Porous Polymer Monoliths: Preparation of Sorbent Materials with High-Surface Areas and Controlled Surface Chemistry for High-Throughput, Online, Solid-Phase Extraction of Polar Organic Compounds

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Porous monolithic materials with high surface areas have been prepared from commercial 80% divinylbenzene. The pore properties of these materials are controlled by the type and composition of the porogenic solvent and by the percentage of cross-linking monomer (divinylbenzene) in the polymerization mixture. Surface area was found to increase with the divinylbenzene content of the monolith. Using high-grade divinylbenzene and a suitable porogenic solvent, monolithic materials with specific surface areas as high as 400 m²/g yet still permeable to liquids at reasonable back pressure were obtained for the first time. A macroporous material with hydrodynamic properties optimized for solid-phase extraction has been designed and its permeability and adsorption ability was demonstrated by adsorbing phenols at flow velocities that exceed those of current materials by a factor of 30. A unique set of polymerization conditions had to be developed to allow the incorporation of polar 2-hydroxylethyl methacrylate into the hydrophobic nonpolar backbone of the divinylbenzene monolithic material. This improves wettability while high-flow properties are maintained and unusually high recoveries of polar compounds are allowed.

Introduction

In addition to "classical" use in ion-exchange, macroporous polymeric materials with controlled pore properties are finding numerous new applications in high-end technologies such as catalysis, chromatography, enzyme immobilization, combinatorial chemistry, and solid-phase extraction (SPE). Currently, sorption materials in bead shape are most frequently used in these applications as a result of their commercial availability.[1-4] The polymeric materials have numerous intrinsic advantages compared to inorganic silica-based adsorbents. For example, their use with liquids within the entire range of pH is possible due to the virtually unlimited hydrolytic stability of typical styrene- and methacrylate-based beads.

The inherent problem of all particulate separation media is their inability to completely fill the available space. This may not be critical for applications in columnlike tubular formats, where the length of the packed bed partly compensates for the effect of the irregular interparticular voids. However, it is very difficult to avoid channeling between particles packed in a thin layer that has the aspect ratio typical of applications such as SPE.[5] This has led to the development of disk formats that include disks with embedded sorbent particles or HPLC type beads tightly retained between two screens.[2] Although the syringe barrel is also amenable to the disk format, specifically designed holders, pipet tips, and 96-well microtiter plates are currently more popular, since they allow easy integration into robotic systems for high-throughput screening protocols.[2,6] In addition to the typical offline applications, online adsorption devices are also used in combination with HPLC methods.[7,8]

Recently, we have introduced macroporous polymers in a completely new shape: monoliths prepared by direct polymerization within a mold.[9,10] The macroporous structure of our monolithic materials is readily controlled and consists of a system of interconnected pores of different sizes. Smaller pores provide the surface area required for the desired interactions, while the large macropores allow liquid flow at low back pressures. Mass transport is greatly improved by convective flow through the monolithic structures. The simplicity of the "molding" process permits the reproducible preparation of devices of all sizes. Our previous research on these monolithic materials has mainly focused on the preparation of columns for the rapid chromatography of large molecules, such as biological and synthetic polymers,

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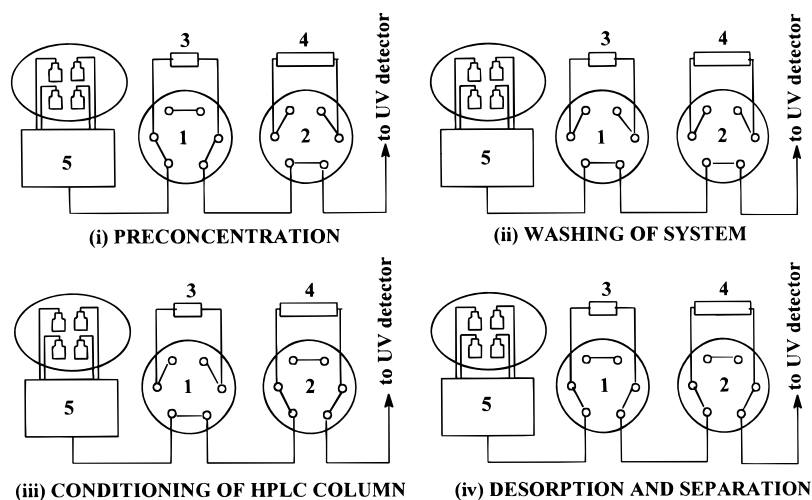(10) Svec, F.; Fréchet, J. M. J. *Science* **1996**, *273*, 205.

