v/v) with other solvents not suitable for resin treatment. While the dicarboxylic acid derivative of **II** shows a pK_1 of 4.5 and a pK_2 of 8.0, titration of all copolymerized resins revealed only one mean pK_a value at 6.6 ± 0.1. Since the steric and electronic situation of the carboxylic acid groups is not changed drastically in the polymer compared to the monomer, this single pK_a value for a polydicarboxylic acid is believed to result rather from kinetic effects than from one single, quasi equlibrated dissociation constant for all carboxylic acid groups within the resin.

General Requirements for SPE. Examples for Sample Clean-up. SPE represents a well-established procedure for the concentration and clean-up of analytes.[1,3,31,33] Furthermore, water and air purification by special resins may be regarded as an up-scaled SPE. In order to be useful for solid-phase extraction, a resin must fulfill certain requirements. In addition to a suitable particle size, usually in the range of 40−60 μm, a selective interaction with the analyte, often performed in form of a combination of reversed-phase (RP) and ion exchange mechanisms, plays an important role. A possible way to characterize new resins in terms of their retention characteristics, efficiency as well as selectivity, is to investigate their interaction with various analytes in different matrices. In this context, the corresponding breakthrough curves, describing the maximum amount of each compound beeing held back by the resin, as well as the total recovery, describing the efficiency of elution, are of major interest. In the present investigation, aqueous mixtures of strong and weak amines (lutidines and anilines) as well as volatile, airborne amines have been investigated.

A 10 ppm solution of 16 different anilines and lutidines (compounds **1**−**16**, Table 2) dissolved in a mixture of methanol/water (20:80) was passed through a SPE column filled with small amounts (50 mg) of carboxylic-acid-functionalized resin. The significantly lowered amounts of polymers used for these investigations compared to standard procedures, which usually employ 0.5−10 g of adsorbent, were chosen in order to contribute to a generally desired miniaturization. The actual points of breakthrough were determined under competitive conditions from a mixture of all 16 amines for each analyte and are shown in Table 2. Entire breakthrough curves have been recorded for a mixture of selected amines and are shown in Figure 5. The advantage of a mixed standard containing the same amount of different analytes for the characterization of a stationary phase is the fact that it does not only allow for a drastically reduced time of analysis but also for the investigation of effects, which result from the interaction and competition of the different analytes. Table 2 shows a brief summary of these results in comparison to those obtained with the 10-fold amount of a standard COOH-derivatized silica-based material. Keeping the total amount of each analyte below the point of its breakthrough, excellent recoveries were obtained. Additional chromatographic parameters such as capacity factors (k') as well as the number of theoretical plates (N) have been determined[42] for a representative selection of analytes. The high values for the number of theoretical plates (N) up to 19000/m again underline the high efficiency of these materials.

A comparison of these recoveries with the pK_a values of the corresponding conjugated acids of compounds **1**−**16** reveals that a significant cation exchange mechanism must be present. The

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Table 2. Recoveries of Selected Anilines and Lutidines in Comparison to Commercially Available Silica-Based Resins[a]

