Chem. Mater. **2006,** *18,* 6308−6315

Epoxy-Based Monoliths. A Novel Hydrophilic Separation Material for Liquid Chromatography of Biomolecules

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Received March 17, 2006. Revised Manuscript Received September 29, 2006

In our efforts to develop novel hydrophilic monolithic porous materials for use as supports in liquid chromatographic separation of proteins, polymers based on epoxy monomers and diamines as curing agents were synthesized. The epoxy dispersed phase was emulsified in an aqueous phase containing the amine with the aid of a nonionic polymeric surfactant, and the resulting emulsions were thermally polymerized. Various factors, namely, the type of epoxy component, levels of reactants, type and concentration of diluents, and curing procedures, were studied to obtain suitable morphology and adequate mechanical properties for their intended use. Characterization of their morphologies and porous properties was done using scanning electron microscopy, nitrogen adsorption/desorption measurement (BET method), mercury intrusion porosimetry, and X-ray photoelectron spectroscopy.

Introduction

Monolithic materials have gained substantial interest as chromatography separation media and supports for flow-through systems, e.g., immobilized catalysts, adsorbents, and sensors.[1] For these applications macroporous monolith media are characterized by micrometer-sized pores responsible for convective flow and smaller pores in the nanometer size range, which contribute mainly to the total surface area—a factor vital for the sorption capacity for small solutes. While silica-based monoliths have proven excellent column efficiencies in separations of both small molecules[2] and macromolecules,[3] the organic polymer-based counterparts have found their use mainly in biomolecule technology[4−6] and for separation of synthetic macromolecules.[7,8] Typically, the macropores of organic polymer-based monoliths are more irregular, and micropores in the low nanometer size range cause low column efficiency, especially with small molecules. Macromolecules are sterically excluded from entering such micropores, and therefore, their separations are less affected by their existence.

The preparation of organic polymer-based monoliths is quite simple. In the majority of cases, it is based on free radical polymerization of vinylic monomers, whereby a chromatography column is filled with a mixture of monofunctional monomer(s), polyfunctional monomer(s) as cross-linker(s), an initiator, and a set of porogen solvents with suitable Θ values relative to the polymer formed. The polymerization is often initiated thermally,[9,10] by UV radiation at lower temperature,[11] or more recently also by highly penetrating γ radiation.[12] The resulting porous materials consist of mesoporous microglobules aggregated in clusters, interspaced by macropores that are occupied during preparation by the porogen, which is the inferior solvent for the polymer when more than a single porogenic solvent is used. Removal of the porogens by flushing with an appropriate solvent and drying the material results in a permanently porous bed with two pore families, large interconnecting pores for convective flow and smaller pores between and within the microglobules. Monolithic materials derived from vinylic polymers [typically copolymers of (meth)acrylic acid or styrene and their derivatives] have been extensively studied and successfully applied to biomolecule separations.[13−15]

The majority of the monolith research has been focused on free radical polymerization of vinyl polymers, and only a few attempts have been made to investigate other polymer systems. The most widely studied system based on nonradical polymerization chemistries is ring-opening metathesis polymerization.[16] Monoliths have also been prepared from

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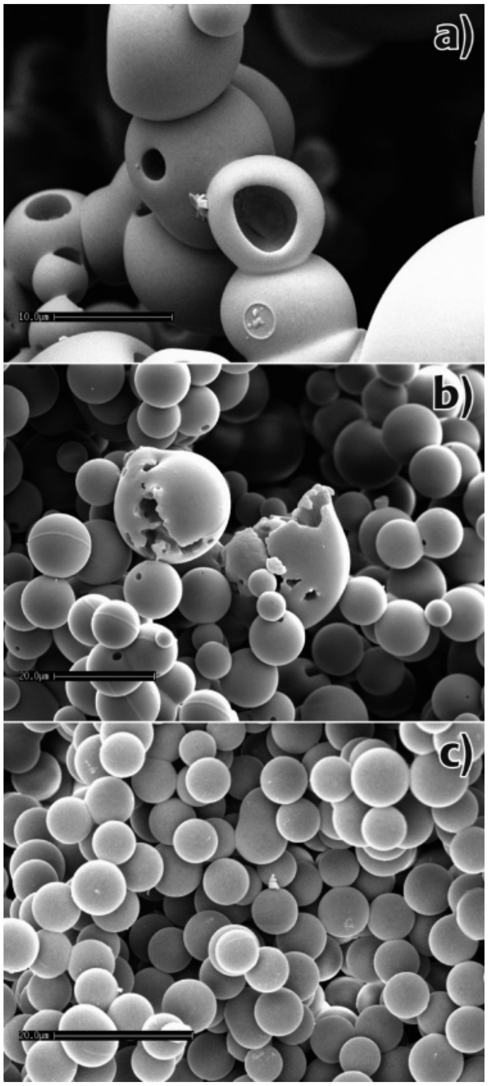

Figure 1. SEM micrographs from scouting syntheses of epoxy monoliths from emulsions containing 10% (w/w) epoxy phase dispersed by various surfactants into an aqueous phase containing 0.1 M $CaCl_2$ and a stoichiometric (two epoxy groups per amine group) amount of DAH: (a) BADGE: BDGE = 40:60 (w/w), with 15% (w/w) Pluronic L101, cured at 60 °C for 36 h; (b) BDGE with 20% (w/w) Span 80, cured at 60 °C for 48 h; (c) BDGE with 10% (w/w) Pluronic P123, cured at 70 and 80 °C, each step for 24 h. All emulsions were placed in the oven for curing directly after mixing.

urea–formaldehyde resins.[17] Hosoya and co-workers[18] recently presented a brief report on the preparation of epoxy-based monoliths possessing highly ordered structures by phase separation polymerization in polyethylene glycol media for use as separation materials. Polymers derived from epoxide monomers and polyamine curing agents possess an inherent hydrophilicity, a valuable property of supports for most proteins, peptides, and nucleic acids, and also afford possibilities of modifications through residual surface epoxide and amine groups after curing. The materials are, therefore, of interest in our efforts to find better separation supports for biomolecules, especially when preservation of their native states after separation is of great concern.