Figure 1. Setup of the experimental system used to study adsorption properties of monoliths.

and on immobilized biological catalysts.[10,11] We have demonstrated that monoliths with specifically designed porous structures and moderate surface areas in a range of 10−50 m²/g are well-suited for these applications. The relatively small surface area largely results from the low number of micropores and mesopores with diameters less than 2 nm and 2−50 nm, respectively, in contrast to the much larger pores (800−10 000 nm) that are present to afford good hydrodynamic properties.[9−12,15]

In contrast to rapid chromatographic separation, polymeric materials with surface areas in the range of hundreds of square meters per gram are generally required for processes controlled by adsorption. Our previous studies of both porous polymer beads and monoliths with various chemistries have demonstrated that an increase in the percentage of cross-linking monomer often leads to an increase in specific surface area.[11−14] Although this approach allows the preparation of monoliths with larger surface areas, their pore size decreases rapidly. For example, poly(styrene-co-divinylbenzene) monolith with a surface area of 160 m²/g had the mean pore size of only 70 nm, which is much too small to enable flow-through applications.[12] Therefore, a new generation of porous materials had to be designed. These materials should have a different morphology that involves both large pores with sizes in the range of several hundreds of nanometers to maintain the excellent flow-through properties and a large number of small mesopores and micropores to achieve the required surface area.

This study explores the preparation of new permeable macroporous monoliths with large surface areas and their use for solid-phase extraction. For the first time the hydrophilic monomer 2-hydroxyethyl methacrylate (HEMA) has also been incorporated in a framework of a permeable highly cross-linked divinylbenzene mono-

lith to afford unique internal surfaces with a balance of hydrophilic and hydrophobic character. These novel materials are well-suited for the normally difficult solid-phase extractions of polar organic compounds from very dilute aqueous solution.[16]

Experimental Section

Preparation of Porous Polymer Monoliths. A threaded poly(ether ether ketone) (PEEK) tube (20 × 1 mm i.d., Upchurch Scientific, Oak Harbor, WA) was placed in a glass vial that was filled with a polymerization mixture consisting of a solution of azobisisobutyronitrile (AIBN, 1 wt % with respect to monomers) in a mixture of freshly distilled monomers, typically commercial divinylbenzene (80% and 55% active components and 20% and 45% ethylstyrenes, respectively; Aldrich) or experimental 91% divinylbenzene (Dow Chemicals) and 2-hydroxyethyl methacrylate (97%, Aldrich), a higher aliphatic alcohol, and toluene (porogenic solvents; purchased from Aldrich and used without any treatment), so that the tube was completely covered. Specific polymerization conditions are shown in the captions to Tables and Figures.

Caution: *High-grade divinylbenzenes (80 and 91%) have been reported as suspected carcinogens, while 2-hydroxyethyl methacrylate and higher alcohols are known irritants. Proper precautions should be taken while handling these materials.*

The vial was sealed and the polymerization allowed to proceed at a temperature of 70 ºC for 24 h, at which time the glass was broken and the tube retrieved. The excess of polymer on the outside of the tube was mechanically removed, then the tube was provided with end fittings and attached to a chromatographic system. Methanol (20 mL) and water (1 mL) were pumped through the cartridge at a flow rate of 0.2 mL/min to remove the porogenic solvents and any remaining soluble compounds present in the monolith. The monolith formed by polymerization outside of the mold was recovered, cut to small pieces, extracted with methanol in a Soxhlet for 12 h to remove all soluble compounds, vacuum-dried at 60 °C overnight, and used in porosimetric studies.

Characterization of the Materials Porous Properties. Pore size distribution curves were determined in the dry state using a mercury porosimeter (Autopore III 9400, Micromeritics Instrument Corp., Norcross, GA) and used for the calculation of median pore diameter. A surface area and porosimetry system (ASAP 2010, Micromeritics) was used for the measurement of specific surface areas. Since the equilibration times between each nitrogen addition during the measurement were relatively long for polymers with large surface areas and the

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measurement took up to 24 h, only adsorption at increasing relative pressure was monitored.

Adsorption of Phenols. Figure 1 shows the experimental setup for the online SPE measurement that includes two Rheodyne six-port switching valves (1 and 2), the monolithic cartridge (3), and a Symmetry C18 reversed-phase HPLC column (4) (150 × 4.6 mm i.d., Waters Corp.) inserted between the quaternary solvent pump (5) and the UV detector of a commercial Hewlett-Packard HPLC 1050 system. Flow can either be directed to pass through the cartridge and the HPLC column separately, or through both at the same time.

