

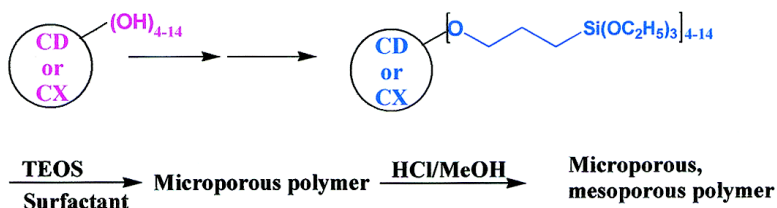
Article

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J. Am. Chem. Soc., **2003**, 125 (21), 6452-6461 • DOI: 10.1021/ja0213930 • Publication Date (Web): 02 May 2003

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A Novel Family of Ordered, Mesoporous Inorganic/Organic Hybrid Polymers Containing Covalently and Multiply Bound Microporous Organic Hosts

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Abstract: We have prepared a new family of periodic hybrid polymers containing microporous cavities provided by covalently bound organic hosts. Cyclodextrin (CD) or calixarene (CX) hosts are attached to four or more trialkoxysilyl groups, which are polymerized to form a polysilsesquioxane matrix. Structural integrity is provided by copolymerization with tetraethoxysilane, which produces a polysilicate co-matrix. Periodic order is created by carrying out the polymerization in the presence of a surfactant, cetyltrimethylammonium bromide. The resulting as-synthesized polymers from these three starting materials were characterized by solid-state nuclear magnetic resonance spectroscopy. The ¹³C and ²⁹Si spectra provided evidence for intact polysilsesquioxane, polysilicate, organic host, and surfactant. Removal of the surfactant by washing produced a polymer containing cavities of mesoporous dimensions, in addition to the microporous host cavities. The purpose of introducing mesoporosity is to allow enhanced access of guests to the microporous hosts. Transmission electron microscopy demonstrated that both as-synthesized and solvent-extracted polymers have a periodic structure. All polymers are completely insoluble in water. The as-synthesized CD-containing polymers extracted up to >99% of 4-nitrophenol from aqueous solution, and the solvent-extracted CX-containing polymers extracted up to 67% of Fe³⁺ and lesser amounts of other metal cations from aqueous solution, with interesting selectivity patterns. Simple filtration then removes the polymer containing the extracted organic molecule or metal cation. These extraction abilities are superior to previous materials.

Introduction

We recently reported the preparation, characterization, and binding properties of a new family of polysilsesquioxane polymers containing covalently bound organic hosts.¹ Cyclodextrins (CDs) and calixarenes (CXs), which normally are water soluble, are rendered entirely insoluble when made an integral structural component of these polymers. These hosts offer microporous cavities capable of binding guests such as organic molecules or inorganic cations. The host-containing polymers proved very effective in removing guests from aqueous solutions.¹ Because of their insolubility, the guest-impregnated materials are separated from the water solution simply by filtration. The CD-containing polymers moreover are insoluble in organic solvents, but their organic guests are not. Consequently, the polymers are renewable through washing with organic solvents. The ease of preparation, high stability, favorable binding properties, facile separation, and good renewability suggest a variety of uses in water reclamation, drug delivery, catalysis, and separations.

We prepared these polymers by sol-gel polymerization of monomers of the type (RO)₃SiR', in which R' contains CD or

CX. The gels proved to be amorphous, aperiodic, and lacking any pore structure.¹ The only available cavities are those provided by the cyclodextrin or calixarene hosts. It is likely, although not proved, that the accessible host sites are those closest to the solid surfaces. Nitrogen adsorption porosimetry indicated very low Brunauer-Emmett-Teller (BET) surface areas (1.1–1.7 m² g⁻¹). The materials thus are likely to have low catalytic activity and poorly accessible microporous host sites.

Surfactant templation has proved to be an effective method for preparing periodic mesoporous materials. In 1992, the first such synthetic material, called MCM-41, was reported.² The procedure involved polymerization of a tetraalkoxysilane in the presence of a surfactant such as cetyltrimethylammonium bromide (CTAB). In water, the surfactant possesses a highly ordered structure. As the siliceous polymer is formed, it layers over and around the surfactant, retaining the original periodic structure. Calcination or solvent washing can remove the surfactant and leave behind the silica-like polymer containing cavities or mesopores that retain the shape of the absent surfactant. Silica formed from the aqueous polymerization of

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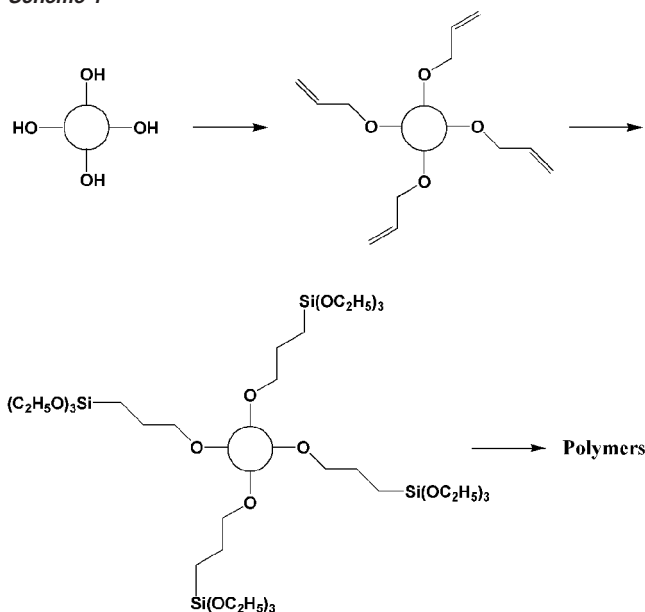
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tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) alone is irregular and broadly distributed in pore size. Silica formed from the same starting materials templated in the presence of a surfactant that is subsequently removed has a periodic structure with uniform pore sizes ranging from 15 Å to more than 100 Å. The material termed MCM-41 possesses hexagonal symmetry, in the presence or absence of the surfactant. Variations with cubic symmetry or containing other metals such as titanium also have been prepared.² The micellar structure originally present in solution, however, is not always retained during polymerization and self-assembly of the inorganic precursor in the presence of the surfactant.

The purely inorganic materials formed by this procedure of templation followed by washing or calcination have favorable properties but are synthetically limited. A second generation of materials was produced by surface grafting of organics onto MCM-41 and related templated polymers or by assembly of ordered silica with attached organic groups.³ Because of the mode of synthesis, the organic portions in general protruded into the pores. Three groups⁴ reported almost simultaneously in 1999 that polymerization of bridged silsesquioxane monomers, $(RO)_3Si-B-Si(OR)_3$, or copolymerization of TEOS with bridged silsesquioxane monomers in the presence of a surfactant produced MCM-41-related materials in which the organic portions were an integral part of the channel walls. Subsequent removal of the surfactant created a periodic mesoporous hybrid organosilica polymer. The comonomer TEOS/TMOS provided structural integrity but was not always necessary. The organics in these copolymers do not block the channels. They convey fundamental changes to the nature of polymer, and they may be broadly varied to produce novel polymer properties.⁵ Materials containing both terminal $((RO)_3SiR')$ and bridged polysilsesquioxanes have been synthesized,⁶ and recently the first example of copolymerization with a silsesquioxane having an organic group attached to three silicon atoms (three-point attachment) was reported.⁷ Various names have been given to these inorganic/organic hybrid polymers, such as *periodic mesoporous organosilicas*. The imprecise term "organosilica" is used intentionally to include both the polysilsesquioxanes and the interlocked silicate lattice formed from TEOS or TMOS.