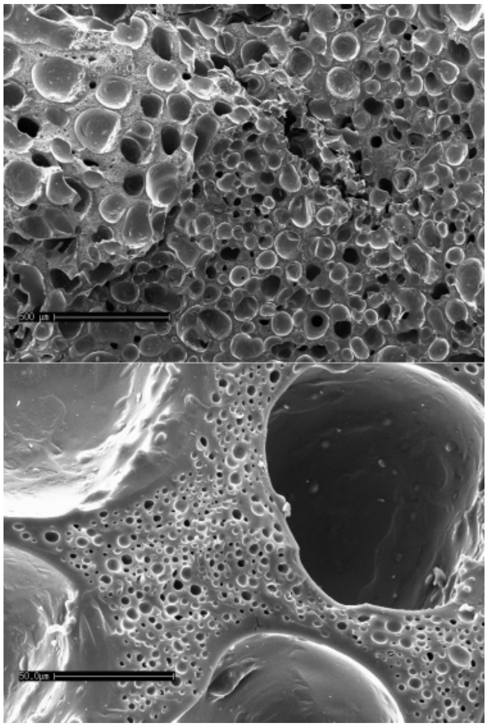

Figure 2. SEM micrographs at two different magnifications of a monolith, with the epoxy polymer forming the continuous phase, made from 30% (w/w) BDGE cured by DAH (80% of the stoichiometric amount), cooled by cold water directly after emulsification, and kept at room temperature overnight before thermal polymerization.

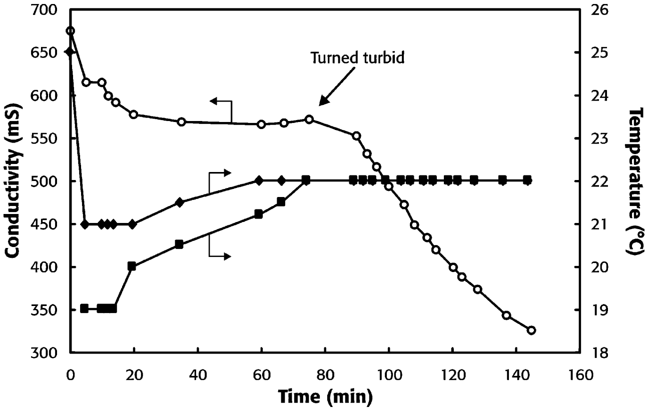

Figure 3. Measurements of the electrolytic conductivity in the polymerization mixture and temperatures in the middle of the polymerization vessel (◆) and in the water bath (■) during the prepolymerization stage for a monolith based on 30% (w/w) BDGE with 60% of the stoichiometric amount of DAH and Pluronic P123 (10% of the weight of the organic phase) as the surfactant.

In this paper we present our first series of attempts to prepare macroporous epoxy-based monoliths intended for use as stationary phases for liquid chromatography. The approach chosen is emulsification of a dispersed phase composed of epoxy monomers and organic solvents as diluents and an aqueous phase containing a nonionic surfactant and a diamine curing agent with $CaCl_2$ as the electrolyte. Polymerization takes place thermally at controlled temperature. The porosity of the resulting monoliths is established by the aqueous phase and the organic diluents in the dispersed phase.

Experimental Section

Materials. The epoxy components 1,4-butanediol diglycidyl ether (BDGE) and bisphenol A diglycidyl ether (BADGE; epoxy equivalent weight of 172–176), polyTHFs with molecular weights

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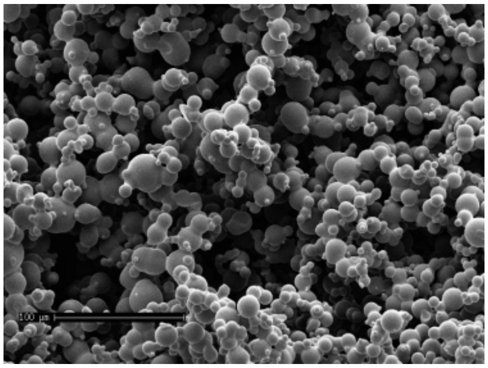

Figure 4. SEM micrograph of an epoxy monolith with 20% (w/w) neat BDGE or 30% dispersed phase containing DEGDE as the diluent with BDGE:DEGDE = 2:1, cured by DAH (80% of the stoichiometric amount).