The absorption capacities at different percentages of break-through were calculated as the weight of absorbed phenol obtained from retention volume divided by the overall weight of sorbent in the cartridge (5.3 mg). The weight of absorbed phenol was determined from the breakthrough curve measurements in the frontal elution mode. The breakthrough was measured by pumping an aqueous 10 μg/mL solution of 2-nitrophenol through the cartridge at a flow rate of 0.8 mL/min (flow velocity of 102 cm/min or 51 bed volumes/min) and recording with a UV detector at 280 nm. Water was purified by an EASYpure RF Compact Ultrapure Water System (Barnstead, Dubuque, IA). Since SPE of phenols occurs typically from untreated samples of surface or drinking water, no attempt was made to change or adjust the pH of the phenol solutions used for the absorption.

Recovery Experiments. Recovery experiments were carried out separately by pumping 4.8 mL of a 10 μg/L solution of substituted phenol in water through the column at a flow rate of 0.8 mL/min. The amount of 2-nitrophenol absorbed was determined from its peak area in the chromatogram obtained using the Symmetry HPLC column. This chromatographic process helps avoid interference with the peak of the measured analyte from trace impurities present in water. The chromatographic separation was achieved at a flow rate of 0.5 mL/min using a 10 min solvent gradient from 30 to 100% acetonitrile in acidified water (trifluoroacetic acid, pH 2.5) followed by 5 min elution with 100% acetonitrile. For more highly retained compounds such as trichlorophenol and pentachlorophenol, the elution gradient was started at 50% acetonitrile.

All measurements were repeated three times and the average values are shown.

Results and Discussion

Design of Permeable Poly(ethylstyrene-*co*-divinylbenzene) Monolithic Materials with Enhanced Surface Area. The pore properties of macroporous materials are controlled in a rather complex fashion by variables such as the polymerization temperature, composition of porogenic solvent, and the percentage of cross-linking monomer in the polymerization mixture.[12] Since a very large surface area is a favorable feature of adsorbents, our current efforts aim at the preparation of new materials with vastly enhanced surface areas to increase both sorption capacity and recovery while the advantageous flow properties of the original monoliths are maintained. Table 1 shows the effect of the percentage of divinylbenzene in the polymerization mixture on the pore properties. While typical commercial DVB that contains 55% of divinyl compounds and 45% ethylstyrenes (ES) affords monoliths with only a moderate specific surface area of 50 m²/g, a surface area of almost 400 m²/g is obtained for monoliths prepared from the higher grade monomer (80% DVB and 20% ES). Since pure divinylbenzene and ethylstyrene were not available for our experiments, the other percentages of DVB used in the various polymerizations were achieved by mixing these two common commercial grades. The specific surface area is a linear function of the percentage of

Table 1. Pore Properties of Poly(ethylstyrene-*co*-divinylbenzene) Monoliths Prepared by Polymerization of Mixtures Containing Different Percentages of Cross-Linking Monomer[a]

Composition of the Monomer Mixture					
divinylbenzene,[b] %	80.0	73.75	67.5	61.25	55.0
ethylstyrene, %	20.0	26.25	32.5	38.75	45.0
Composition of Porogenic Solvent Mixture					
dodecanol, wt %	52.0	52.1	52.4	52.6	52.9
toluene, wt %	8.0	7.9	7.6	7.4	7.1
Pore Properties					
median pore diameter,[c] μm	6.19	6.57	6.70	6.63	6.09
pore volume,[c] mL/g	2.08	2.03	2.12	2.11	2.13
specific surface area,[d] m²/g	398	275	217	203	50

[a] Polymerization conditions: PEEK cartridge 20 × 1 mm i.d.; polymerization mixture: monomer mixture (divinylbenzene + ethylstyrene) 40 wt %, porogenic solvent mixture (dodecanol + toluene) 60 wt %, AIBN 1 wt % (with respect to monomers); 70 °C; 24 h. [b] Percentage of divinylbenzene was adjusted by mixing 80% and 55% grade monomers. [c] According to mercury intrusion porosimetry. [d] Specific surface area determined from nitrogen adsorption/desorption isotherm.

