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Solid Phase Host−Guest Properties of Cyclodextrins and Calixarenes Covalently Attached to a Polysilsesquioxane Matrix

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A new family of silicon-based polymers has been prepared with covalently bound hosts. The polymer is a polysilsesquioxane formed by the sol−gel process, and the hosts are cyclodextrins (CD) or calixarenes (CX). The organic and silicon structures are supported by solid-state NMR spectroscopy. The nanoporous polymer is relatively stable to a variety of aqueous conditions. It is a water-insoluble material, which binds with and extracts both organic compounds and metal cations from water. The polymer containing the guests is then removed by filtration. The objective achieved can be either removal of impurities from water or recovery of materials dissolved in water. The CD-based polymer may be renewed by treatment with ethanol. Its binding ability is equal or superior to that of other available materials such as activated charcoal.

Introduction

The use of the solid state in synthetic organic chemistry conveys enormous advantages in terms of separation and purification of materials, particularly in multistep syntheses. Starting with the work of Merrifield in the synthesis of polypeptides[1] and continuing with that of Khorana and of Letsinger in the synthesis of polynucleotides,[2] attachment of substrates to a solid material has enabled chemists to remove byproducts and impurities readily over many high yield steps. The method has become a central feature in the synthesis of organic materials with repetitive units. The solid state also provides unique opportunities to control organic reactions.[3]

Solid inorganic silicates that include clays and zeolites have provided a framework for separations and catalysis utilizing naturally occurring mesoporous cavities.[4] The use of organics as templates has allowed such cavities to be created with designed shapes.[5] Silicate cavities offer acidic and basic sites for interaction with guest molecules. Specially designed organic clathrates also can provide cavities or channels in which guests may reside. The insoluble nature of these mesoporous inorganic and organic hosts permits their use in heterogeneous contexts, whereby purifications (such as removal of water by molecular sieves) can be effected and the host and bound impurity removed by simple filtration.

The most famous organic hosts include crown ethers, cyclodextrins, calixarenes, and spherands.[6] These molecules usually are soluble in aqueous or organic solvents and serve as hosts for a wide variety of neutral organics, cations, and anions. Their uses now are legion, including drug delivery, catalysis, and purification. Cyclodextrins (abbreviated herein as CD) are cyclic oligomers of glucose, which possess a hydrophilic exterior and a hydrophobic interior into which a variety of small, usually neutral, molecules may be introduced. Calixarenes (abbreviated herein as CX) are cyclic oligomers in which aligned phenols, connected by methylene units, serve to complex metals ions and other cations in particular. These hosts offer cavities on the nanometer scale, generally smaller than the zeolitic cavities. Moreover, in contrast to zeolites, CDs and CXs usually are handled in solution, and the host−guest interactions occur within the single liquid phase.

We have sought to bring together these three chemical strands: solid-state manipulations, silicon-based polymers, and nanoporous organic hosts. There are several reports of insoluble versions of these organic hosts. Typically, the hosts are incorporated into polymers either by direct synthesis or by coating or grafting the host onto a stationary phase. In particular, authors Ma and Li connected CD to urethane polymers to create highly cross-linked, insoluble materials, which they envisaged as useful for environmental separations.[7] Huq et al. incorporated CD into mesostructured silica noncovalently by co-condensation.[8] Davis and co-workers attached CD units to insoluble organic polymers to create new drug delivery systems.[9] There also have been

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(1) (a) Merrifield, R. B. *Science* **1965**, *150*, 178−185. (b) Stewart, J. M.; Young, J. D. *Solid-Phase Peptide Synthesis*, 2nd ed.; Pierce Chemical Company: Rockford, IL, 1984.

(2) (a) Jacob, R. M.; Khorana, H. G. *J. Am. Chem. Soc.* **1965**, *87*, 368−374. (b) Letsinger, R. L.; Caruthers, M. H.; Jerina, D. M. *Biochemistry* **1967**, *6*, 1379−1388.