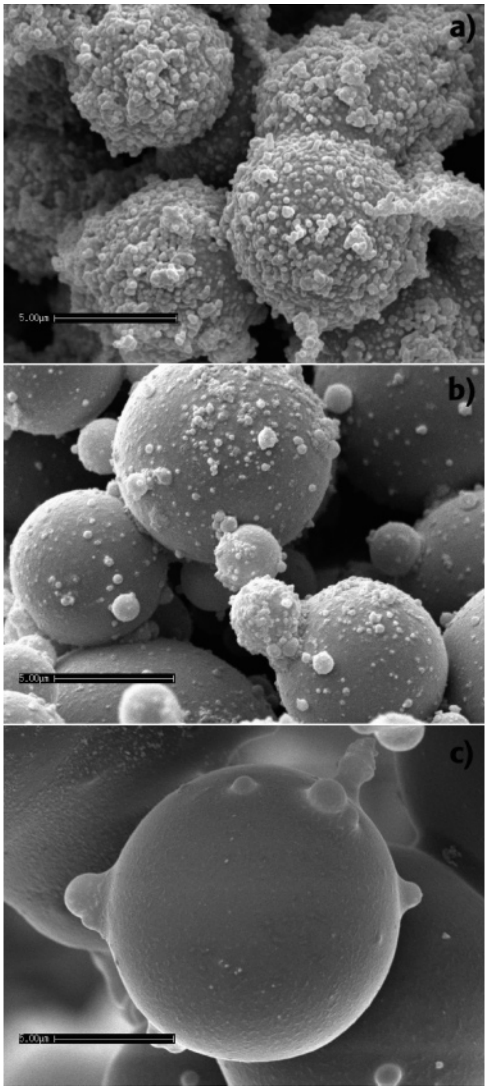

Figure 5. SEM micrographs of epoxy monoliths with 30% (w/w) neat epoxy mixture (BDGE:BADGE = 70:30, w/w) or 45% dispersed phase including diluents (epoxy mixture:diluent = 2:1, w/w), cured by DAH (80% of the stoichiometric amount). Diluents in the dispersed phases were (a) DEGDE, (b) DEGDB, and (c) polyTHF 2900.

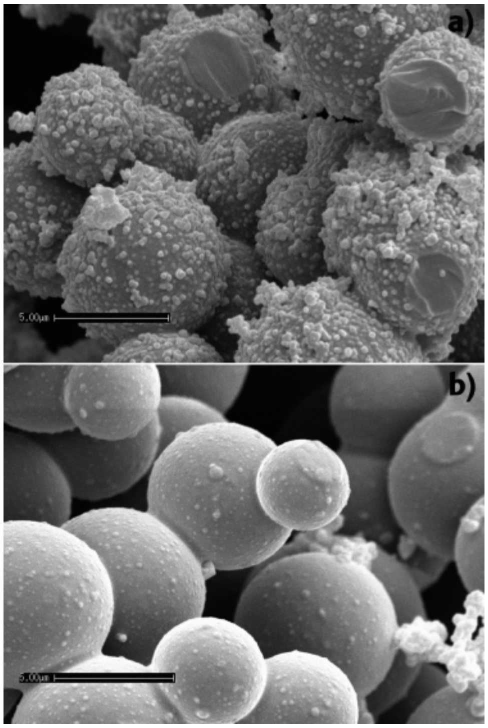

Figure 6. Epoxy monolith with 30% (w/w) neat epoxy mixture (BDGE: BADGE = 70:30, w/w), cured by DAH (80% of the stoichiometric amount): (a) DEGDE in the dispersed phase (epoxy mixture:DEGDE = 2:1, w/w); (b) same amount of DEGDE as in (a), but it was dissolved in the aqueous phase.

of 250, 650, 1400, and 2900, and Span 80 (sorbitan monooleate) were purchased from Aldrich (Schnelldorf, Germany). The diluents diethylene glycol dibutyl ether (DEGDB), diethylene glycol diethyl ether (DEGDE), diethylamine (DEA), and the amine component 1,6-diaminohexane (DAH) were supplied by Fluka (Buchs, Switzerland). The surfactants Pluronic L101 and Pluronic P123, poly[ethylene oxide−propylene oxide−ethylene oxide] block copolymers of compositions $(EO)_4-(PO)_{59}-(EO)_4$ and $(EO)_{20}-(PO)_{70}-(EO)_{20}$, respectively, were products of BASF (North Mount Olive, NJ), and calcium chloride (p.a.) was from Merck (Darmstadt, Germany). All chemicals were used as received. Water was purified by an UltraQ system (Millipore, Bedford, MA).

Monolith Preparation. Dispersed phases containing epoxy monomers, surfactant, and an organic diluent were first well mixed before subsequent addition to and mixing with the aqueous phases, composed of the DAH curing reagent in 0.1 M aqueous $CaCl_2$. Emulsification was conducted manually in disposable polypropylene (PP) syringes. Appropriate volumes of the epoxy and amine component mixtures were taken up in separate syringes to a combined volume corresponding to the volume of a single syringe (2 or 5 mL). The syringes were then connected head to head by a PP Luer connector (model FTLLC, Value Plastic, Ft. Collins, CO), with care taken to avoid trapping air bubbles in the connector. Mixing was accomplished by pushing the plungers of the interconnected syringes back and forth 4−5 times in rapid succession. The shear force by passage through the connector orifice was sufficient to create an emulsion after a few passages. The syringes containing the emulsions were thereafter capped. Emulsions containing high epoxy loadings (above 20%) were left at room temperature overnight for a prepolymerization step prior to the final curing. In some experiments the syringes were also placed in cold tap water (∼4−8 °C) for 4 h to prevent phase separation due to rapid heating caused by the autocatalytic nature of the epoxy/amine reaction. Final curing took place in a circulating air oven with a temperature program of 60 °C for 24 h and 80 °C for another 4 h, unless otherwise stated. The surfactant remaining on the monolithic polymers was removed by Soxhlet extraction with methanol for 24 h, and the final products were dried in a vacuum oven at ∼40 °C before being subjected to further characterizations.