Numerous bridges ($-B-$) have been explored in these periodic mesoporous organosilicas, including methylene, ethano, etheno, ethyno, 1,4-phenylenyl, thiopheno, ferrocenyl, and 1,3,5-trisubstituted phenyl.^{4,5,7} The bridges have not, however, been viewed as conveying specific cavities themselves. Heretofore, the cavities usually were restricted to the mesoporous structures

Scheme 1



abandoned by the template, and the bridge served to alter properties of the polymer. There are a few examples in the literature in which the organic host also provided independent complexing properties.⁸ Mercier and co-workers prepared mesoporous silicas containing covalently attached cyclodextrins serving primarily in the role of a terminus for extraction of organics. Corriu et al. attached cyclams to mesoporous frameworks to assist in the extraction of transition metals.

In the present work, we have incorporated bridges that contain the same organic hosts we utilized in our previous study, cyclodextrins and calixarenes.¹ We have copolymerized CD- and CX-bridged silsesquioxanes with TEOS in the presence of a surfactant and subsequently removed the surfactant. The host organics have four or more points of attachment to silicon, exceeding previous structures.^{4,5,7,8} The resulting robust periodic organosilicas should be both mesoporous (from the cavities created by the removal of the surfactant) and microporous (from the CD or CX hosts in the bridges). We view the two types of cavities as symbiotic, as together they may be superior to either alone. Thus, the mesopores may provide greater accessibility to the CD/CX micropores, with the result that the micropores may have improved complexing or extracting abilities in comparison with the polymers prepared without templation.¹ The Experimental Section is found in the Supporting Information.

Results and Discussion

Synthesis. Scheme 1 provides a diagrammatic description of the synthesis. The CD or CX rings are represented by the interior circle. We used β -cyclodextrin, which is a cyclic oligosaccharide containing seven glucose molecules with 1,4 connections, and calix[4]arene, in which four phenol units are connected by methylene groups to form a macrocycle. Allyl groups were attached to two hydroxyls in each CD glucose ring (for a total of 14 allyls per CD unit), and allyl groups were attached to all

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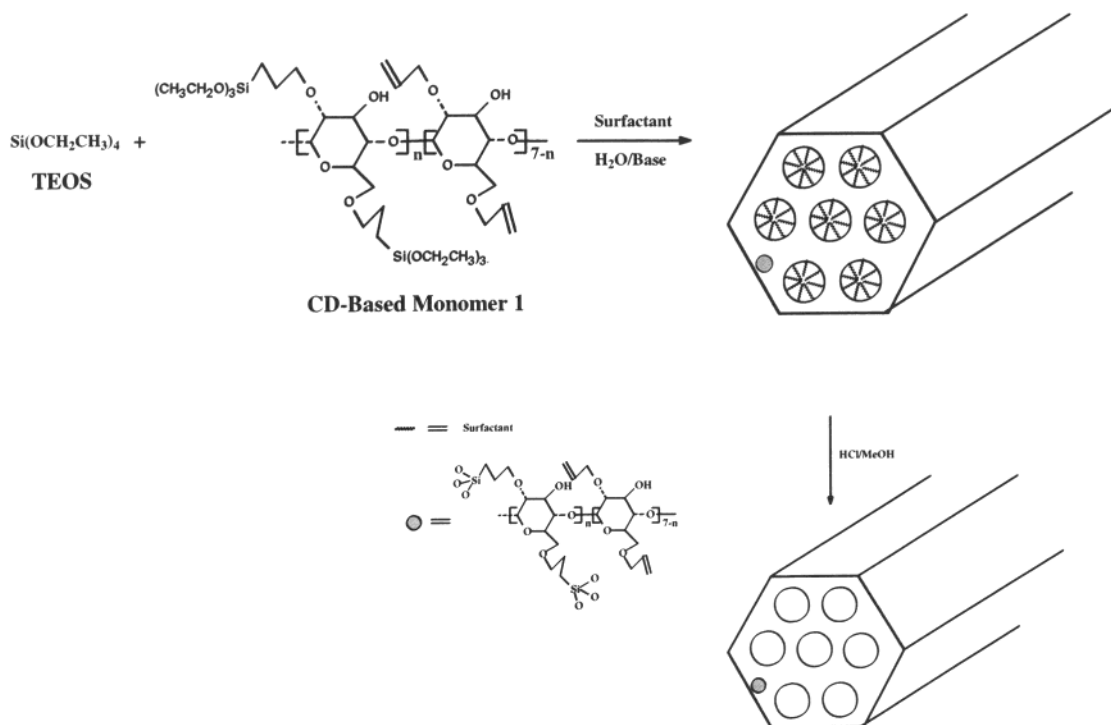


Figure 1. Synthetic route to ordered CD-based mesoporous organosilicon materials. TEOS/Monomer 1 (in Si atom ratio) = 1/0 (**1a**, **1a'**); 0.9/0.1 (**1b**, **1b'**); 0.75/0.25 (**1c**, **1c'**); 0.5/0.5 (**1d**, **1d'**); 0.25/0.75 (**1e**, **1e'**). Note that the figures are not drawn to scale.

four para carbons in each CX. Synthetic details for these derivatizations have been published previously.¹ Thus, by design each CD unit has seven remaining hydroxyls, and each CX has four hydroxyls to assist in binding with guests. The second structure in Scheme 1 loosely represents the product of the first synthetic step, although the CD would have 14 protruding allyl groups.

The allyl groups then were hydrosilylated to form the third structure in Scheme 1. The organic portion in this structure constitutes the bridge. The silylated CD has up to 14 points of attachment to silyl groups (the hydrosilylation yield was not 100%), and the silylated CX has four points of attachment to silyl groups. These bridging groups provide more silylated arms for polymerization than those used previously, compared with one for terminal cases $\text{T}-\text{Si}(\text{OR})_3$,³ two for most previous examples of the type $(\text{RO})_3\text{Si}-\text{B}-\text{Si}(\text{OR})_3$,^{4,5} and three for the 1,3,5-trisubstituted phenyl.⁷

To retain our original notation,¹ the CD product was termed Monomer 1 and the CX product was termed Monomer 3. In our previous study, we carried out the sol-gel polymerization of these materials in aqueous tetrahydrofuran. Gelation occurred rapidly, and polymers were allowed to cure for a week. The dried materials respectively were called Polymer 1 and Polymer 3.¹ Both polymers were amorphous, aperiodic, and low in surface area. Nonetheless, they had excellent complexation properties, respectively extracting organic molecules (Polymer 1) and inorganic cations (Polymer 3) from aqueous solution.

There may be a fundamental structural difference between the CD and CX structures. In the CD monomer, there are up to seven arms extended from each of the CD faces, because the original alkylation reaction placed one allyl group on the primary hydroxyl and one allyl group on one secondary hydroxyl of each glucose ring (primary and second hydroxyls are on opposite faces of cyclodextrin). In Polymer 1, polymerization clearly

occurred from both CD faces. On the other hand, the CX monomer contains a hydrophobic face on which the allyl groups were placed and a hydrophilic face from which phenolic hydroxyls protrude. There is some conformational flexibility, but in aqueous solution all hydroxyls likely point in the same direction. All allyl groups in Scheme 1 and their silylated products then point in the other direction from the core. In Polymer 3, polymerization thus occurred, although probably not exclusively, from only one CX face.