DVB within the measured range ($r = 0.963$). Adjustments in the composition of the porogenic solvent are used to keep the median pore diameter (pore size at the maximum of the distribution curve determined by mercury porosimetry) within the 6−7 μm range to retain the high flow properties. This study clearly demonstrates the tremendous effect of the DVB content on the surface area of the new material.

Sorption Capacity and Recovery in Solid-Phase Extraction. Porous materials are often used in applications in which adsorption is the driving force. Since adsorption occurs typically on surfaces, the amount of surface area available is critical for the desired use. We used solid-phase extraction as a model process to demonstrate that our new monoliths characterized by surface areas in the range of several hundreds of square meters per gram, an unprecedented value for this class of materials, can be used in high-end adsorption processes.

Sorption capacities of these monoliths were determined using frontal elution with an aqueous solution of 2-nitrophenol (10 μg/mL) at the very high flow velocity of 102 cm/min (51 bed volumes/min). Since most of the nitrophenol is adsorbed at the surface of the pores, the amount of absorbed compound should be directly proportional to the available surface area, provided the pores are sufficiently large to allow penetration. Therefore, adsorbents with as large specific surface areas as possible (typically several hundred m²/g) are preferred in solid-phase extraction devices.[3] Indeed, Figure 2 demonstrates that an increase in capacity is observed for all of the tested monoliths as the percentage of DVB in the monolith is increased. Interestingly, the amount of nitrophenol adsorbed is not a simple linear function of either DVB content or specific surface area. While the capacities at all three determined breakthrough points (1, 10, and 50% breakthrough) increase only slowly with the increase in DVB content within the 55−74% range, a steep increase in capacity is achieved for the monolith prepared from 80% DVB. This might be due to a substantial change in pore size distribution in the region of very small pores, as such slight changes are not readily observed in simple measurements of overall surface areas.
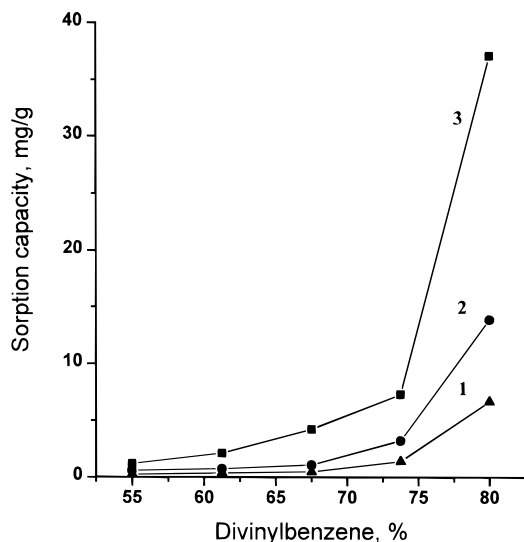
Figure 2. Effect of divinylbenzene percentage in the polymerization mixture on sorption capacity of porous poly-(ethylstyrene-*co*-divinylbenzene) monoliths for 2-nitrophenol from 10 μg/mL solution at a flow velocity of 102 cm/min; for polymerization conditions see Table 1. Curves: capacity at 1% (1), 10% (2), and 50% (3) breakthrough.
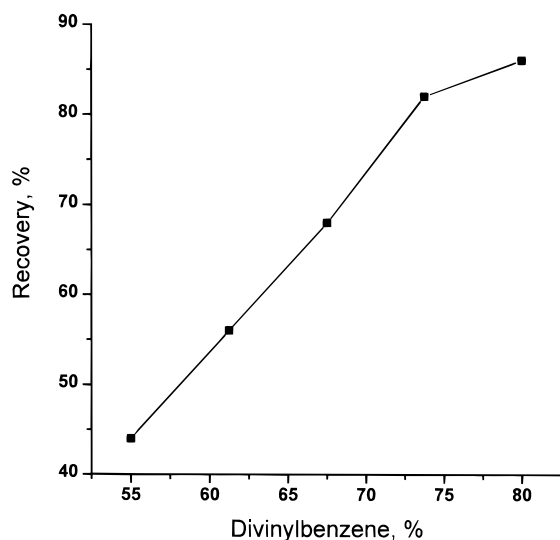

Figure 3. Effect of divinylbenzene percentage in the polymerization mixture on recovery of 2-nitrophenol from porous poly(ethylstyrene-*co*-divinylbenzene) monoliths; for polymerization conditions see Table 1; adsorption from 4.8 mL of a 10 μg/L solution, elution with a gradient of acetonitrile in water at a flow velocity of 102 cm/min.