	amine	pK_a	500 mg silica-CO_2H[d] recovery ± s[b]	50 mg resin C recovery ± s[b]	breakthrough vol.[c,e]	N[f]	N per meter[f]	k' for resin C	90 mg resin C recovery ± s[c]	50 mg poly(**I**) recovery ± s[b]
1	2,6-lutidine	6.99	70 ± 6	100 ± 8.8	40				32 ± 5	91 ± 1
2	2,4-lutidine	6.63	79 ± 23	103 ± 8.3	40				69 ± 13	97 ± 10
3	aniline	4.63	5 ± 1	20 ± 1.8	25				6 ± 1	10 ± 1
4	*N*-methylaniline	4.82	69 ± 11	101 ± 8.0	35	56	2800	92 ± 32	33 ± 1	66 ± 4
5	*N*,*N*-dimethylaniline	5.15	86 ± 6	101 ± 6.6	85	77	3850	119 ± 18	84 ± 12	83 ± 1
6	2-chloroaniline	2.65	0	95 ± 6.3	35	31	1550	89 ± 10	41 ± 4	15 ± 1
7	2,6-dimethylaniline	3.95	0	97 ± 6.6	35	25	1250	69 ± 2	40 ± 8	15 ± 0
8	3-chloroaniline	3.46	0	63 ± 4.6	35	49	2450	225 ± 41	28 ± 2	22 ± 4
9	2-aminobenzonitrile	0.95	0	31 ± 6.2	25			61 ± 8	14 ± 1	1 ± 0
10	3-aminobenzonitrile	2.8	0	13 ± 2.1	17	68	3400		7 ± 1	7 ± 2
11	2-nitroaniline	−0.05	0	100 ± 6.5	50				50 ± 1	55 ± 2
12	2,6-di-*i*-propylaniline		86 ± 15	102 ± 5.9	130	380	19000	1080	109 ± 11	78 ± 7
13	4-aminobenzonitrile	1.75	0	8 ± 1.0	17	53	2650	66 ± 12	6 ± 1	3 ± 0
14	3-nitroaniline	2.47	0	44 ± 3.8	25	115	5750	113 ± 28	13 ± 2	14 ± 0
15	1-naphthylamine	3.92	35 ± 4	61 ± 2.6	60	81	4050	309 ± 66	21 ± 4	23 ± 5
16	diphenylamine	0.85	90 ± 9	105 ± 4.6	>190			2335	96 ± 5	104 ± 4

[a] Resin C (3.9 mequiv/g). [b] Determined in methanol/water 20:80 (v/v), 5 mL of mixed standard (10 ppm each of 1−16). [c] Determined in water using 1000 mL of mixed standard (50 ppb each of **1**−**16**). [d] ICT-Bond-elut, capacity: ca. 1 mequiv/g. [e] Expressed in multiples of the column volume. [f] Number of theoretical plates.

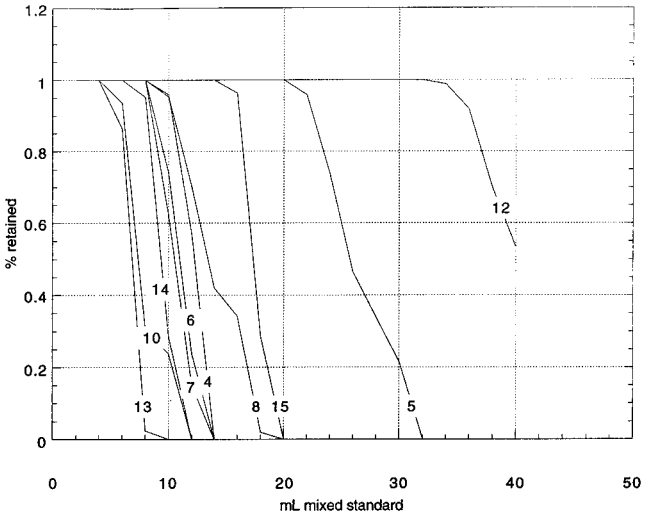

Figure 6. Breakthrough curves for selected anilines on resin C (50 mg, 3.9 mequiv/g); mixed standard of compounds indicated (50 ppm each) in water/methanol (80/20, v/v). Quantification by GC-MS.