(3) (a) Curtin, D. Y.; Paul, I. C. *Chem. Rev.* **1981**, *81*, 525−541. (b) McBride, J. M. *Acc. Chem. Res.* **1983**, *16*, 304−312.

(4) Langley, P. J.; Hulliger, J. *Chem. Soc. Rev.* **1999**, *28*, 279−291, and references therein.

(5) Polarz, S.; Smarsly, B.; Bronstein, L.; Antonietti, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4417−4422, and references therein.

(6) (a) Vögtle, F. *Supramolecular Chemistry*; Wiley: Chichester, U.K., 1991. (b) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; Wiley: Chichester, U.K., 2000.

(7) Ma, M.; Li, D. *Chem. Mater.* **1999**, *11*, 872−874.

(8) Huq, R.; Mercier, L.; Kooyman, P. J. *Chem. Mater.* **2001**, *13*, 4512−4519.

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several reports of insoluble CXs immobilized noncovalently on organic supports such as polymer beads.[10]

The creation of insoluble organic hosts could provide new materials that can be used to transport ions and molecules. Analogous to the concept of solid state synthesis, the concept of solid state hosts implies that purification, catalysis, and material transport can be carried out with the ability to remove the host along with the encapsulated material simply by filtration. To achieve these ends, there must be a happy marriage of the host (CD, CX) and the polymer support. For biological applications, neither must be toxic. For separations, the properties of the support must enhance those of the host, or at a minimum not counteract them.

Whereas past approaches have embedded organic hosts in organic polymers,[8−10] we have taken a new direction by attaching the hosts covalently to modified silicate matrixes. In contrast to silicates, in which each silicon is bonded to four oxygens, and, in contrast to silicones, in which silicon generally is bonded to two oxygens and two organic groups, silsesquioxanes contain silicon bonded to three oxygens and one organic group.[11] The bulk silsesquioxane matrix is very silicate like, but the single Si−C bond allows a variety of organic functionalities to be attached, with control of chemical and physical properties including porosity, thermal stability, hydrophobicity, dielectric properties, optics, and chemical sensitivity. To date, the use of polysilsesquioxanes for host−guest applications has relied on natural cavities, cavities produced by imprinting, or noncovalently attached organic hosts. Such approaches lack the flexibility and robustness that would attend the presence of covalently attached organic hosts. Very few such applications have been reported.[12]

We report herein the synthesis, characterization, and host−guest properties of a new family of materials that combines the physical (bulk) properties of silica gel with the host properties of CDs and CXs. The polymers are superior to silica gel because they may be easily modified synthetically, and they differ from most CD and CX hosts by being entirely insoluble in organic and aqueous media, thereby permitting facile separations.

Experimental Section

Materials. Cycloheptaamylose (β-CD) was obtained from Aldrich Chemical Co., Inc., purified by recrystallization from H_2O three times, and dried at 110 °C for 12 h. Calix[4]arene was prepared according to published literature procedures.[15]

Instrumentation. FTIR spectra were recorded on KBr pellets using a FTS60 spectrophotometer. Liquid state ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 spectrometer operating at 400.2 MHz (^1H) and 100.6 MHz (^{13}C). Liquid state ^{29}Si NMR spectra were recorded on a Varian Inova 400 spectrometer operating at 79.5 MHz. High-resolution ^{13}C and ^{29}Si solid-state NMR spectra were run at 75.5 and 59.6 MHz, respectively, on a Varian VXR300 spectrometer with a ZrO_2 rotor and two aurum caps. The spinning speed ranged between 3 and 4 kHz. Mass spectra were recorded on either a negative-ion mode JEOL DX-303 spectrometer or a Varian MAT 311A EI instrument. UV−vis spectra were recorded at 25 °C with a Varian Cary 1E double beam UV−vis spectrophotometer. The ICP-AES data were obtained with a Thermal Jarrell Ash Atomscan model 25 sequential inductively coupled plasma atomic emission spectrometer. The XRD patterns were obtained with a Rigaku DMAX-A diffractometer using Cu Kα radiation. The BET surface areas were determined by N_2 adsorption at liquid nitrogen temperature with a Micromeritics ASAP 2010 porosimeter. SEM images were acquired on a Hitachi S4500-II scanning electron microscope with an acceleration voltage of 3 kV. TEM images were recorded on a Hitachi HI8100 200-kV transmission electron microscopy.