In the present study, we have followed the templating and extraction procedures that lead to periodic mesoporous organosilicas.⁴ Monomers 1 and 3 were co-condensed at room temperature with tetraethoxysilane (TEOS) in the presence of the surfactant cetyltrimethylammonium bromide (CTAB) to produce the as-synthesized polymers. The TEOS-to-monomer ratio was varied to produce a series of polymers in each case. The surfactant was removed by treatment with methanol containing aqueous hydrochloric acid to produce the periodic mesoporous organosilicas. Figures 1 and 2, after Asefa et al.,⁶ respectively illustrate the synthetic procedures. The final materials should have the hexagonal structure of MCM-41, in which the mesopores provide better access to the hosts in comparison with the amorphous, aperiodic materials we prepared previously.¹

Polymer Characterization. The ratio of TEOS to the monomer was varied to produce two series of polymers defined in Table 1, designated **1** for the CD polymer and **2** for the CX polymer. The as-synthesized products are unprimed, and the solvent-extracted products are primed. Polymer **1a** and its extraction product **1a'** were prepared entirely from TEOS and thus contain no host molecule (CD or CX) (**2a** and **2a'** would be redundant and are not listed). The ratio of TEOS to monomer is expressed in percentages as an atom ratio of silicon (TEOS contains one silicon, the CD-based Monomer 1 contains 14

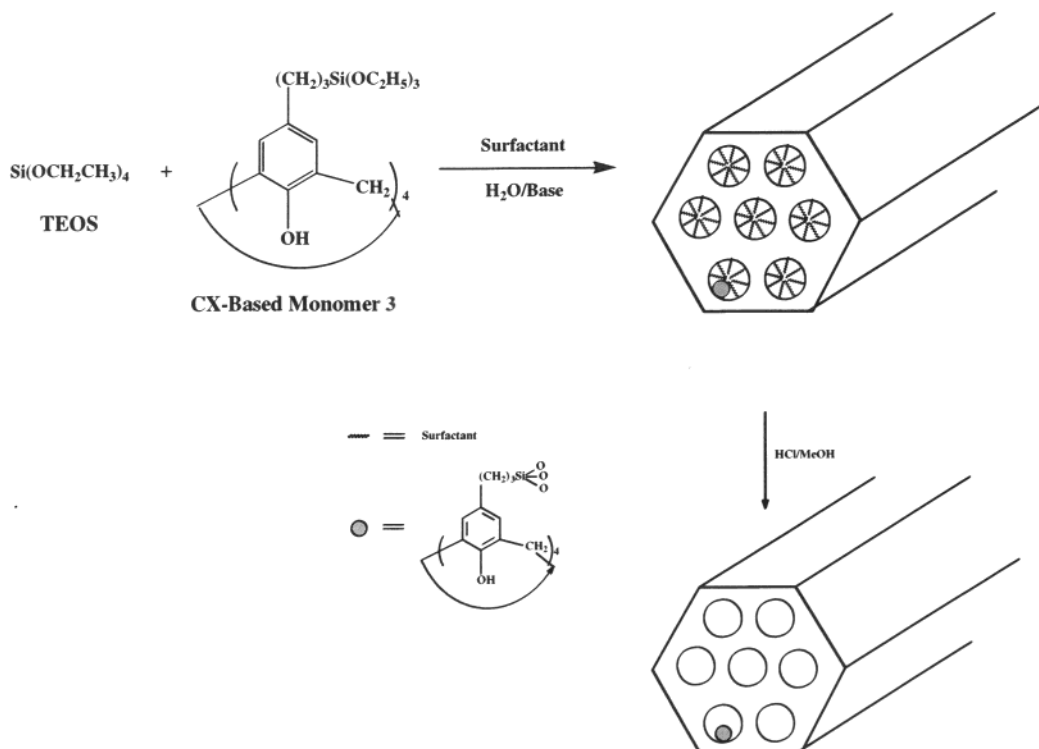


Figure 2. Synthetic route to ordered CX-based mesoporous organosilicon materials. TEOS/Monomer 3 (in Si atom ratio) = 0.9/0.1 (**2b**, **2b'**); 0.75/0.25 (**2c**, **2c'**); 0.5/0.5 (**2d**, **2d'**); 0.25/0.75 (**2e**, **2e'**). Note that the figures are not drawn to scale.

Table 1. Polymer Products

host	designation ^a	% TEOS/ ^b % monomer ^b	host	designation ^a	% TEOS/ ^b % monomer ^b
—	1a	100/0	CD	1c''	75/25
CD	1b	90/10	CX	2b	90/10
CD	1c	75/25	CX	2c	75/25
CD	1d	50/50	CX	2d	50/50
CD	1e	25/75	CX	2e	25/75
—	1a'	100/0	CX	2b'	90/10
CD	1b'	90/10	CX	2c'	75/25
CD	1c'	75/25	CX	2d'	50/50
CD	1d'	50/50	CX	2e'	25/25
CD	1e'	25/75			

^a Unprimed materials are as synthesized with surfactant. Primed materials are solvent extracted to remove the surfactant. The doubly primed material **1c''** was prepared in the absence of surfactant. ^b Atom ratios based on Si.

silicons, and the CX-based Monomer 3 contains four silicons). Thus, equimolar amounts of these three monomers exhibit a 1/14/4 atom ratio. The amount of monomer was increased in the order 10, 25, 50, and 75% (atom ratios). Polymers were not prepared with 100% monomer (no TEOS), as they were expected to be amorphous and to lack structural robustness.

Solid-State NMR Spectra. The product polymers were insoluble in solvents; as a result their structural characteristics were examined by solid-state NMR with cross polarization and magic angle spinning. Figure 3 contains the ¹³C spectra of the as-synthesized CD polymers **1b–1e**, as well as the spectrum of polymer **1a** from only TEOS. The six sharp peaks visible in the bottom spectrum of polymer **1a** are from the surfactant CTAB. These peaks persist in the remaining spectra but broaden and weaken in intensity. The broad peaks in the region δ 110–140 are background from the rotor. As the proportion of CD builds from **1b** to **1e** by addition of Monomer 1, new peaks emerge that document the structural integrity of the sugar rings.

The peak at about δ 100 is from the anomeric carbon C1, indicating that the glucose rings are intact. The other C–O carbons in the sugar rings and from the first carbon of the OCH₂CH₂CH₂Si connector are found in the region δ 60–90. The other two carbons in the connector (OCH₂CH₂CH₂Si) are found at δ 9 and 23. Thus, all peaks in the ¹³C spectrum are readily accounted for, and the polymerization process has in no way degraded the CD structure.

The solid-state ²⁹Si spectrum of **1a** (pure TEOS with the surfactant) contains only Q peaks (SiO₄) at δ –100 and –110, in addition to the broad background peak from the rotor, centered at δ –52. These peaks decrease in intensity as Monomer 1 is added to the mix. The T² and T³ peaks (CSiO₃) from the silicon atoms attached to the connector carbon in the polymerizing monomer grow in at δ –55 to –60 first as shoulders on the background peak and eventually as the major peaks. The T peaks document the integrity of the C–Si bond between the CD units and the polysilsesquioxane silicons.

Figure 4 contains the solid-state ¹³C spectra of the solvent-extracted CD polymers **1b'–1e'**, as well as the spectrum of the solvent-extracted polymer **1a'** from TEOS alone. The spectrum at the bottom of the TEOS polymer **1a'** is pure silicate and lacks all carbon resonances except those from the background. Solvent extraction has effectively removed all of the surfactant. The CD resonances grow in from **1b** to **1e** and closely resemble those in Figure 3. Thus, solvent extraction had no effect on the integrity of the CD structure. The ²⁹Si spectra of the solvent-extracted polymers **1'** closely resemble those of the as-synthesized polymers **1**.