weakly basic chloro-, nitro-, and cyano-substituted anilines showed a reduced retention compared to the much stronger alkyl substituted anilines and lutidines. Nevertheless, even weak bases such as diphenylamine were retained quite efficiently (see Figure 6). This suggested that a second mode of interaction is present. Due to the polymerization technique, the backbone of the new resins represents a highly unsaturated hydrocarbon. As a consequence, a large amount of π-electrons, which may give raise to π-donor−π-acceptor interactions, is available. If these unsaturated moieties of the resin are responsible for the strong retention of weak, yet π-electron-accepting amines, the underivatized resin, i.e., only hydrocarbon-based resin poly(**I**) prepared by the same technique, should also favor the retention of this type of analytes. A comparison between an underivatized resin, prepared by ROMP of **I**, and carboxylic-acid-functionalized resins using the same mixture of analytes allows a rough estimation of the degree of reversed-phase mechanism for each compound, which is responsible for the adsorption properties of the resin. This mode of adsorption seems to be mainly resonsible for the strong adsorption of amines with pronounced π-acceptor character such as diphenylamine (Table 2), demonstrating the considerable high reversed-phase part in the retention of rather apolar amines. On the basis of these findings, this reversed-phase mechanism was found to be strong enough for the extraction of almost any type of organic compounds from water. When the carboxylic-acid-functionalized type-1 resins are used, alcohols, phenols, carboxylic acids, carbonyl compounds, halogenated hydrocarbons, *N*-nitrosoamines and polycyclic aromatic hydrocarbons have been extracted almost quantitatively.[43]

Table 3. Recoveries for Compounds **17** and **18** on Resin C (3.75 mequiv/g)[a]

	amine	recovery ± s (methanol)[b]	recovery ± s (air)[c]
17	pentamethyldiethylentriamine	120.3 ± 3.6	105.7 ± 10.4
18	1,4-diazabicyclooctane (DABCO)	105.4 ± 3.0	98.6 ± 7.8

[a] General conditions: bed-volume 50 mg, elution with methanol/NEt_3 50:50 (v/v); quantification by GC-MS using 2,6-di-*i*-propylaniline as an internal standard. [b] Standard mix containing 260 ppm of **17** and 240 ppm of **18** in methanol. [c] Air containing 100 ppm of **17** and 75 ppm of **18**, sampling rate 200 mL/min.

The new, high-capacity carboxylic-acid-derivatized materials have also been used for solid-phase extraction and water clean-up, respectively, at the ppb level. A solution of compounds **1**−**16** in water at a concentration of 50 ppb was again passed over a column filled with carboxylic-acid-derivatized particles. Sufficient retention, at least for the more apolar compounds, was observed. The more electronegatively substituted and therefore more polar and less basic anilines were hardly retained due to their increased solubiliy in water as well as their reduced basicity. These findings, as well as the stability of the material and the fact that it is wetted by water alone, let these new sorbents appear as attractive polymers for the clean-up of waste water.

Another area of interest was the investigation of the retention behavior of the new materials versus that of volatile basic compounds. In order to obtain information about the retention behavior of the new resin toward volatile amines and to develop an efficient elution system, solutions of methanol containing two volatile amines, pentamethyldiethylentetramine (PMDTA) and 1,4-diazabicyclooctane (DABCO), were passed over the resin. Recoveries (Table 3) and breakthrough curves (Figure 7) were obtained consecutively. An exceptionally high total uptake of over 20% of the theoretical capacity of the resin was

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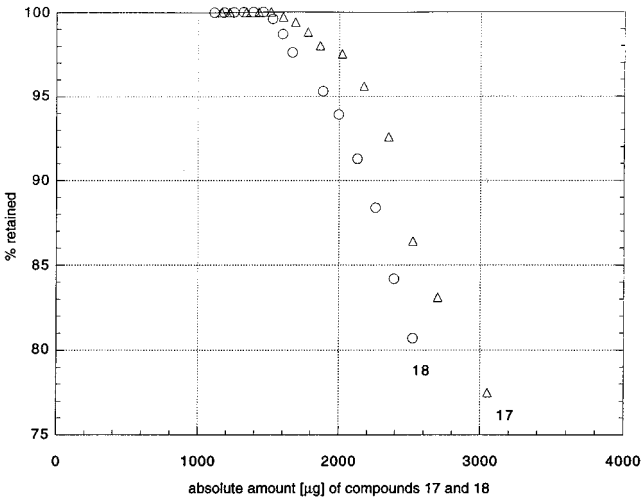

Figure 7. Breakthrough curves for pentamethyldiethylentriamine (**17**) and diazabicycloundecane (**18**) on polymer A (35 mg, 3.75 mequiv/g). Mixed standard containing 175 ppm of **17** and 125 ppm of **18** in ethyl acetate. Quantification was by GC-MS (internal standard 2,5,8,11,14-pentaoxapentadecane).