In contrast to this exponential increase in capacity, a plot of percentage recovery vs DVB is essentially linear, though it levels off as it approaches values close to the theoretical 100% (Figure 3). However, even these results support our hypothesis concerning a change in the fine pore structure. The inability of the adsorbents with lower DVB contents to fully retain all of the nitrophenol also leads to its early breakthrough and low recovery.

High flow rates are generally desirable for the design of high throughput devices. Figure 4 shows the effect of flow velocity on 1% breakthrough capacity using monolith prepared from 80% DVB. As expected from theory,[2] the curve shows that sorption capacity at the highest flow velocity is only about $^1/_{10}$ of the initial value.

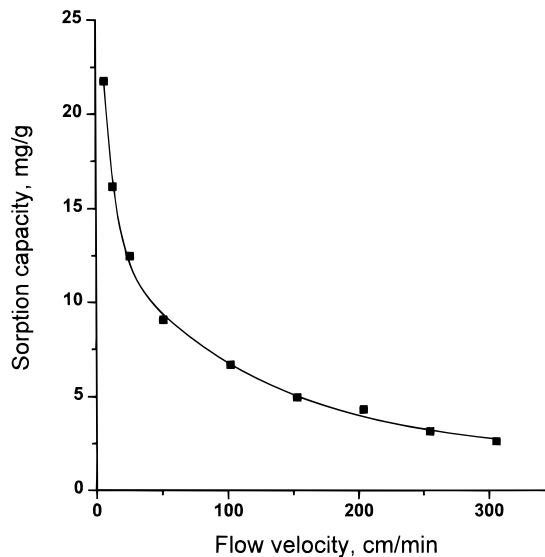**Figure 4.** Effect of flow velocity on sorption capacity of porous poly(ethylstyrene-*co*-divinylbenzene) monolith for 2-nitrophenol from a 10 μg/mL solution; monolith prepared from commercial 80% divinylbenzene in the presence of 8% toluene and 52% dodecanol.

Obviously, shallower breakthrough curves result from the increase in flow velocity, reflecting the increasing effect of mass transfer resistance within the sorbent.[2] Consequently, this leads to both earlier elution of nitrophenol and lower capacity. However, the capacity of 2.6 mg/g achieved at a remarkably high flow velocity of 300 cm/min (150 bed volumes/min or 2.4 mL/min) is still rather good and documents again the excellent mass transfer properties of our new sorbent material. In comparison, the typical flow velocities used with current thin-disk-format SPE media are less than 10 cm/min.[6]

Quite high recoveries of about 85% are achieved in the independent experiments for the entire range of flow velocities used in these experiments. The "missing" 15% of the sorbate is not the result of the insufficient sorption capacity of the material. Indeed, a simple calculation shows that the total sorption capacity of the 20 × 2 mm i.d. cartridge that contains 5.3 mg of monolithic sorbent is 13 μg, as determined at 1% breakthrough for nitrophenol at 300 cm/min. This is more than enough for 100% sorption, since 4.8 mL of the 10 μg/L solution contains only 0.048 μg nitrophenol. Therefore, incomplete recovery likely results from incomplete elution and as a small amount of phenol remains retained within the porous polymer matrix during the time selected for the elution cycle.

Effect of Pore Size on Flow, Capacity, and Recovery. Pore size distribution is the key factor that controls the hydrodynamic properties of the monolithic material. Table 2 shows the variation of pore sizes within the broad range of 0.39−7.59 μm at a constant total pore volume of 1.7 mL/g. These changes were achieved by adjusting the composition of the porogenic mixture.

Resistance to flow through the porous monolithic materials was found to obey approximately the Hagen−Poiseuille law, as it decreased exponentially with an increase in the median pore size.[12] Back-pressure data (Table 2) obtained at a flow velocity of 102 cm/min

Table 2. Pore Properties of Poly(ethylstyrene-*co*-divinylbenzene) Monoliths Prepared by Polymerization of Mixtures Containing Different Percentages of Toluene Coporogen[a]

Porogenic Mixture							
toluene, %	2	4	6	7	8	10	12
decanol, %	58	56	54	53	52	50	48
Pore Properties							
median pore diameter,[b] μm	7.59	4.56	1.99	1.06	0.71	0.39	0.23
pore volume,[b] mL/g	1.65	1.69	1.67	1.73	1.76	1.75	1.70
specific surface area,[c] m²/g	188	206	270	289	329	348	376
back pressure,[d] MPa	2.6	3.4	5.3	6.3	8.2	15.1	na[e]

[a] Polymerization conditions: PEEK cartridge 20 × 1 mm i.d.; divinylbenzene (80% grade) 40 wt %, porogenic mixture 60 wt %, AIBN 1 wt % (with respect to monomer); 70 °C; 24 h. [b] According to mercury intrusion porosimetry. [c] Specific surface area determined from nitrogen adsorption/desorption isotherm. [d] Measured with water at a flow rate of 0.8 mL/min. [e] Back pressure cannot be measured since it exceeds tolerable limits of the equipment (40 MPa).