In one experiment, the temperature and conductivity of the emulsion were monitored during the precuring step to determine the course of the reaction. A small hole was made in the center of

Table 1. Experimental Design for Shrinkage in the Dry and Reswollen State

						diameter change over a dry/reswell cycle[d] (%)		
expt	run no.	[BADGE],[a] % (w/w)	[DAH],[b] % (w/w)	dispersed phase concn,[c] % (w/w)	apperance after curing	dry state	water	methanol
N1	1	10	60	30	homogeneous, yellow	13.7	3.2	1.6
N2	8	50	60	30	almost homogeneous	9.7	3.9	3.6
N3	10	10	80	30	homogeneous, yellow	15.3	6.3	3.6
N4	4	50	80	30	homogeneous, white	13.3	9.0	3.6
N5	7	10	60	45	phase separated, yellow[e]	N/A	N/A	N/A
N6	9	50	60	45	homogeneous, white	10.5	4.9	3.6
N7	5	10	80	45	phase separated, yellow[e]	N/A	N/A	N/A
N8	3	50	80	45	homogeneous, white	14.9	14.5	3.6
N9	2	30	70	37.5	homogeneous, white	16.5	10.6	2.4
N10	11	30	70	37.5	homogeneous, white	16.5	10.1	1.6
N11	6	30	70	37.5	homogeneous, white	16.1	9.5	3.6

[a] Percentage of BADGE in the epoxy component. [b] Percentage of the stoichiometric ratio (two epoxy groups per amine). [c] Percentage of the total emulsion weight. [d] Percentage decrease in diameter after drying and reswelling in water or methanol. [e] Syntheses discarded as “phase separated” were not entirely separated but substantially harder at the bottom of the syringe compared to the top.

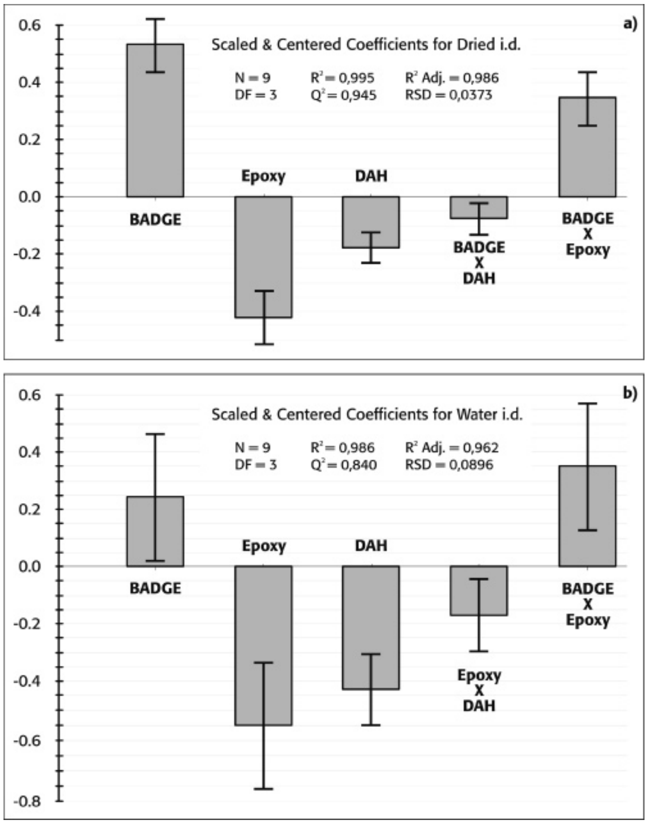

Figure 7. Multivariate regression analysis for significant factors for dry-state and water-swollen-state shrinkage.

the rubber septum part of a 5 mL syringe plunger, and two 0.4 mm diameter stainless steel wires were pushed through the septum, parallel to each other and ∼5 mm apart on opposite sides of the drilled hole, so that they protruded ∼10 mm into the syringe. When the mixing was accomplished, the emulsion was transferred to another syringe; the rubber septum holding the electrodes was fitted in the syringe, and a K type thermocouple was immersed in the emulsion through the hole in the center of the septum, so that the sensing part of the thermocouple was situated as close to the center of the syringe as possible. The conductivity electrodes were then connected to a laboratory conductivity meter, and a digital multimeter was used for recording the temperature by means of the thermocouple. No attempts were made to calibrate the conductivity setup since the intention was only to measure changes taking place over the course of the reaction.

Characterization of the Monolithic Polymers. Surface areas were determined by nitrogen gas absorption according to the BET principle, using a Micromeritics FlowSorb II 2300 (Norcross, GA). The instrument was calibrated by injecting 1 mL of nitrogen gas at room temperature and adjusting the surface area readings to the corresponding value at the same temperature and pressure as the actual ones.

The pore size distribution was determined by mercury intrusion porosimetry (MIP) with a Micromeritics Autopore II and was performed in both low-pressure and high-pressure mode, with results combined to obtain the overall distribution.

The morphologies of the epoxy monoliths were visualized by scanning electron microscopy. The samples were placed on sticky carbon foils (used to increase conductivity) attached to standard aluminum specimen stubs. Two successive layers of carbon and gold of ∼50 Å each were coated onto the samples using a combined system of an Edwards (Crawley, U.K.) model S150A sputter coating unit and a modified Edwards E14 vacuum unit, incorporating an automatic tilting and rotation device. Microscopic analysis of all samples was carried out by an S-360 iXP scanning electron microscope (Leica Cambridge Ltd., Cambridge, U.K.) operated at 10 kV, 100 pA probe current, and 0° tilt angle. Final images were recorded from randomly chosen areas at the magnification indicated in each SEM image.

Surface elemental analysis was performed by X-ray photoelectron spectroscopy (XPS), and spectra were recorded with a Kratos Axis Ultra electron spectrometer using a monochromated Al Kα source operated at 150 W. To compensate for surface charging, a low-energy electron gun was used. The existence of elements on the material surfaces was confirmed by matching the experimentally determined binding energies with corresponding values taken from the NIST XPS database.