observed, making this type of material highly interesting for air clean-up. This high uptake may be explained by the fact that both compounds represent strongly basic di- and triamines, respectively. In a second step, air, containing both compounds at a concentration of approximately 75−100 ppm, was passed over a short column containing 35 mg of COOH-derivatized resin. As expected, the triamine (PMDTA) was absorbed stronger than the diamine (DABCO). After adsorption, quantitative desorption (Table 3) was achieved by elution with methanol containing triethylamine (50% v/v). Recoveries for both compounds were found to be around 100%. Again, after elution and transformation into the H^+ form with 2 N hydrochloric acid, the materials may be used at least 20 times without any loss of performance.

Outlook

The high reproducibilty in the synthesis of these resins as well as the broad applicability of the synthetic concept for the polymerization of various functional groups prompted us to extend our investigations to other applications such as the separation of lanthanides[44] and other transition metals[45] as well as to the polymerization of other functional monomers.[46] A wide field of applications in the area of separation chemistry such as membrane-embedded polymers, the preparation of chiral stationary phases suitable for HPLC, and the chemistry of polymer-bound enzymes is currently under investigation.

Experimental Section

I. Synthesis. All experiments were performed by standard Schlenk techniques unless stated otherwise. Reagent grade pentane, diethyl ether, THF (tetrahydrofuran), DME (dimethoxyethane), and toluene were distilled from sodium benzophenone ketyl under argon. Reagent grade dichloromethane was distilled from CaH_2 under argon. Purchased starting materials as well as the investigated amines were used without any further purification. Other educts or reagents were prepared according to literature procedures and checked for purity by NMR.

II. Analytical Details. NMR data were obtained in the indicated solvent at 25 °C on a Bruker AM 300 and Varian EM 360L unless stated otherwise and are listed in parts per million (ppm) downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in hertz. IR spectra were recorded on a Midac FTIR. Mass spectra were obtained on a CH-7 (MAT). A Philips PU-7000 was used for all ICP measurements. GC-MS experiments were carried out on a Fisons GC-MS system (GC 8000 series, MD 800) using a 95%-poly(dimethylsiloxane)−5%-poly(diphenylsiloxane)-coated column (SE 54 cappillary column, 30 m, 0.25 mm i.d. 0.1−0.15 μm film thickness, Mega). Values for the specific surface were determined by the BET (Brunauer, Emmett, Teller) method (multi-point measurement), using a Quantachrome/NOVA 2000 (Institut für Mineralogie und Petrographie, Universität Innsbruck). Sample Preparation: 2 h at 50 °C, measurement with nitrogen 5.0. Molybdenum was quantified on a Philipps PU-7000 inductively coupled plasma (ICP) after breakdown of 0.5 g of the resins using peroxosulfuric acid/nitric acid (1:1). Titrations were performed on a Metrohm 686 Titroprocessor. Values for the specific pore size and specific surface[36−38] of resin C were determined by GPC using a Waters 717 Autosampler, a Waters column heater (35 °C), a Waters 510 HPLC pump, a Waters 490E UV-detector, a Waters 410 RI detector, and a Millenium work package.

III. Solid-Phase Extraction. For SPE experiments, 1 mL filtration columns (0.8 cm i.d.) equipped with 20 μm polypropylene frits (both IST, Isolute Accessories) were used. The amounts of polymer used are given in the text and Table 2. Solutions containing the analytes in the concentration indicated in Table 2 were passed over the columns filled with the corresponding material. For the determination of the breakthrough curves, every 2 mL samples were checked for analytes by GC-MS. Recoveries were determined by elution of the columns with triethylamine in ethyl acetate (50:50 v/v) and subsequent quantification by GC-MS (full scan, 70 eV) using 2,4-dinitrochlorobenzene as an internal standard. For the determination of the capacity factors (k'), a 6 cm steel column (0.4 cm i.d.), equipped with 20 μm steel frits, was used. The column was connected to a Waters 501 HPLC pump, and a total volume of 25 mL of a mixed standard of anilines (50 ppm of compounds **1**−**16** each) was passed over 90 mg of the sorbent (resin C). According to Hlavay et al.,[42] an equilibrium is reached after passing the solution at least 10 times over the resin. Concentrations of the anilines were determined again by GC-MS. Values were counterchecked by elution of the adsorbed anilines with triethylamine ($pK_a = 11.1$)/ethylacetate (50:50) and subsequent quantification by GC-MS.