Tetradecakis-2,6-*O*-allylcycloheptaamylose (1′) was prepared in 67% yield after recrystallization according to the method of Bergeron and Meeley. MS (negative-ion FAB) *m*/*z* 1694 (17, M−1).[13]

Heptakis-3-*O*-methyltetradecakis-2,6-*O*-allylcycloheptaamylose (2′) was prepared in 76% yield after recrystallization according to the method of Bergeron and Meeley.[13]

Tetradecakis-2,6-di-*O*-[3-(triethoxysilyl)propyl]cycloheptaamylose (Monomer 1). A 100-mL, round-bottomed flask containing 0.5 g (0.3 mmol) of **1′**, and equipped with a reflux condenser, a magnetic stirrer, and a two-way stopcock, was evacuated and charged three times with dry N_2. The flask was charged with 45 mL of tetrahydrofuran (THF) and 0.5 mL of a THF solution of Cp_2PtCl_2 (1 mg/mL).[14] The mixture was stirred at room temperature for 30 min, and 5.7 mL (31 mmol) of triethoxysilane was added. The resulting mixture was stirred and subsequently warmed to 60 °C for 72 h. The solvent and excess triethoxysilane were removed in vacuo under N_2. The product Monomer 1 was obtained as a white sticky solid. ^1H NMR ($CDCl_3$) δ 0.60 (m, $SiCH_2$), 0.91 (m, SiCH), 1.22 (t, $\mathrm{C}\mathit{H}_3\mathrm{CH_2O}$), 1.55 (m, $\mathrm{SiCHC}\mathit{H}_3$), 1.70 (m, $\mathrm{SiCH_2C}\mathit{H}_2$, $\mathrm{C}\mathit{H}_3\mathrm{CH{=}CH}$), 3.2−4.0 (m, $SiOCH_2$, H4, H5, H6, H2, H3, $\mathrm{C}\mathit{H}_2\mathrm{{-}CH{=}CH_2}$, $\mathrm{CH_2OC}\mathit{H}_2\mathrm{{-}CH{=}CH_2}$), 4.7−5.1 (m, $\mathrm{CH{=}C}\mathit{H}\mathrm{{-}CH_3}$, $\mathrm{C}\mathit{H}_2\mathrm{{=}CH}$, H1), 5.9−6.3 (m, $\mathrm{C}\mathit{H}\mathrm{{=}CH{-}CH_3}$, $\mathrm{C}\mathit{H}\mathrm{{=}CH_2}$). ^{13}C NMR ($CDCl_3$) δ 6.4, 6.8, 9.6, 10.3, 10.8, 12.3, 12.7, 18.2, 18.3, 18.5, 23.2, 58.4, 59.3, 68.9, 70.6, 72.4, 73.4, 74.1, 75.4, 80.5, 83.4, 98.9, 101.9, 116.9, 134.6, 145.9. ^{29}Si NMR ($CDCl_3$) δ −45.8.