Supporting Information Figure 1 contains the solid-state ¹³C spectra of the as-synthesized CX polymers **2**. In this case, the spectrum from pure TEOS is omitted, as it would be the same as **1a** in Figure 3. The illustrated spectra show the decrease in

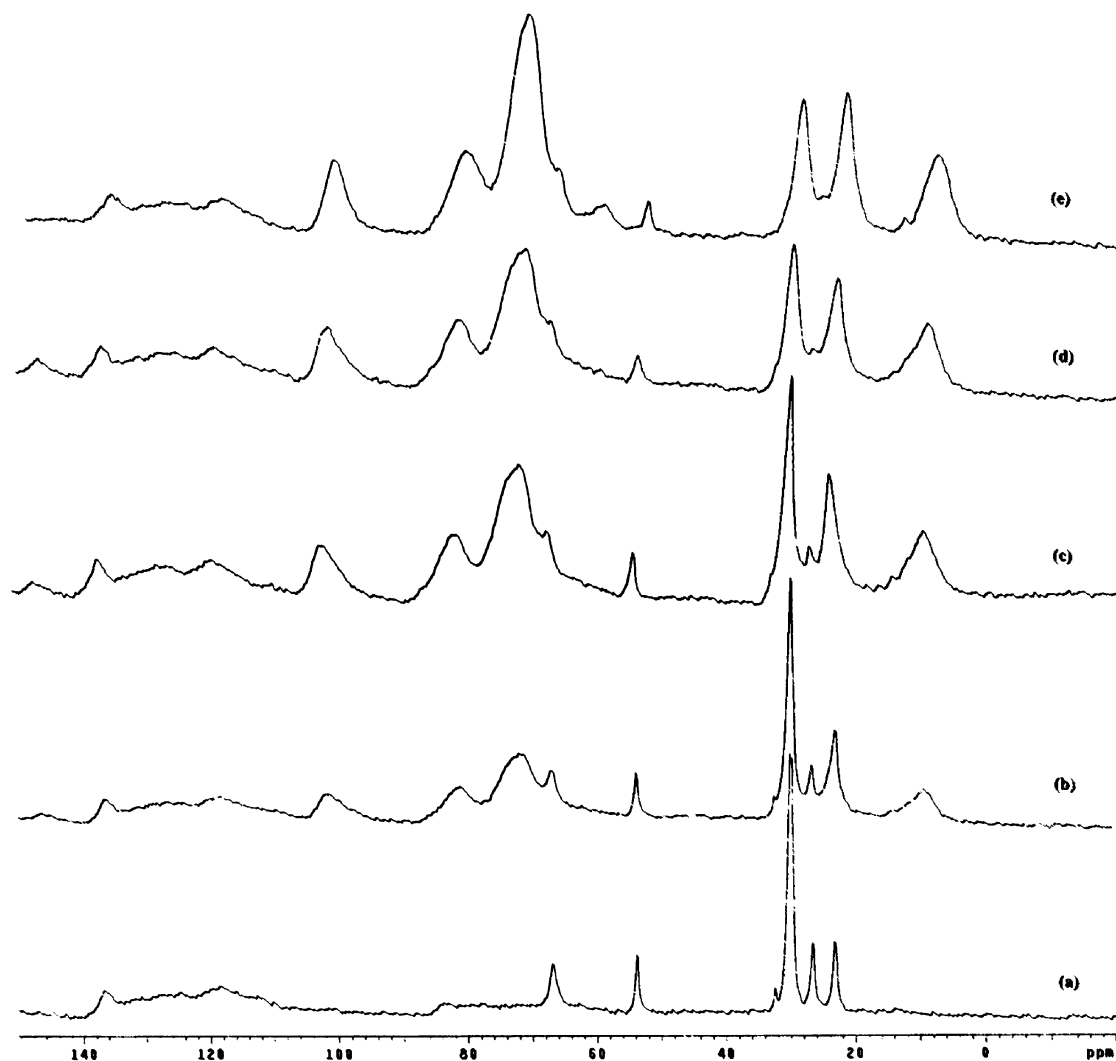


Figure 3. ^{13}C MAS NMR spectra of the as-synthesized CD-based polymers. (a) **1a**, (b) **1b**, (c) **1c**, (d) **1d**, and (e) **1e**.

intensity of the surfactant resonances at δ 23, 27, 30, 33, 54, and 67 and the growth of the CX resonances as the TEOS/Monomer 3 ratio decreases. The aromatic resonances are found in the region δ 110–140 (and bear no resemblance to the background resonances in this area seen in Figures 3 and 4). The resonances of the CX inter-ring methylene group and of the first methylene in the connector $\text{ArCH}_2\text{CH}_2\text{CH}_2\text{Si}$ are found at δ 20–40. The other connector resonances ($\text{ArCH}_2\text{CH}_2\text{CH}_2\text{Si}$) appear at δ 14 and probably 23. Thus, all major peaks are accounted for by the expected CX carbons. The solid-state ^{29}Si spectrum contains decreasing Q peaks at δ –100 and –109 from the TEOS polymer (as the proportion of TEOS decreases) and increasing T peaks at δ –54 to –65 from the polysilsesquioxane polymer (as the proportion of Monomer 3 increases), closely resembling the results from the CD polymer.

Supporting Information Figure 2 illustrates the solid-state ^{13}C spectra for the CX polymers after solvent extraction. The surfactant resonances disappear, and the CX resonances indicate no degradation of the calixarene structure. The solid-state ^{29}Si spectra follow the same trend, with decreasing Q peaks and increasing T peaks as the proportion of Monomer 3 increases at the expense of TEOS. The presence of dominant T peaks confirms that the polysilsesquioxane structure is retained with intact Si–C bonds.

Infrared Spectra. Fourier transform IR spectra were recorded for all 18 polymers. The dominant peak in all cases was the Si–O–Si stretch in $1050\text{--}1150\text{ cm}^{-1}$, characteristic of siloxane condensation.

Powder X-ray Diffraction. Small-angle XRD measurements on the polysilsesquioxanes obtained from Monomers 1 and 3 by sol–gel polymerization showed no ordering or periodicity.¹ In contrast (Figure 5), the as-synthesized templated polymer **1** from Monomer 1 containing CD units shows a single peak in the region $2\theta \approx 2.2^\circ$, indicating values of $d_{100} \approx 4.0\text{ nm}$. The distance from pore center to pore center is 1.15 times this value, or ca. 4.6 nm. Table 2 gives the d_{100} values in the second column. This order is lost as the proportion of TEOS decreases and that of Monomer 1 increases. As seen in Figure 5, the peak at 2.2° decreases in intensity as the percentage of TEOS goes from 90 to 50% and is absent at 25%. Thus, polymer **1e** remains amorphous, in agreement with our previous work on polysilsesquioxanes.¹ It is the templated TEOS polymer that provides long-range order. Cross-linking in the polymer from Monomer 1 occurs extremely rapidly, as the monomer contains up to 42 hydrolyzable groups, compared with only four for TEOS. The templating role of the surfactant may be vitiated in the face of rapid condensation and cross-linking at high proportions of Monomer 1.