The multivariate evaluation of significant parameters in the recovered diameter experiment was done using MODDE 6.0 (Umetrics, Umeå, Sweden) software. The coefficient plots shown in Figure 7 were modeled in the multilinear regression mode.

Results and Discussion

In preliminary studies we tested several surfactants in attempts to find a system where the epoxy phase was dispersed in the aqueous amine phase, producing a monolithic structure. Another factor that was scouted for was the curing temperature and time. A representative subset of the experiments that were carried out is accounted for below, with Figure 1 showing typical samples of the early monolithic

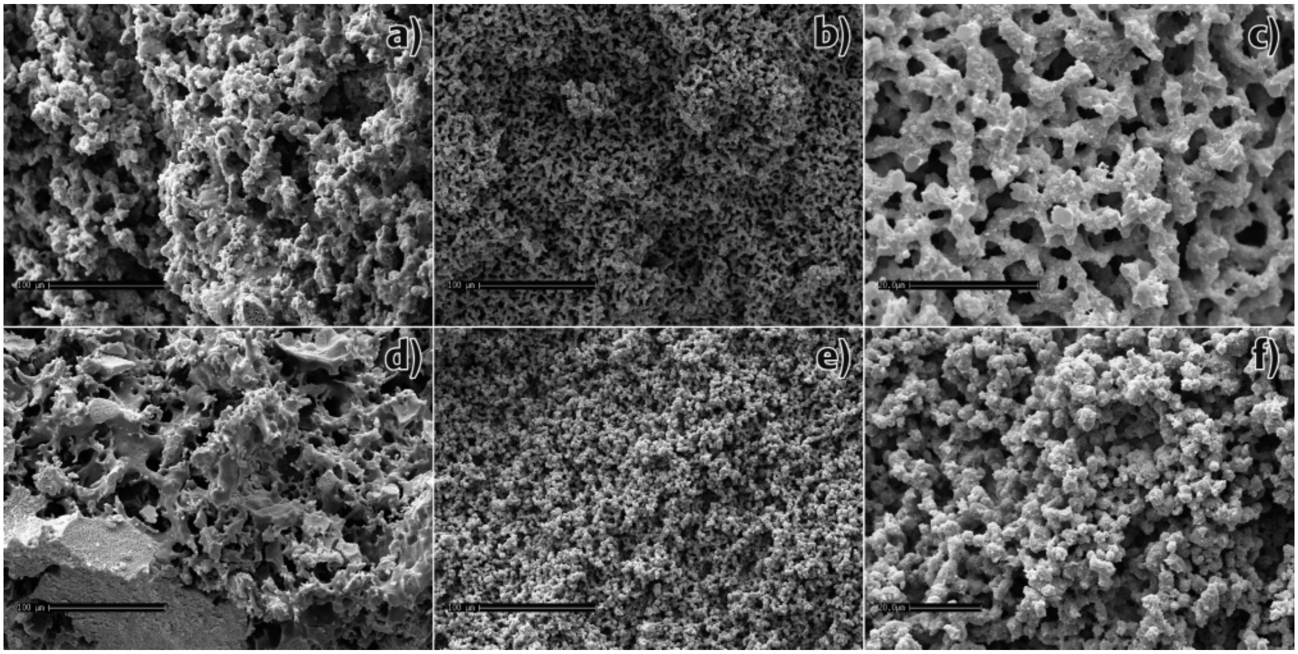

Figure 8. SEM micrographs of epoxy monoliths with 30% (w/w) neat epoxy mixture or 45% dispersed phase (epoxy mixture:DEGDB = 2:1, w/w), DEGDE in the aqueous phase as the cosurfactant (DEGDE:aqueous phase = 1:4): (a) BDGE:BADGE = 70:30, w/w, DAH (60% of the stoichiometric amount); (b) BDGE:BADGE = 50:50, w/w, DAH (60% of the stoichiometric amount) at a magnification of 327×; (c) as in (b), but at 2000× magnification; (d) BDGE:BADGE = 70:30, w/w, DAH (80% of the stoichiometric amount); (e) BDGE:BADGE = 50:50, w/w, DAH (80% of the stoichiometric amount); (f) as in (e), but at 2000× magnification.

Table 2. Surface Areas of Epoxy Monoliths Prepared with Different Diluents

sample description			
BADGE:BDGE, % (w/w)	diluent	dispersed epoxy phase concn,[a] %	surface area (m^2/g)
0:100	DEGDE	20	0.6
30:70	DEGDE	25	1.06
50:50	DEGDE	25	1.26
50:50	DEGDB	30	1.74
50:50	DEGDB[b]	30	1.85
30:70	polyTHF 1400	25	0.92
30:70	polyTHF 2900	25	0.4

[a] Dispersed epoxy phase comprised of an epoxy mixture, diluent, and surfactant. [b] In addition, 18% DEGDE (w/w) was added to the aqueous phase (SEM images are in Figure 8b,c). No DEGDE was added to the other samples.

Table 3. XPS Analysis of the DEA-Functionalized Epoxy Monolith[a]

peak	bond energy (±0.1 eV)	chemical structure	atomic concn, %
N $1s_2$	400.1	$C-NH-C$	6.48
N $1s_3$	402.0	$C-NH_2^+-C$	0.83
N $1s_1$	399.1	$C-NH_2$	1.15
Si $2p_{3/2}$	102.1	$[-Si(Me)_2-O-]_n$	1.43
Si $2p_{1/2}$	102.7	$[-Si(Me)_2-O-]$	0.71

[a] Prepared from an epoxy mixture (70:30 = BDGE:BADGE) without a diluent in the epoxy phase and an aqueous phase containing DEGDE, DAH, and $CaCl_2$.

structures. Figure 1a shows a close-up of the elements making up the monolith for a BADGE/BDGE mixture with Pluronic L101 as the surfactant and a stoichiometric amount of DAH in the aqueous phase, which had been thermally cured directly after mixing. The interfacial polymerization process produced spheres with a polymeric shell that subsequently ruptured. Their internal cavities, visible in the close-up, appear to be due to a collapse of the shell, possibly during the sample preparation for SEM. The nature of the interfacial polymerization can also be seen in the fracture surface in the lower part of Figure 1a, where the connecting point between the particles that have been snapped apart during the preparation of the sample has the form of a crater and lacks the characteristic roughness of a fracture surface. It was obvious that the curing conditions were insufficient, since the particle cores had been able to empty their presumably still liquid content. The polydispersity of the particle phase was also substantial with Pluronic L101, so another polymeric surfactant was sought.