Heptakis-3-*O*-methyltetradecakis-2,6-di-*O*-[3-(trimethoxysilyl)propyl]cycloheptaamylose (Monomer 2). A 100-mL, round-bottomed flask containing 0.5 g (0.3 mmol) of **2′**, and equipped with a reflux condenser, a magnetic stirrer, and a two-way stopcock, was evacuated and charged three times with dry N_2. The flask was charged with 30 mL of THF and 0.5 mL of a THF solution of Cp_2PtCl_2 (1 mg/mL).[14] The mixture was stirred at room temperature for 30 min, and 2.5 mL (19.5 mmol) of trimethoxysilane was added. The resulting mixture was stirred and subsequently warmed to 60 °C for 72 h. The solvent and excess trimethoxysilane were removed in vacuo under N_2. The product Monomer 2 was obtained as a light yellow sticky solid. IR (KBr) 2931 (C−H), 1645 ($CH_2{=}CH$), 1093 ($Si{-}OCH_3$). ^1H NMR ($CDCl_3$) δ 0.60 (m, $SiCH_2$), 0.68 (m, $SiCH_2$), 1.66 (m, $\mathrm{SiCH_2C}\mathit{H}_2$), 3.21−4.25 (m, OCH_3, $SiOCH_3$, H4, H5, H6, H2, H3, $\mathrm{C}\mathit{H}_2\mathrm{{-}C{=}C}$, $\mathrm{OC}\mathit{H}_2\mathrm{{-}C{=}C}$), 5.11, 5.20−5.29 (m, $CH_2{-}C$, H1), 5.89 (m, $CH{=}C$). ^{13}C NMR ($CDCl_3$) δ 6.6, 6.9, 24.4, 50.3, 50.9, 51.6, 62.5, 70.5, 72.4, 72.8, 74.4, 81.2, 82.1, 83.2, 100.6, 116.6, 136.2, 136.3. ^{29}Si NMR ($CDCl_3$) δ −42.3, −42.7.

25,26,27,28-Tetrahydroxycalix[4]arene (3′) was prepared by the method of Gutsche and Lin[16] in 73% yield after recrystallization, mp 313−315 °C. MS (EI, 90 eV) *m*/*z* 424 (100, M).

25,26,27,28-Tetra(allyloxy)calix[4]arene (4′) was prepared by the method of Gutsche et al.[17] in 64% yield after recrystallization, mp 184−185 °C. MS (EI, 90 eV) *m*/*z* 584 (100, M).

5,11,17,23-Tetraallyl-25,26,27,28-tetrahydroxycalix[4]arene (5′) was prepared according to the method of Gutsche et al.[17] in 69% yield after chromatography. MS (EI, 90 eV), *m*/*z* 584 (100, M).

5,11,17,23-Tetraallyl-25,26,27,28-tetra(allyloxy)calix[4]arene (6′). A suspension of **5′** (1.17 g, 2.0 mmol), anhydrous K_2CO_3 (4.42 g, 32.0 mmol), allyl bromide (3.87 g, 32.0 mmol),

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[9] Gonzalez, H.; Hwang, S. J.; Davis, M. E. *Bioconjugate Chem.* **1999**, *10*, 1068−1074.

[10] Alexandratos, S. D.; Natesan, S. *Macromolecules* **2001**, *34*, 206−210, and references therein.

[11] (a) Baney, R. H.; Itoh, M.; Sakakibara, A. *Chem. Rev.* **1995**, *95*, 1409−1430. (b) Shea, K. J.; Loy, D. A. *Chem. Rev.* **1995**, *95*, 1431−1442.

[12] Duhart, A.; Dozol, J. F.; Rouquette, H.; Deratani, A. *J. Membrane Sci.* **2001**, *185*, 145−155.