Figure 6. Effect of pore diameter on sorption capacity at 1% breakthrough and recovery determined for porous poly(ethylstyrene-*co*-divinylbenzene) monoliths with 2-nitrophenol; for polymerization conditions see Table 2; constant flow of 10 μg/mL 2-nitrophenol solution at a velocity of 102 cm/min was used for sorption capacity measurements; for recovery experiments, adsorption from 4.8 mL of a 10 μg/L solution followed by elution with a gradient of acetonitrile in water at a flow velocity of 102 cm/min was used.
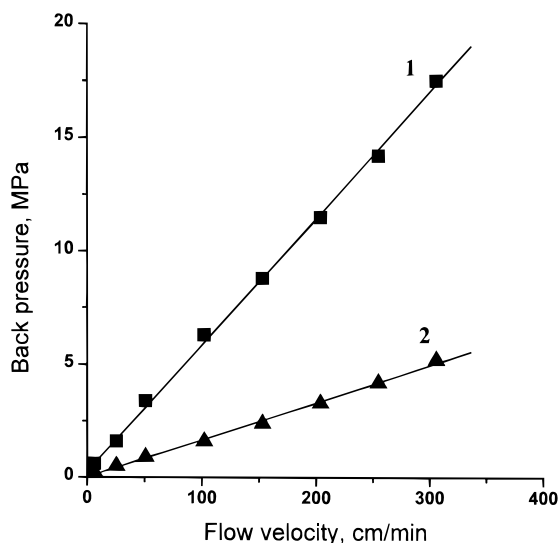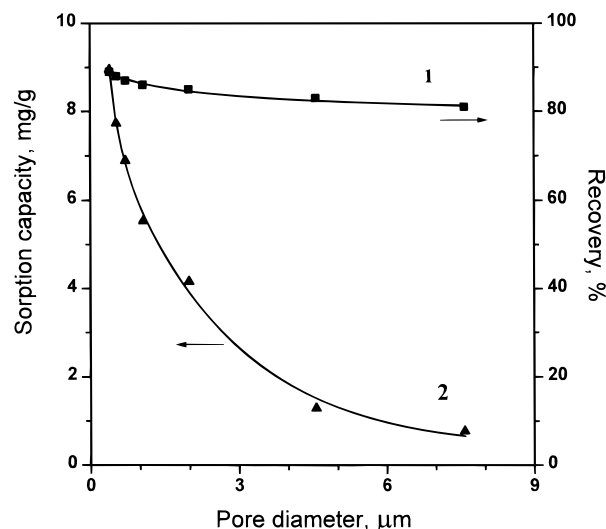

Figure 5. Back pressure of porous poly(ethylstyrene-*co*-divinylbenzene) monolith at different flow rates of water (1) and acetonitrile (2); monolith prepared from commercial divinylbenzene (80% grade) in the presence of 7% toluene and 53% decanol.

confirm this trend. As an example, Figure 5 shows the moderate back pressures for both water and acetonitrile pumped at different flow rates through the monolith with a median pore diameter of 1060 nm. The back pressure remains well below an acceptable value of 20 MPa (2800 psi), even at the very high flow velocity of 300 cm/min, and it is only about one-third of that value if the less viscous solvent acetonitrile is used.

It is clear from Figure 6 that a balance between the flow properties resulting from the presence of large pores and adsorption properties resulting from small pores must be achieved. For example, Figure 6 shows a sharp decrease in sorption capacity in the SPE experiments from 8.9 to 0.77 mg/g, resulting from an increase in median pore diameters from 0.39 to 7.59 μm. Yet, small pores, which lead to both the large surface area and high sorption capacity favored for SPE, result in a higher back pressure within the cartridge. For example, back pressures of 27.5 and 15.1 MPa were observed for a monolith with a 0.39 μm pore size and 348 m²/g surface area at a flow rate of 0.8 mL/min for a 60/40 acetonitrile−water mixture and for water alone, respec-

tively. A monolith prepared with 7% toluene porogen in the polymerization mixture seems to be optimal, as its capacity for absorption of 2-nitrophenol is 5.5 μmol/g while back pressure reaches only 6.3 MPa, even at the high flow velocity of 102 cm/min. In contrast to sorption capacity, nitrophenol recovery does not change very much with pore size (Figure 6). Only a small decrease from 89% recovery for the monolith with the largest surface area to 81% for the monolith with the largest pores was measured.