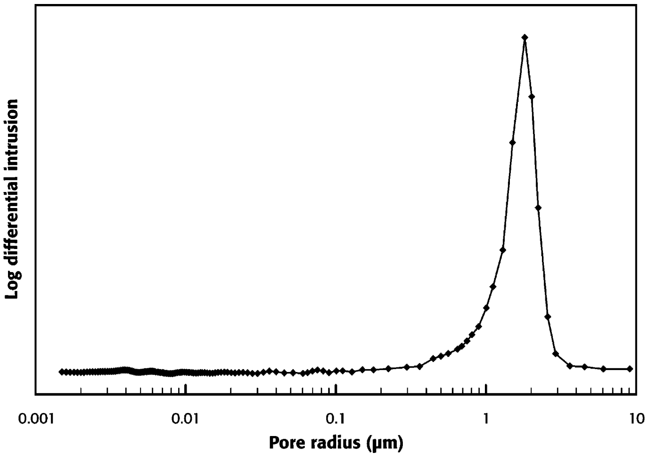

Figure 9. Mercury intrusion porosimetry characterization of the epoxy monolith shown in Figure 8b,c.

The next dispersing agent that was used was Span 80, producing the material shown in Figure 1b. The polydispersity of the particles was high, with the larger spheres (seen in the center) appearing to be fractured and collapsed, whereas many of those of intermediate size had an equatorial crack indication, evident in the lower left part of Figure 1b. Span 80 was therefore also discarded.

The next surfactant tested in the scouting experiments was Pluronic P123, which was found to be capable of forming a finely dispersed emulsion with BDGE (Figure 1c). The hollow and fractured spheres that are seen in Figure 1a,b were absent, the diameter of the spherical entities was in the range of HPLC packing particles (7−10 μm), and the monodispersity was significantly better than with the other surfactants tested. Despite a significant shrinkage in the dried state and insufficient mechanical strength, the BDGE/P123 material had high hydrophilicity and an open structure which gave rise to high permeability, which are both attractive features. It should be noted that due to shrinkage and a low degree of connectivity the particles may appear more closely packed in the SEM images than they actually were in the wet state. The monomer loading in this synthesis was low, and since we were aiming toward monolithic sorbents and not monodisperse particles, we needed a higher extent of fusion between spheres, characteristic of monolithic materials. Efforts were therefore made to achieve these goals by manipulating a number of factors we believed to be most likely to affect the polymer morphology, e.g., emulsion composition, emulsification, and polymerization procedures. The first and most obvious step was to increase the organic loading.

When the level of the epoxy dispersed phase was increased to 25% (w/w) of the total emulsion and higher, with correspondingly larger amounts of the diamine in an aqueous phase of lower volume, the heat released by the polymerization accelerated the reaction and resulted in phase separation. Cooling the two phases prior to mixing was not possible because of an excessive viscosity of the epoxy phase. Attempts were therefore made to cool the emulsions immediately after preparation by immersing the syringes into a beaker with cold tap water and letting them stay there overnight before starting the final curing. This prevented a catastrophic phase separation, but emulsions of the water-in-oil (W/O) type with a bimodal distribution of dispersed aqueous-phase droplet sizes were obtained instead of oil-in-water (O/W) emulsions, with a representative morphology shown in Figure 2. Although the cooling decreased the temperature of the reaction medium to such an extent that an accelerating reaction was largely prevented (Figure 3), the phase inversion was believed to be a consequence of an increase in hydrophobicity of the $(PO)_m$ block,[19] which made W/O emulsions more favored during the unavoidable temperature increase transient that followed immediately upon mixing. The course of the reaction is evident from the difference in temperature between the center of the syringe and the surrounding water bath; after 70 min the temperature difference had disappeared, and at the same time the mixture turned visibly turbid. We conclude that, at this stage, the reaction had progressed to a point where most of the epoxy phase in the interfacial regions had reacted and diffusion of amine into the epoxy phase was severely impeded by formation of an interfacial membrane. Unfortunately, it was not possible to monitor the temperature immediately after mixing, as fitting the thermocouple/electrode assembly took a few minutes. It is still clear from the first datum point that the initial reaction is both fast and exothermal. Cooling was successful for preventing total breakup of the emulsion, but the hydrophile−lipophile balance (HLB) value of the surfactant was changed beyond the point of phase inversion. Absence of a connected pore system prevented the use of the resulting materials in flow-through applications.