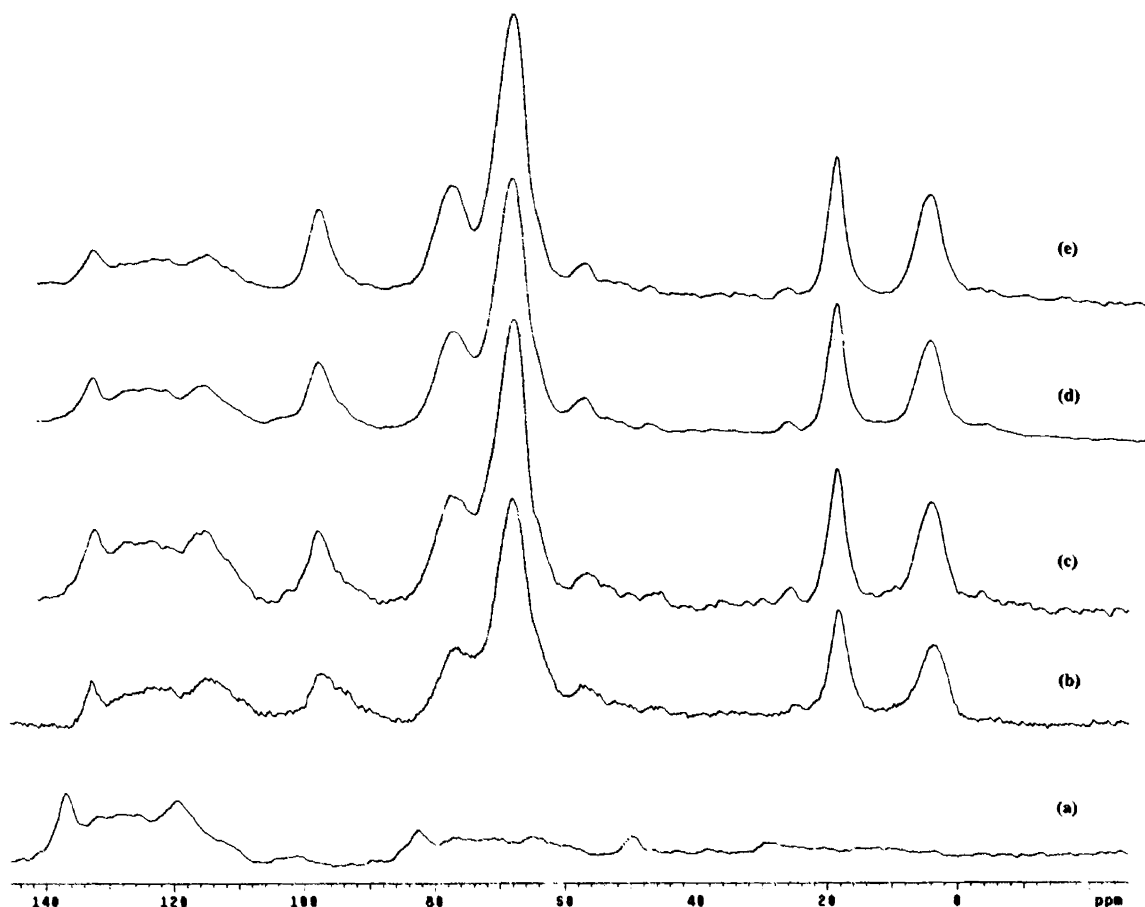


Figure 4. ^{13}C MAS NMR spectra of the surfactant-extracted CD-based polymers. (a) **1a'**, (b) **1b'**, (c) **1c'**, (d) **1d'**, and (e) **1e'**.

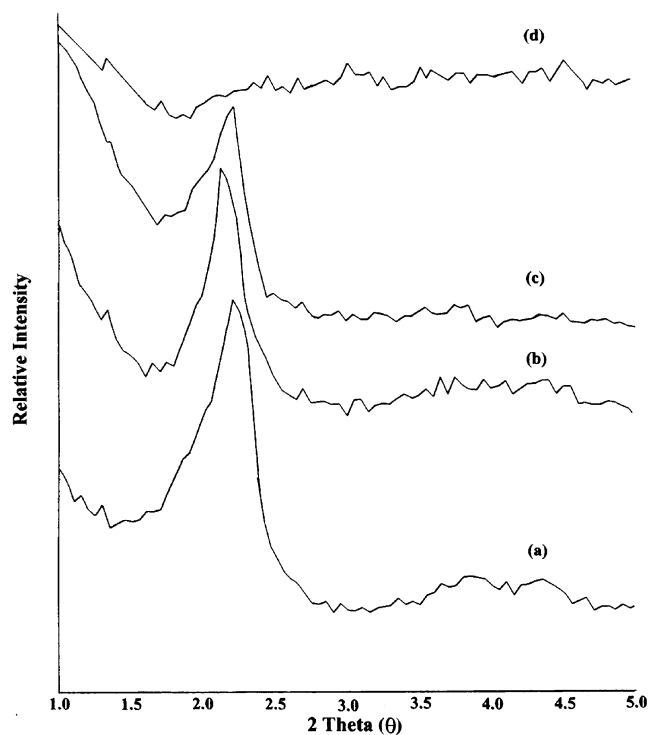


Figure 5. Powder X-ray diffraction patterns of as-synthesized CD-based mesoporous samples containing different proportions of TEOS and CD-based Monomer **1**. (a) **1b**, (b) **1c**, (c) **1d**, (d) **1e**.

After surfactant extraction from polymers **1** to produce polymers **1'**, a major peak in the powder XRD pattern (see

Table 2. Physical and Surface Properties of CD-based and CX-based Materials

material	XRD d -spacing (100) (nm)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	mesopore diameter (nm) ^a
1a	4.02	—	—
1a'	3.97	1080	3.0
1b	4.01	—	—
1b'	3.85	670	2.9
1c	4.08	—	—
1c'	3.77	560	2.9
1c''	—	11	—
1d	3.95	—	—
1d'	—	250	2.9–3.9
1e	—	—	—
1e'	—	190	3.9
2b	4.06	—	—
2b'	3.93	650	2.4
2c	3.89	—	—
2c'	3.77	570	2.4
2d	3.92	—	—
2d'	—	260	2.5
2e	—	—	—
2e'	—	210	2.7

^a Calculated from the desorption branch by the BJH method.

Supporting Information Figure 3) remains at $2\theta \approx 2.3^\circ$, indicating values of $d_{100} \approx 3.9$ nm (Table 2) for polymers with more than 50% TEOS. Following surfactant removal there appears to be a slight contraction in the distance from pore center to pore center. For the case of **1b'**, small peaks at 3.9 and 4.4° respectively correspond to d_{110} and d_{200} , suggestive of longer-range order.

Similar observations were made with the CX polymers **2** and **2'**. The presence of periodicity in the solid was indicated by a peak $2\theta \approx 2.2^\circ$ at higher levels of TEOS for the as-synthesized polymers **2**, with values of d_{100} contracting slightly on removal of the surfactant to form polymers **2'** (Table 2, second column, and Supporting Information Figure 4). As with the CD polymers, periodicity disappears when TEOS was under 50%. When 50% TEOS (or higher) was used, CD polymer **1d'** and CX polymer **2d'** underwent collapse during solvent extraction.

Surface Area and Pore Size. The polymers we previously obtained from the sol-gel polymerization of Monomers **1** and **3** alone possessed very low surface areas.¹ The Brunauer-Emmett-Teller (BET) values from nitrogen adsorption experiments were in the range 1.1–1.7 m² g⁻¹. For the present polymers, measurements were not made on the as-synthesized polymers, in which the surfactants presumably filled all voids. Table 2 gives the BET surface areas for the surfactant-extracted polymers in the third column. The value of 1080 m² g⁻¹ for polymer **1a'**, which corresponds to MCM-41, compares favorably to literature values¹¹ and indicates high surface area. Both CD polymers **1'** and CX polymers **2'** had BET values of 500–700 m² g⁻¹ when the percentage of TEOS was above 50% and values of 200–300 m² g⁻¹ when the percentage of TEOS dropped below 50%. Thus, surface areas decrease with higher percentages of Monomers **1** or **3**, but are still 2 orders of magnitude higher than those of the polysilsesquioxanes produced in the absence of templation and extraction.¹ The present method of processing clearly has led to polymers with much higher surface areas.