Monoliths of Poly(2-hydroxyethyl methacrylate-*co*-ethylstyrene-*co*-divinylbenzene). The results shown above demonstrate that monolithic materials consisting of poly(ethylstyrene-*co*-divinylbenzene) can be used successfully for high flow rate applications. For example, the high-speed adsorption of many substituted phenols with a high average recovery of 80% compares favorably to devices containing poly(styrene-*co*-divinylbenzene) beads.[17] Owing to their high hydrophobicity, these sorbents are particularly well-suited for the extraction of nonpolar compounds. In contrast, more polar compounds are less well retained and may even breakthrough during the sorption step. This leads to a decrease in recovery of polar compounds and errors in the quantitation of results.[18,19] For example, a recovery of only 58% is achieved with more polar compounds such as phenol on a divinylbenzene monolith. Similar shortcomings of highly nonpolar surfaces that have also been noted by other groups[18,19] have been attributed to the low wettability of the pore surfaces. Therefore, various approaches to increase the polarity of the polymer

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Table 3. Pore Properties and Capacities of Poly(ethylstyrene-*co*-divinylbenzene) (EST-DVB) and Poly(2-hydroxylethyl methacrylate-*co*-ethylstyrene-*co*-divinylbenzene) (HEMA-EST-DVB) Monoliths[a]

	EST-DVB	HEMA-EST-DVB
median pore diameter,[b] μm	0.53	0.60
pore volume,[b] mL/g	1.76	1.88
specific surface area,[c] m²/g	329	367
capacity (1%), mg/g[d]	7.73	21.4
capacity (10%), mg/g[d]	18.0	23.7
capacity (50%), mg/g[d]	39.0	31.4

[a] Polymerization conditions: divinylbenzene (80% grade) 40 wt %, decanol 51 wt %, toluene 9 wt % (for EST-DVB) or 2-hydroxylethyl methacrylate 4.85 wt %, divinylbenzene (91% grade) 35.2 wt %, tetradecanol 57.5 wt %, toluene 2.5 wt % (for HEMA-EST-DVB), AIBN 1 wt % (with respect to monomers); 70 °C; 24 h. [b] According to mercury intrusion porosimetry. [c] Determined from nitrogen adsorption/desorption isotherm. [d] Adsorption capacity of monoliths determined with a 10 μg/mL aqueous solution of 2-nitrophenol at indicated percent breakthrough at a flow velocity of 102 cm/min.

Table 4. Recovery of Phenols from Porous Poly(ethylstyrene-*co*-divinylbenzene) (EST-DVB) and Poly(2-hydroxylethyl methacrylate-*co*-ethylstyrene-*co*-divinylbenzene) (HEMA-EST-DVB) Monoliths[a]

	recovery, [b]%	
	EST-DVB	HEMA-EST-DVB
phenol	58	92
4-nitrophenol	77	90
2-chlorophenol	82	97
2-nitrophenol	88	96
2,4-dinitrophenol	76	91
2,4-dimethylphenol	85	95
4-chloro-3-methylphenol	88	99
2,4-dichlorophenol	79	97
4,6-dinitro-2-methylphenol	80	94
2,4,6-trichlorophenol	82	96
pentachlorophenol	91	97
average	80	95

[a] For the pore properties of these monoliths, see Table 3. [b] Recovery of phenols was determined at a flow velocity of 102 cm/min.

surface have been tested in order to improve both the wettability and adsorption of polar compounds. For example, excellent adsorption is achieved with the recently introduced cartridges that contain porous poly-(divinylbenzene-*co*-*N*-vinylpyrrolidone) beads.[20] Similarly, the surface of ST-DVB beads has been chemically modified to include sulfonic acid groups[21] and carboxyl,[22] hydroxyl, and acetoxy functionalities,[17,23] or the resin was coated with a hydrophilic polymer.[24,25]

An increase in polarity and wettability of the internal surface of the divinylbenzene monolith can be easily achieved by the addition of a more polar monomer such as HEMA to the polymerization mixture. Unfortunately, previous experiments with typical polymerization mixtures for the preparation of HEMA-containing monoliths failed to afford materials with large pores.[26] Therefore, we developed a new polymerization procedure that allows the preparation of more polar monolithic materials containing significant amounts of hydrophilic HEMA. This requires the use of a porogenic mixture containing a higher aliphatic alcohol such as tetradecanol with only a small amount of toluene and 91% grade divinylbenzene (Table 4).