and CH_3CN (200 mL) was stirred and refluxed for 48 h. After evaporation of the solvent, the mixture was added to 100 mL of CH_2Cl_2 and washed with 3% HCl (2 × 100 mL) and H_2O (2 × 100 mL). The organic layer was dried (Na_2SO_4), the solvent was evaporated, and the residue was purified by flash chromatography over silica gel 60 with 1:1 petroleum ether/CH_2Cl_2 to afford 0.97 g (65%) of **6′** as white crystals. ^1H NMR ($CDCl_3$) δ 6.79 (s, 8H, ArH), 5.94−5.80 (m, 8H, CH=C), 5.16−4.97 (m, 16H, CH_2=C), 4.10 (s, 8H, OCH_2), 3.57 (s, 8H, CH_2C=), 3.18 (s, 8H, $ArCH_2Ar$). ^{13}C NMR ($CDCl_3$) δ 37.6, 39.9, 71.4, 115.3, 115.6, 131.1, 132.8, 133.8, 134.3, 138.3, 154.2. MS (EI, 90 eV) *m*/*z* 744 (100, M). Anal. Calcd for $C_{52}H_{56}O_4$: C, 83.87; H, 7.53. Found: C, 83.81; H, 7.58.

CX-Based Dimer (7′). According to the method of Hajek et al.,[19] a solution of **5′** (1.26 g, 2.15 mmol) in dry THF (60 mL) was charged with NaH (0.345 g, 14.4 mmol). The mixture was stirred under N_2 for 20 h at room temperature, and $SiCl_4$ (0.3 mL, 2.61 mmol) was added in one portion. The mixture was stirred at room temperature for another 3 h, the solvent was removed, and the solid thus-obtained was dissolved in 100 mL of ethyl ether. The insoluble solid was removed by filtration, and the solvent in the filtrate was removed by rotary evaporation to afford a light yellow solid. The solid was purified by flash chromatography (1:1 CH_2Cl_2/hexane) to provide 0.62 g (48%) of **7′** as a white solid, mp 300 °C. ^1H NMR ($CDCl_3$) δ 3.12 (d, 8H, $ArCH_2C$=), 3.31 (d, 4H, $ArCH_2Ar$), 3.40 (d, 4H, $ArCH_2Ar$), 4.46 (d, 4H, $ArCH_2Ar$), 4.54 (d, 4H, $ArCH_2Ar$), 4.94−5.12 (m, 16H, CH_2=C), 5.80−6.08 (m, 8H, CH=C), 6.74 (s, 4H, ArH), 6.88 (s, 8H, ArH), 6.93 (d, 4H, ArH). ^{13}C NMR ($CDCl_3$) δ 33.7, 34.5, 39.6, 39.9, 40.0, 115.5, 115.8, 115.9, 128.5, 128.5, 129.5, 129.8, 129.9, 130.4, 132.9, 133.8, 134.2, 135.8, 137.6, 137.8, 137.9, 145.5, 146.7, 148.9. ^{29}Si NMR ($CDCl_3$) δ −112.33.

5,11,17,23-Tetrakis[3-(triethoxysilyl)propyl]-25,26,27,-28-tetrahydroxycalix[4]arene (Monomer 3). A 100-mL, round-bottomed flask containing 0.32 g (0.54 mmol) of **5′**, and equipped with a reflux condenser, a magnetic stirrer, and a two-way stopcock, was evacuated and charged three times with dry N_2. The flask then was charged with 30 mL of THF and 0.5 mL of a THF solution of Cp_2PtCl_2 (1 mg/mL). The mixture was stirred at room temperature for 30 min, and 1.07 g (6.5 mmol) of triethoxysilane was added. The resulting mixture was stirred and subsequently warmed to 60 °C for 72 h. The solvent and excess triethoxysilane were removed in vacuo under N_2. The product CX-based Monomer 3 was obtained as a light yellow sticky solid. ^1H NMR ($CDCl_3$) δ 0.65 (m, 8H, $SiCH_2$), 1.22 (t, 36H, OCH_2CH_3), 1.65 (m, 8H, $SiCH_2CH_2$), 2.42 (m, 8H, $SiCH_2CH_2CH_2Ar$), 4.22 (br d, 4H, $ArCH_2Ar$), 3.44 (br d, 4H, $ArCH_2Ar$), 3.81 (q, 24H, OCH_2CH_3), 6.84 (s, 8H, ArH, 10.19 (s, 4H, OH). ^{13}C NMR ($CDCl_3$) δ 10.5, 18.5, 25.2, 32.2, 38.7, 58.5, 128.1, 128.9, 135.9, 146.7. ^{29}Si NMR ($CDCl_3$) δ −45.0.