Epoxy Monoliths Based on the Aliphatic Epoxy BDGE with Different Diluents. To increase the dispersed phase loading without causing a thermal runaway, and at the same time create a monolith with a mesoporous structure, a number of different organic compounds ranging from small molecules (DEGDB and DEGDE) to polymers (polyTHFs with MWs of 250, 650, 1400, and 2900) were tested as inert diluents in the dispersed epoxy phase. The ratio of epoxy to diluent was maintained at 2:1 (w/w) throughout the experiments. Simultaneously, the DAH curing reagent level was also reduced to 80% of the stoichiometric amount, and the emulsions were kept at room temperature overnight before thermal curing to slow the reaction. With emulsions containing 20% BDGE in the dispersed phase, stable O/W emulsions and homogeneous monolithic polymers could only be obtained when neat BDGE was used, or when polyTHF 650, polyTHF 1400, or DEGDE was added to the epoxy as a diluent in a 2:1 (w/w) ratio. When the materials in Figures 1c and 4 are compared, it is obvious that the connectivity that was almost absent in Figure 1c had become excessive in Figure 4. However, the regularity of the interconnected spheres was severely distorted, with sizes varying from a few to tens of micrometers. All the products shrunk upon drying and swelled again quite readily in polar solvents (methanol, ethanol, and acetone were tested) to regain almost their original size and shape. The materials were also reswollen by water, but to a lower extent than by organic solvents. All the monoliths produced were furthermore quite elastic, even after a dry/swell cycle. The monoliths produced with DEGDB, polyTHF 650, and polyTHF 2900 as diluents suffered from slight phase separation, evident from an aqueous layer on top of the emulsion after the initial polymerization, and a gradient of decreasing polymer density from bottom to top was evident after curing. In the case of polyTHF 250, the material obtained was derived from a W/O emulsion and had a closed cell structure of the type shown in Figure 2. The shorter $[-(CH_2)_4O-]_n$ hydrophobic segment and the high level (>30%) of polyTHF 250 in the epoxy phase could account for its function as a W/O emulsifier, while in polyTHFs with higher molecular weights the hydrophobic segments are too dominant to allow the terminal hydroxyls to express interfacial activities. It is likely that 20% of neat BDGE or 30% of the dispersed phase (including diluents in a 2:1 ratio) was close to the upper limit for stable emulsions. Attempts to use the mentioned diluents at 25% BDGE loading all failed, due to either phase inversion or phase separation.

Epoxy Monoliths Based on Mixtures of the Aliphatic BDGE and Aromatic BADGE Epoxies with Diluents. A further attempt to raise the organic loading and to enhance the mechanical properties of the polymers was to partly replace the aliphatic epoxy BDGE by BADGE, which is usually used to prepare rigid epoxy polymers. In addition, BADGE has a higher epoxy equivalent weight compared to BDGE (174 vs 101) and therefore required less diamine on the basis of weight. It should consequently lead to less heat

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[19] Mortensen, K. *Colloids Surf., A* **2001**, *183−185*, 277−292.

formation from the exothermic polymerization reaction per unit weight of the dispersed phase. In fact, not only did BADGE produce materials that were less elastic, but it was also possible to produce more stable emulsions so that levels of 25−30% neat epoxy or 37.5−45% in the dispersed phase could be reached with all diluents, and the first polymerization step could be done without cooling below room temperature.

When the levels of BADGE were increased, the surfaces of the spherical entities of materials became rougher, with nodular elements protruding from the surface when DEGDE and polyTHF 650 were used as diluents (Figure 5a). In the case of polyTHF 1400 and 2900 diluents, the particles were larger and the smooth appearance of the surfaces hardly changed (Figure 5c). The surface morphology with DEGDB as the diluent was somewhere in the middle of the two extremes (Figure 5b). This could be provisionally explained by the more polar diluents DEGDE and polyTHF 650 being present at higher levels in the skin formed in the initial interfacial polymerization, causing leakage of unreacted epoxy monomer into the amine-containing aqueous phase during the curing process.

Epoxy Monoliths Based on BDGE and BADGE with DEGDE. On the basis of SEM observations from numerous screening experiments not accounted for here, DEGDE seemed to produce spherical entities with more narrow size distribution than other diluents. Besides, the presence of this low molecular weight diluent produced a dispersed phase of relatively low viscosity, which facilitated the initial mixing process. DEGDE could, in contrast to DEGDB, be dissolved at the appropriate concentration in both the dispersed and the aqueous phases, and it was interesting to note that DEGDE had an ability to stabilize the emulsions regardless of which phase it was added to. High epoxy loadings could consequently be achieved. The stabilizing effect of DEGDE could be a result of the higher density of ether oxygens (hydrogen-bonding acceptors) in the molecule compared to that of DEGDB and the polyTHFs. Cyclic and linear ethers have been well documented as retarding agents for polyaddition reaction of epoxy resins by polyamines.[20] The appearance of the surfaces of the materials that resulted from adding DEGDE to the epoxy phase and to the aqueous phase (Figure 6) strengthens the assumption that the roughness seen in Figure 5a was due to migration of DEGDE from the epoxy phase into the aqueous amine phase.

As mentioned in the initial part of the discussion, shrinkage is an issue when the materials are dried or exposed to different solvents. An experimental design was therefore made to determine the critical parameters for maintaining the dimensions over a dry/swell cycle. On the basis of scouting experiments, the factors chosen as variables were the percentage of BADGE in the BADGE/BDGE epoxy mixture, the percentage of DAH compared to the stoichiometric amounts (calculated on the basis of the epoxy equivalent), and the dispersed phase as a percentage of the total emulsion weight. The design and the coefficient plot of the multiple linear least-squares regression are summarized in Table 1 and Figure 7.