The mesopore diameters were calculated from the desorption branch of the nitrogen adsorption-desorption isotherms by the BJH method and were found to be in the range of 2.4–3.9 nm (last column of Table 2). The distance must correspond to the diameter of the pores vacated by the surfactant, as they are much too large for the interior dimensions of CD or CX hosts. The nitrogen adsorption-desorption isotherm for the surfactant-extracted CD-based sample **1c'** (Figure 6a) showed a type-IV isotherm, characteristic of mesoporous materials, with a BET surface area of 560 m² g⁻¹ and a narrow pore size distribution centered at 2.9 nm (Figure 6b).

Polymers **1a'** and **1b'** showed similar behavior, but at higher levels of CD (**1d'** and **1e'**) the pore size distribution widened and developed a second maximum at 3.9 nm (see Supporting Information Figure 5). These materials also lacked the order characterized by a $d(100)$ spacing of ca. 4 nm (Table 2, second column). These higher levels of CD have a deleterious effect on the polymer order and the mesopore size.

Electron Microscopy.¹² Scanning electron microscopy (SEM) indicated that the materials consisted of coarse particles with diameters in the 10–100 μm range. High-resolution transmission electron microscopy (TEM) images showed hexagonal arrangements of pores with uniform pore size throughout the sample. Figure 7 provides the TEM images for the as-synthesized

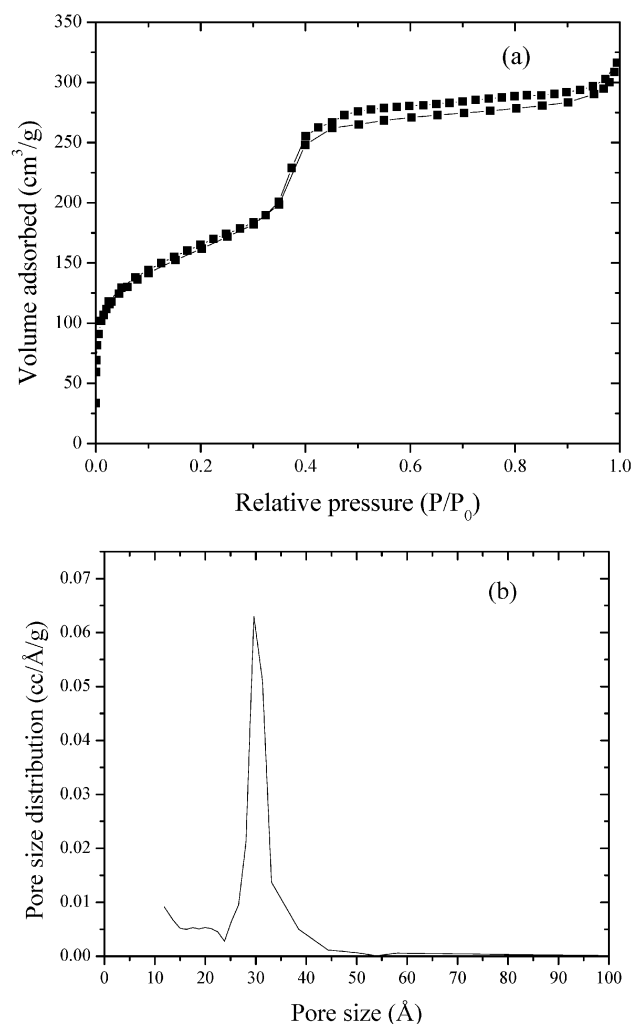


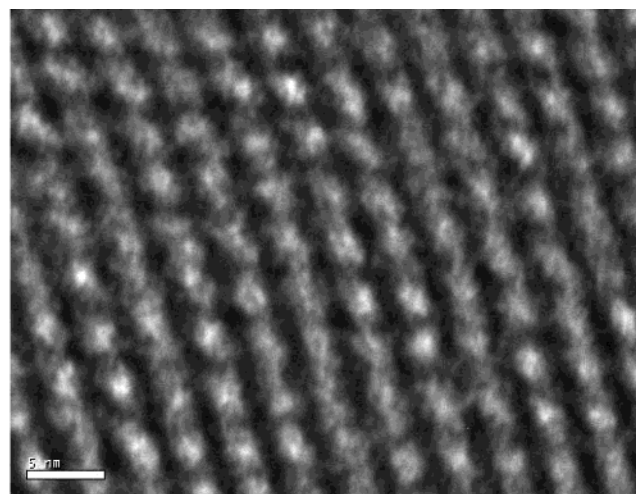
Figure 6. Nitrogen adsorption-desorption isotherms (a) and pore size distribution plot (b) of the surfactant-extracted CD-based polymer **1c'**.

polymer **1c** and its surfactant-extracted product **1c'**. Thus, the quality of the hexagonal mesostructure is retained as Monomer **1** or **3** is added and as the surfactant is extracted. The distances from pore center to pore center were measured to be 3.8–4.5 nm, corresponding very closely to the same distances calculated from powdered XRD (Table 2, column 2).

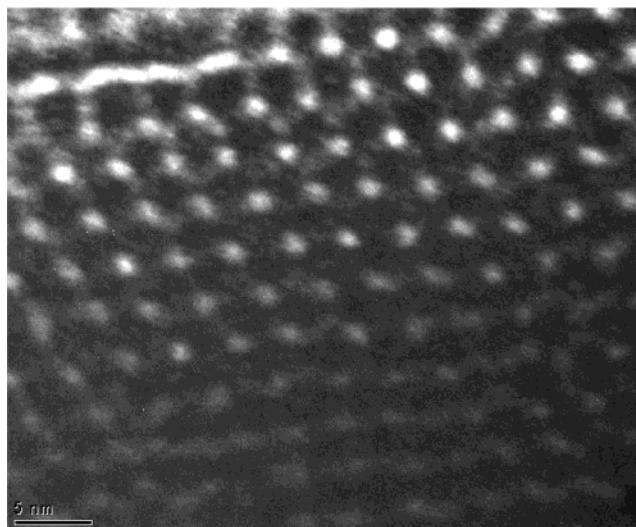
There is some question as to whether the hosts protrude from the polymer into the mesopore or are embedded within the polymer body (Scheme 2, respectively, left and right). The structure of the CD polymers strongly suggests that the host is embedded within the polymer (also see Figure 1). With up to seven silyl groups on the top CD face and seven silyl groups on the bottom face, it is likely that polymerization and cross-linking occur in all directions from the CD unit, thereby encasing it in polysilsesquioxane polymer. Thus, we expect the CD polymer **1** to follow the diagram on the right side of Scheme 2. This model contrasts with that of Huq et al.,⁸ whose polymers were not so extensively cross-linked. When the CD in T is attached to 2.8 silicon atoms,⁸ polymerization moves away from the CD unit, leaving it to protrude into the mesopore, as in the model on the left side of Scheme 2.

To the extent that all four hydroxyls are on the same side of the CX unit, polymerization moves away from the CX unit and allows it to protrude into the mesopore (also see Figure 2).

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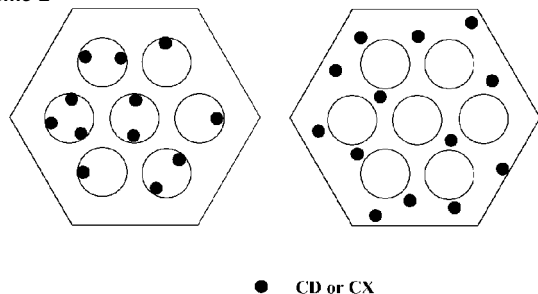
(a)



(b)

Figure 7. TEM images of the well-ordered mesostructure of CD-based materials (a) as-synthesized **1c**, and (b) after surfactant-extraction **1c'**.