Breakthrough Volumes in Different Solvents. Breakthrough volumes were recorded in the indicated solvents using GC-MS detection. The amount and type of resin indicated in Table 2 was treated with 2 mL portions of the mixed standards. Selected breakthrough curves are given in Figures 6 and 7.

Monomers and Catalysts. 1,4,4a,5,8,8a-Hexahydro-1,4,5,8-*exo,endo*-dimethanonaphthalene[47] (**I**), *endo,endo*-[2.2.1]bicyclohept-5-ene-2,3-dicarboxylic anhydride (**II**),[48] and the initiators, $Ru(PCy_3)_2Cl_2CH$-p-F-C_6H_4,[17] Mo(*N*-2,6-*i*-Pr_2-C_6H_3)$CHCMe_2Ph(OCMe(CF_3)_2)_2$ (**III**),[49] Mo(*N*-2,6-Me_2-C_6H_3)$CHCMe_2Ph(OCMe(CF_3)_2)_2$,[49] and Mo(*N*-2,6-*i*-Pr_2-C_6H_3)$CHCMe_2Ph(OCMe_3)_2$,[49] were prepared according to the literature. Additional analytical data for **II** are given below. Since the initiator is very sensitive toward water and acids, any trace of moisture was excluded carefully during the course of the whole synthesis in order to prevent partial hydrolysis of the carboxylic anhydride functionality to the corresponding 1,4-dicarboxylic acid. All analytical data of compounds **I**−**III** were identical to those reported earlier.

***endo,endo*-[2.2.1]Bicyclohept-5-ene-2,3-dicarboxylic anhydride:** ^{1}H NMR (C_6D_6) δ 5.84 ("t", $J = 1.8$, C═C*H*), 2.82 (m, 2 H, C*H*), 2.31 (dxd, 2 H, $J_1 = 2.6$, $J_2 = 1.4$, C*H*CO), 0.86 (dxt, $J_1 = 9.0$, $J_2 = 1.4$, C*HH*); ^{13}C NMR δ 171.5 (CO), 135.6 (C═C), 53.2 (CH_2), 47.2 (*C*H), 46.2 (*C*H).

Polymer Syntheses. Preparation of Poly(I). Underivatized resins (poly(**I**)) were prepared by adding a solution of the initiator (**III**, 50 mg, 65.3 μmol) to a stirred solution (350 rpm) of the cross-linker (**I**, 1.0 g, 6.3 mmol) in methylene chloride (50 mL). After 1 h,

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benzaldehyde (0.5 mL) was added and the mixture was stirred for additional 30 min. Filtration, subsequent washing with methylene chloride and removal of all volatiles under high vacuum yielded poly(**I**) quantitatively. The average particle diameter was 50 ± 10 μm. Specific surface area: 30 m^2/g. Following the same procedure and using the same amount of toluene instead of methyene chloride resulted in the quantitative formation of poly(**I**) with a higher specific surface (150 m^2/g). Prior to filtration, 50 mL of pentane was added. After filtration, the material was ground up. The material was not suitable for SPE.