SPE tests were run again to verify the effect of the incorporated HEMA on the surface chemistry. Figure 7 shows the breakthrough curve for a poly(2-hydroxyethyl methacrylate-*co*-ethylstyrene-*co*-divinylbenzene) monolith (Table 4) compared to that of a poly(ethylstyrene-*co*-divinylbenzene) monolith with similar pore properties. The more hydrophilic HEMA monolith affords better sorption kinetics, leading to both a much steeper breakthrough curve (curve 1, Figure 6) and a capacity 3-fold larger at 1% breakthrough. This results from both the improved wettability and the concomitant

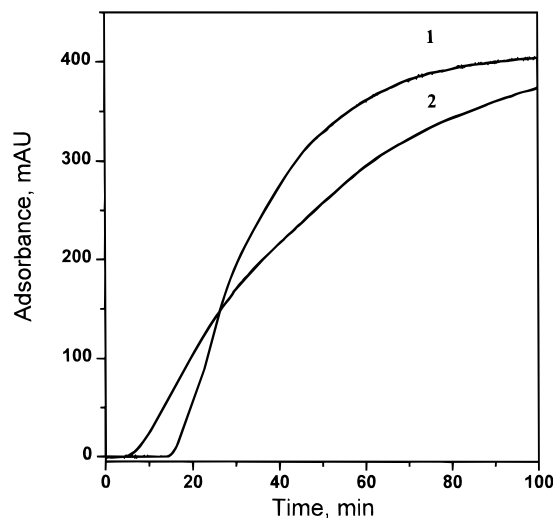**Figure 7.** Break through curves determined using a 10 μg/mL aqueous solution of 2-nitrophenol for poly(ethylstyrene-*co*-divinylbenzene) (curve 2) and poly(2-hydroxylethyl methacrylate-*co*-ethylstyrene-*co*-divinylbenzene) monoliths (curve 1) at a flow velocity of 102 cm/min; for polymerization conditions and material properties, see Table 3.

increase in mass transfer rate. In contrast, the breakthrough profile for the second monolith without HEMA is shallower and crosses curve 1 at about 30% breakthrough. As a result, the overall sorption capacity of the poly(ethylstyrene-*co*-divinylbenzene) monolith is somewhat larger than that of poly(2-hydroxyethyl methacrylate-*co*-ethylstyrene-*co*-divinylbenzene). Table 4 shows the capacities for 2-nitrophenol at different percentages of breakthrough for both monoliths.

Following the encouraging results with the sorption of 2-nitrophenol, comparative studies of recovery for a whole range of different phenols was carried out with the poly(2-hydroxyethyl methacrylate-*co*-ethylstyrene-*co*-divinylbenzene) and the matching poly(ethylstyrene-*co*-divinylbenzene). Table 4 summarizes the results that clearly demonstrate the generally higher recoveries obtained with the more polar sorbent. This is particularly true for phenol, for which the recovery from the HEMA-based monolith is almost twice as high (95 vs 58%). The average recovery calculated for all 11 phenols

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is close to the theoretical value and reaches a remarkable value of 95%. This is 15% more than the average value determined for the nonpolar DVB monolith.

Conclusion

Variations in polymerization conditions that play on the percentage and grade of cross-linking monomer, the composition of the porogenic solvent mixture, and the addition of functional monomer may be used to obtain monolithic materials with large surface areas and excellent hydrodynamic properties. The fine control of polymerization conditions allows the design of novel monolithic materials that are well-suited for the preparation of SPE devices that require both high flow rates and tailored selectivities. Monolithic materials with optimized pore properties and surface chemistry exhibit both excellent capacity and high recovery for adsorption and preconcentration of compounds from highly dilute solutions. Convective flow through the pores of the material substantially improves mass transfer and accelerates the sorption process. The high recovery of polar organic compounds at high flow velocities confirms the great potential of monolithic porous materials for use in high throughput sample preparation and purification using the solid-phase extraction approach. This makes our new materials well-suited for use in combinatorial chemistry, drug screening, clinical testing, and environmental analysis.

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