Scheme 2



Because CX units are conformationally mobile, however, it is possible that it can assume a conformation in which one hydroxyl faces opposite to the other three. Such a conformation then could result in CX embedded in the polymer, as on the right side of Scheme 2, or a mix of the two models.

Because of the large size of the organic hosts, they may be difficult to incorporate into relatively thin walls of the ordered material. The extensive cross-linking of the organic units may

Table 3. Extraction Percentages of 4-Nitrophenol from Aqueous Solution^a

polymer	loading level (wt %)	absorbed (%)	polymer	loading level (wt %)	absorbed (%)
1a	0.2	81	1b'	0.2	41
	5.0	32		5.0	5
1b	0.2	84	1c'	0.2	60
	5.0	39		5.0	10
1c	0.2	>99	1d'	0.2	92
	5.0	49		5.0	17
1d	0.2	>99	1e'	0.2	86
	5.0	57		5.0	12
1e	0.2	96	1c''	0.2	51
	5.0	41			
1a'	0.2	20			
	5.0	1			

^a Reaction time 18 h, concentration of 4-nitrophenol 8.63×10^{-5} M.

create a distinct disordered phase. Such a situation would imply that the ordered domain of these materials derives entirely from pure silica. This is clearly not the case. Polymer **1a'** represents pure silica from polymerization of TEOS in the absence of the organic host, followed by solvent extraction of the surfactant (Table 1). The $d(100)$ spacing for pure silica (**1a'**) prepared in the presence of the surfactant thus is 3.97 nm. As the proportion of cyclodextrin (**1b'**, **1c'**) or calixarene (**2b'**, **2c'**) increases, the $d(100)$ spacing contracts to 3.77 nm. The changes in d -spacing and mesopore diameters indicate that the ordered domains are not pure silica but rather silica containing the organic hosts. Moreover, the narrow distribution of mesopore size (Figure 6) for **1c'** suggests that the material contains relatively uniform mesopores.

Association Properties. Our previous experiments¹ with polysilsesquioxanes obtained by sol-gel polymerization demonstrated that the CD-based polymers had high affinity for small organic molecules in aqueous solution and the CX-based polymers had specific and modest affinity for iron and for some other cations in aqueous solution. The present association experiments were carried out to determine whether the ordering imposed by templating and the mesopores formed by solvent extraction enhance the binding abilities of the micropores provided by the covalently bound CD and CX structures.

Table 3 presents the percentage of 4-nitrophenol extracted from aqueous solution by polymer **1** under conditions comparable to those used previously in association experiments with the sol-gel polymers containing covalently bound CD.¹ Results are given for two loading levels, defined as the weight of the guest in grams divided by the weight of the host in grams converted to percentage. The as-synthesized polymers **1c** and **1d** removed 4-nitrophenol to below the detection limit of the UV assay (>99%) when the loading level was 0.2%. The percentage removed dropped below 85% when there was over 75% TEOS and to 96% when there was only 25% TEOS for the as-synthesized polymers. The as-synthesized polymer MCM-41 (**1a**) without CD is reasonably effective in removing the organic (81%), but the presence of the organic host makes a polymer that is far superior in its ability to remove the organic from aqueous solution (>99% removal). The typical values for the sol-gel Polymer **1** under similar conditions were 89–92%.¹ Thus, polymerized TEOS, surfactant, polysilsesquioxane, and covalently bound CD work synergistically to provide the optimal result. The polymers are subject to saturation, as the extraction percentage falls at higher loading levels. The 57% removal of

4-nitrophenol by **1d** compares with 25% by the sol-gel polymer¹ under comparable conditions for a loading level of 5.0%. The new polymers thus perform better than the sol-gel polymers at higher loading level. Either the new polymer has more surface binding sites or the interior micropores are more accessible. The renewability of the as-synthesized polymers was tested by washing the polymers that had been charged with 4-nitrophenol with ethanol for 24 h. The percentage of 4-nitrophenol that was released was 71% for polymer **1c**, 75% for **1d**, and 78% for **1e**.

Similar experiments were carried out on the solvent-extracted CD-based polymers **1'** (Table 3). Optimal results were obtained with polymer **1d'** at 0.2% loading level: 92% removal of 4-nitrophenol. These results are comparable to those obtained with sol-gel polymerization without templation¹ but slightly less than those obtained with the optimal as-synthesized polymers (**1c** and **1d**). Results degrade significantly at higher loading levels. Thus, the as-synthesized polymers still containing the surfactant were uniformly more effective at removing 4-nitrophenol than the solvent-extracted polymers. Apparently the presence of the surfactant in polymers **1** has a slightly more positive effect on extraction of 4-nitrophenol than the presence of mesopores in polymers **1'**. This cooperative effect of the surfactant may result from noncovalent interactions with the substrate, higher levels of surface CD molecules, or destruction of surface CD by the washing process to remove the surfactant. Mesopores alone (**1a'**) in the absence of the microporous CD molecules were the least effective (20%).

These results also contrast with those of Huq et al.⁸ Their polymers, however, were formed from simple terminal monomers, which led to solvent-extracted polymers in which the host protruded into the mesopore. Their solvent-extracted polymers were effective in removal of 4-nitrophenol. Our polymer family **1** probably contains embedded rather than protruding hosts, with the apparent result that guest removal is highly effective with or without surfactants.

As a control, we synthesized polymer **1c''**, with the same concentration as **1c** and **1c'** (75% TEOS and 25% CD-containing monomer) but prepared without any surfactant. The solid-state ¹³C NMR spectrum (see Supporting Information Figure 6) resembled those of the solvent-extracted materials in Figure 4. The nitrogen adsorption-desorption isotherm (see Supporting Information Figure 7) and the powder X-ray diffraction pattern (see Supporting Information Figure 8) indicated that there was no mesopore structure. The BET surface area of 11 m² g⁻¹ is very low. Absorption experiments were carried out with the control polymer **1c''** and 4-nitrophenol. With a loading level of 0.2%, 51% of the substrate (at 8.63 × 10⁻⁵ M) was removed by **1c''**. This polymer thus provides only modest removal of the organic substrate.

Absorption of 4-nitrophenol improves from 2% for pure silicate (prepared from SiCl₄ without surfactant¹) to 51% for 75% TEOS/25% CD without surfactant (**1c''**) to 81% for MCM-41 made from pure TEOS with surfactant (**1a**) to >99% for 50% TEOS/50% CD with surfactant (**1c**). Optimal absorption requires both surfactant and CD.

In our previous work, we found that sol-gel polymers containing covalently bound CX molecules selectively removed Fe³⁺ from aqueous solution.¹ The sol-gel Polymer 3, containing only CX, removed 25–35% of this ion from aqueous solution

Table 4. Extraction from Aqueous Solution of Metal Cations by Surfactant-Templated (Solvent-Extracted) Polymers^a

cation	2b'	2c'	2d'	2e'	cation	2b'	2c'	2d'	2e'
Fe ³⁺ ^b	47.0	67.8	54.1	27.8	Na ⁺ ^d	<1.0	<1.0	<1.0	<1.0
Fe ³⁺ ^c	33.2	34.2	29.7	27.0	Mg ²⁺ ^d	<1.0	<1.0	<1.0	<1.0
K ⁺ ^c	5.5	45.5	28.3	8.2	Ca ²⁺ ^d	<1.0	<1.0	<1.0	<1.0
Cu ²⁺ ^c	6.8	40.7	8.2	3.2	Sr ²⁺ ^d	<1.0	4.8	4.5	3.6
Co ²⁺ ^c	2.1	9.4	3.6	2.1	Ba ²⁺ ^d	<1.0	12.1	9.0	2.4
Ni ²⁺ ^c	<1.0	1.4	<1.0	<1.0	Eu ³⁺ ^d	<1.0	18.9	11.3	8.9
Cr ³⁺ ^c	<1.0	4.3	<1.0	<1.0					