The results show that the epoxy monoliths were swollen well in methanol and regained almost the original dimensions, regardless of the changes in composition of the emulsions; this is indicated by a poor model quality (data not presented). Their dimensions in both the dry state and the water-reswollen state were controlled to certain extents by the investigated factors. Regarding the impact direction of the factors, the models for the dry and water-swollen states had similar patterns (Figure 7), except for the composite interaction terms BADGE × DAH (Figure 7a) and EPOXY × DAH (Figure 7b). The uncertainties of the model coefficients were higher for the water-swollen diameter than those of the dry one; this could be accounted for by high uncertainties of measuring the monolith diameters due to the elasticity of the wet materials. As can be seen in the coefficient plots, higher amounts of epoxy and DAH led to more shrinkage in both cases; this seems to be rational because higher levels of DAH should result in higher cross-linking and more epoxy phase was likely to cause more fusion between the spherical elements. BADGE led to less shrinkage in the dry state, which could be the result of harder resins. Moreover, emulsions with high BADGE levels were more stable than those with less BADGE. Consequently, polymerization of these emulsions produced monoliths composed mainly of spherical elements with low connection or less fusion. The model also showed that the effect of higher BADGE levels was significant for the regained diameter in the water-swollen state, but less so than for the shrinkage in the dry state. However, it could be concluded that the extent of swelling in water from the dry state decreased as the level of the more hydrophobic epoxy BADGE increased.

Although the shrinkage study gave us hints to avoid excessive changes in the dimensions of the epoxy monoliths, other factors such as the regularity of the structure and the mechanical properties caused by fusion between the elements making up the monoliths should also be taken into consideration in the development of materials used as supports for liquid chromatography.

Epoxy Monoliths Based on BDGE and BADGE Epoxy Resin with DEGDE and DEGDB as Diluents. By serendipity it was discovered that an earlier onset of curing drastically changed the morphology of the monolithic epoxy materials. Subsequent experiments also showed that similar effects could be produced by altering the proportion of the aromatic epoxy resin BADGE in the epoxy mixtures, the temperature program during curing, and also the quantity of DAH. On the basis of a series of scouting experiments, a study was therefore designed where (i) DEGDB was used as the diluent in the dispersed phase to increase the proportion of epoxy, (ii) DEGDE dissolved in the aqueous phase was exploited to act as a stabilizer (see above), (iii) the BDGE:BADGE ratios were 70:30 and 50:50 (w/w), (iv) the DAH levels were 60% and 80% of the stoichiometric amounts, and (v) the emulsions were first precured at room temperature for 3 h and then at 40 °C for 3 h, followed by final curings at 60 °C for 24 h and 80 °C for 4 h.

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(20) Tanaka, Y.; Bauer, R. S. In *Epoxy Resins: Chemistry and Technology*, 2nd ed.; May, C. A., Ed.; Marcel Dekker: New York, 1988; pp 285−463.

When this procedure was used, it was found that the previously seen agglomerated sphere morphology was altered dramatically and the monoliths were dominated by connected rodlike structures (Figure 8). Among the SEM images presented in the composite figure, it is apparent that the polymer prepared from the epoxy mixture with a BDGE: BADGE ratio of 50:50 and with DAH at 60% of the stoichiometric amount (Figure 8b,c) had a 3D skeletal morphology similar to that of silica-based monoliths.[2,3]

Material Characterization. Specific surface areas measured by the BET method ranged from 0.4 to 1.8 m^2/g for all materials produced from mixtures of aliphatic and aromatic epoxy monomers with diluents (Table 2). Such low surface areas indicate an essential nonporous skeleton surface. This could be a consequence of the collapse of mesopores as a result of the pronounced shrinkage during the drying steps used in preparing the sample for the BET measurements. However, the low surface area can also be explained by the polymerization mechanism, where an initial interfacial reaction produces a skin structure which is later thickened by diffusion of amine and epoxy through the membrane during the curing at elevated temperature. Another possible explanation can be traces of poly(dimethylsiloxane), which was found in the XPS measurements of materials even after Soxhlet extraction by methanol (Table 3). Poly(dimethylsiloxane) is known to have antisurfactant properties,[21] and the source is silicone lubricant from the syringes used for emulsification. Mercury intrusion porosimetry measurements of the monolith with the 3D skeletal structure showed a rather sharp increase in pore volume in the pore size range equivalent to a cylindrical radius of 0.6−2.9 μm with a maximum at ~1.8 μm, corresponding to the flow-through pore size (Figure 9).

Regarding the nature of the polymerization, it is obvious that the reaction took place at the interface between the aqueous phase containing the DAH hardener and the dispersed epoxy phase. As soon as a thin polymer layer had been formed, diffusion of DAH from the aqueous phase into the epoxy phase became more difficult, which led to a significant amount of epoxy remaining unreacted inside the dispersed phase, at least during the early stages of curing. In addition, the low solubility of DAH in the diluents added to the epoxy phase could also restrict its diffusion. XPS measurements on a DEA-functionalized monolith based on BDGE/BADGE (70:30) without diluent added in the epoxy phase showed no tertiary amine groups resulting from the epoxide−DEA reaction. The dominant groups were secondary amine followed by primary amine (Table 3). This implies that there were no epoxide groups left on the surface of the monoliths after polymerization, and the density of amine groups was higher than expected from the amount of DAH used (70% of the stoichiometric amount).

Conclusions

We report here the synthesis of a new type of hydrophilic macroporous materials based on epoxy polymers. It was found that the chemical composition of the emulsion and the curing procedure were the main factors that could be used to manipulate the morphology of the epoxy-based monoliths over a wide range, allowing us to tailor their use as supports for liquid chromatography. However, due to the nature of the interface polymerization, most of the obtained materials were rigid enough for use in SPE formats, but at present not in HPLC systems at high pressures.

Acknowledgment. We are grateful for financial support from the Swedish Foundation for Strategic Research, the Swedish Science Research Foundation, and the Ministry of Training and Education of Vietnam. We also acknowledge the skilful help of Per Hörstedt and Andrej Shchukarev in preparing the SEM images and XPS spectra, respectively.

CM060645J

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