Carboxylic-Acid-Functionalized Resins. The following procedure using a 1 L round-bottomed flask, is typical for the carboxylic-acid-derivatized, A-B-block-copolymers: The initiator (**III**, 250 mg, 0.33 mmol) was added to a well-stirred (350 rpm) solution of **II** (2.2 g, 13.4 mmol) in methylene chloride (300 mL). The clear solution turned cloudy within 1 min, and the resulting suspension was stirred for 5 h after which the cross-linking agent (**I**, 4.6 g, 29.1 mmol) was added. The reaction mixture was stirred for an additional 5 h, benzaldehyde (2 mL, 20 mmol) was added, and the suspension was stirred for 12 h in order to ensure complete termination of the active polymer ends. The polymer was filtered off (G4 frit), washed thoroughly with methylene chloride, and dried in vacuo. Yield: 6.8 g (100%). Hydrolysis of the anhydride was performed by stirring the polymer in a solution of 20 g of sodium hydroxide in methanol/water (1:4) for 6 h. Filtration, washing with water, and subsequent stirring of the polysodium salt in 10% hydrochloric acid (500 mL) yielded the weak cation exchange resin in its H^+ form. It was filtered off, washed with water, methanol, and diethyl ether, and dried in vacuo. Yield: 6.9 g (98%). Capacity calcd.: 3.9 mmol/g; found 3.75 mmol/g (96.2% accessibilty). For the synthesis of the B-A-block-copolymers, the reaction was started with **I** and followed by the addition of **II**, without changing reaction times. Following these procedures, various resins with different capacities have been prepared. An overview is given in Table 1.

Characterization of the Polymers. Poly(*endo,endo*-[2.2.1]bicyclohept-5-ene-2,3-dicarboxylic anhydride)$_{10}$. *endo,endo*-[2.2.1]-Bicyclohept-5-ene-2,3-dicarboxylic anhydride (**II**, 100 mg, 0.61 mmol) was dissoved in 20 mL of methylene chloride. A solution of the initiator (**III**, 45 mg, 0.06 mmol) in 5 mL of methylene chloride was added, and the reaction mixture was stirred at room temperature for 2 h. Finally, benzaldhyde (0.1 mL, 0.94 mmol) was added, and the solution was stirrred for 1 h. Pentane was added, and the precipitate was collected by filtration. It was washed with pentane and diethyl ether and dried in vacuo. Yield: 90 mg (83%). The backbone structure was determined by ^{1}H NMR to be cis, atactic. For title compound: M_w (calcd) 1862 (including end-groups), M_w (found) 2163, PDI 1.73; FT-IR (KBr) 1854 m, 1771 vs, 1630 m, 1207 m, 1001 s, 922 vs; ^{1}H NMR (C_6D_6) δ 5.70 (t, J = 1.6, $H_{5,5'}$), 2.63 (m, 2 H, $H_{2,2'}$), 2.35 (dxd, 2 H, J_1 = 2.8, J_2 = 1.6, $H_{1,1'}$), 1.05 (dxd, J_1 = 7.8, J_2 = 1.7, $H_{3,4}$).

Poly(dilithium-*endo,endo*-[2.2.1]bicyclohept-5-ene-2,3-dicarboxylate)$_{10}$. Poly(**II**)$_{10}$ (50 mg) was dissolved in 10% LiOD in D_2O: ^{1}H NMR δ 5.57 (m, *H*C═C, 2 H), 3.12−2.92 (m, 4 H), 1.88 (m, 1 H), 1.69 (m, 1 H), (all broad); ^{13}C NMR (D_2O, ext. vs C_6D_6) δ 182.9 (CO_2^-), 133.4 (C_6), 56.1 ($C_{2,3}$), 44.9 ($C_{1,4,cis}$), 40.5 (C_5), 39.2 (C_5).

Poly(*endo,endo*-[2.2.1]bicyclohept-5-ene-2,3-dicarboxylic anhydride)(1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo,endo*-dimethanonaphthalene): FT-IR (KBr) 1855 m, 1777 vs, 1450 w, 1250 m, 1206 s, 1000 s, 922 vs, 750 m.

Determination of the Capacity. The corresponding carboxylic-acid-derivatized resin (H^+ form, 200 mg) was stirred in 10 mL of a mixture of 0.05 M NaOH and methanol (4:1) 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. Experimentally determined capacities are expressed as a mean value of at least three experiments. Standard deviations were less than 3%.

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