^a Concentration of individual metal ions 1.0 × 10⁻⁴ M, 18 h, 25 °C, 0.13 g of polymer in 50 g of aqueous solution. ^b Run 1. ^c Run 2. ^d Run 3.

under various conditions. The sol-gel Polymer 6, containing both CD and CX, also removed up to 35%.¹ Most other ions (Co²⁺, Ni²⁺, Cr³⁺, Sr²⁺, Ca²⁺, Mg²⁺, Na⁺) were not removed (<1%), whereas a few were removed to a small extent (K⁺ 6–23%, Cu²⁺ 3–6%, Eu³⁺ 7–8%, Ba²⁺ 2–3%).¹

These same ions were examined with the present polymers. Table 4 collects the results for three separate runs of metal extraction under conditions comparable to those used with the sol-gel polymers with CX.¹ When Fe³⁺ was the only cation present (run 1), all the solvent-extracted polymers **2'** were extremely effective at removing the cation from aqueous solution. Polymer **2c'** with 75% TEOS was the best, removing a remarkable 67.8% of the metal ion, compared with 33% by the sol-gel Polymer 3 under comparable conditions.¹ In run 2, a collection of metal ions was present, and again all the solvent-extracted polymers were effective in removing Fe³⁺, as well as other cations. Polymer **2c'** in this case removed 34.2% of Fe³⁺, 45.5% of K⁺, 40.7% of Cu²⁺, 9.4% of Co²⁺, and 4.3% of Cr³⁺. The polymers were ineffective in removing Ni²⁺ in all formulations and Cr³⁺ at most levels of TEOS. In run 3, a different collection of metal ions yielded removal by **2c'** of 4.8% of Sr²⁺, 12.1% of Ba²⁺, 18.9% of Eu³⁺, and negligible amounts of Na⁺, Mg²⁺, or Ca²⁺. The templated and solvent-extracted polymers thus are much more effective than the sol-gel polymers¹ in removal of metal cations, presumably because of higher accessibility of the CX cavities. Optimal results were obtained when TEOS was present at the 75% level, but all four solvent-extracted polymers were quite effective. The results degraded at low (**2b'**) or high (**2e'**) levels of Monomer 3. Thus, mesoporous polymers alone should be ineffective.

This higher degree of metal cation removal reveals interesting selectivities. The polymers selectively remove K⁺ in the presence of Na⁺ and (to a lesser degree) Ba²⁺ over Sr²⁺ over Ca²⁺, suggesting a size dependence. All three tripositively charged cations (Fe³⁺, Cr³⁺, and Eu³⁺) were removed to varying degrees. Chromium has been notoriously difficult to extract from aqueous solution but was removed by polymer **2c'** (75% TEOS) to a small extent.

The as-synthesized materials **2** showed extremely low abilities to bind metal cations (Supporting Information Table 1), in contrast to the abilities of as-synthesized **1** to bind 4-nitrophenol. The level of Fe³⁺ extraction by **2** is much lower than with the sol-gel polymers.¹ In the case of metal extraction, the mesopores in **2'** appear to provide a critical role. The presence of the surfactant in polymers **2** is a deterrent to metal extraction, compared with the sol-gel polymers. After surfactant removal, the CX units of polymers **2'** likely protrude into the mesopores (Scheme 2, left side), in contrast to the CD units of polymers

1'. In the presence of surfactant (**2**), metal cations may have a difficult time traveling to the CX units. After extraction (**2'**), the mesopores, although ineffective by themselves to trap the metal ions, provide ready access to the now exposed CX units. Metal cations in the aqueous medium of the mesopores would be more readily extracted by CX units protruding into the mesopores than metal cations in the external aqueous medium. Both the as-synthesized polymers **2** and the sol-gel¹ Polymer **3** may possess a limited number of CX units available for metal complexation, since most CX units were structurally inside the polymer.

Conclusions

We have prepared a novel family of polymers capable of effective and selective extraction of solutes from aqueous solution. In our previous work¹ we prepared sol-gel polymers in which cyclodextrin (CD) and calixarene (CX) were covalently bound to the polysilsesquioxane silicon. These organic hosts provided micropores capable of effective extraction of organic solutes and modest extraction of only Fe³⁺. To enhance the extraction capabilities of silicate polymers containing covalently bound CD and CX, we have used the templating procedure.²⁻⁴ Copolymerization of tetraethoxysilane (TEOS) with the same silsesquioxane monomer covalently bound to CD or CX in the presence of a surfactant produced a robust series of polymers **1** and **2**, respectively. Spectroscopic analysis indicated that the CD, CX, and surfactant structures were fully retained in the as-synthesized polymers. Solvent extraction of the surfactant yielded a second series of polymers **1'** and **2'**, containing hosts CD and CX, respectively. Spectroscopic analysis indicated full retention of the organic hosts but complete removal of the surfactant.

Powder X-ray diffraction, scanning and transmission electron microscopy, and nitrogen adsorption (BET) experiments revealed that the templated polymers have periodic structure with hexagonal symmetry that is largely lost at higher levels of CD and CX. The solvent-extracted polymers **1'** and **2'** have high surface area (210–1080 m² g⁻¹) and mesopores with diameters ca. 3 nm.

The CD-based polymers **1** have extremely high affinity for 4-nitrophenol. The extent of organic extraction depended on the loading level and on the amount of TEOS present. The as-synthesized polymers **1c** and **1d** with 75 and 50% TEOS, respectively, had optimal properties at 0.2 loading level,

Table 5. Extraction Abilities of Various Polymers

	% 4-nitrophenol	% Fe ³⁺	%K ⁺ %	Cu ²⁺
MCM-41 (1a)	81			
1d	>99			
1d'	92			
polymer 1 (sol-gel ^a)	89			
activated charcoal ^a	83			
polyurethane-cd ^b	30			
polymethylsilsesquioxane ^{a,c}	7			
polysilicate ^{a,d}	2			
2c		8.7	3.2	2.1
2c'		67.8	45.5	40.7
polymer 3		24.8	6.5	3.4

^a Reference 1. ^b Reference 13. ^c From MeSi(OMe)₃ in ref 1. ^d From SiCl₄ in ref 1.

extracting >99% of the organic. This level of extraction is higher than that of our previous sol-gel polymers.¹ The solvent-extracted polymers **1'** had somewhat reduced extraction abilities. Polymer **1d'** removed 92% of the organic. In this case the surfactant exerts a synergistic effect on binding.

The solvent-extracted, CX-based polymers **2'** exhibited enhanced binding and selectivity in comparison with the sol-gel polymers.¹ They removed almost 70% of Fe³⁺ and significant amounts of other metal ions, showing interesting selectivities. For example, they removed K⁺ selectively over Na⁺.

Table 5 summarizes the extracting abilities of the new polymers, with comparisons with other species. The CD-based polymers **1** are superior to MCM-41 (no CD), the CD-containing sol-gel Polymer 1, activated charcoal, polyurethane containing CD,¹³ polymethylsilsesquioxane, and polysilicate. The CX-based polymers are optimal in the solvent-extracted form, e.g., **2c'**. The as-synthesized polymer **2c** has little ability to extract metal cations. Thus, the mesopores are critical in making available the CX micropore sites.

Acknowledgment. This research was supported by the Dow Corning Corp. and the National Science Foundation (Grant CHE-0091162).

Supporting Information Available: Eight figures, one table, and the Experimental Section (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0213930

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