5,11,17,23-Tetrakis[3-(trimethoxysilyl)propyl]-25,26,-27,28-tetrakis[3-(trimethoxysilyl)propyloxy]calix[4]-arene (Monomer 4). A 100-mL, round-bottomed flask containing 0.4 g (0.54 mmol) of **6′**, and equipped with a reflux condenser, a magnetic stirrer, and a two-way stopcock, was evacuated and charged three times with dry N_2. The flask was charged with 30 mL of THF and 0.5 mL of a THF solution of Cp_2PtCl_2 (1 mg/mL). The mixture was stirred at room temperature for 30 min, and 2.64 g (21.6 mmol) of trimethoxysilane was added. The resulting mixture was stirred and subsequently warmed to 60 °C for 72 h. The solvent and excess trimethoxysilane were removed in vacuo under N_2. The product CX-based Monomer 4 was obtained as a light yellow sticky solid. ^1H NMR ($CDCl_3$) δ 0.70 (m, $SiCH_2$), 1.8 (m, $SiCH_2CH_2$), 2.4 (m, $Si-CH_2-CH_2-CH_2-Ar$), 3.05−4.20 (m, $Si-CH_2-CH_2-CH_2-O$, $SiOCH_3$, $ArCH_2Ar$), 4.9−5.1 (m, CH_2=C), 5.8−6.0 (m, CH=C), 6.7−6.9 (m, ArH). ^{13}C NMR ($CDCl_3$) δ 9.9, 10.1, 24.0, 25.4, 38.8, 40.2, 50.4, 51.3, 115.1, 128.4, 131.5, 134.2, 138.3, 154.1. ^{29}Si NMR ($CDCl_3$) δ −42.3, −42.7.

CX-Based Monomer 5. A 100-mL, round-bottomed flask containing 0.4 g (0.33 mmol) of **7′**, and equipped with a reflux condenser, a magnetic stirrer and a two-way stopcock, was evacuated and charged three times with dry N_2. The flask was charged with 30 mL of THF and 0.5 mL of a THF solution of Cp_2PtCl_2 (1 mg/mL). The mixture was stirred at room temperature for 30 min, and 1.61 g (13.2 mmol) of trimethoxysilane was added. The resulting mixture was stirred and subsequently warmed to 60 °C for 72 h. The solvent and excess trimethoxysilane were removed in vacuo under N_2. The product, CX-based Monomer 5, was obtained as a light yellow sticky solid. ^1H NMR ($CDCl_3$) δ 0.5−0.8 (m, $SiCH_2$), 1.55−1.81 (m, $SiCH_2CH_2$), 2.28−2.60 (m, $SiCH_2CH_2CH_2$), 3.23−3.54, 4.40−4.61 (m, $ArCH_2Ar$), 3.61 (m, OCH_3), 6.75, 6.87, 6.95 (m, ArH). ^{13}C NMR ($CDCl_3$) δ 9.2, 9.3, 24.3, 24.5, 33.2, 33.5, 35.4, 39.0, 39.7, 52.1, 128.4, 128.6, 129.1, 129.2, 129.3, 130.1, 136.6, 136.8, 137.6, 145.2, 146.8, 148.1. ^{29}Si NMR ($CDCl_3$) δ −41.7, −112.8.

CD-Based Polymer 1. In a 50-mL Schlenk flask under N_2, 2.9 mmol of Monomer 1 and 11.5 mL of dry THF were mixed and stirred vigorously. The aqueous HCl acid catalyst (1.97 mL, 1 N) was premixed with 11.5 mL of dry THF and added in one portion to the flask. The aqueous acid was miscible with the THF solution of Monomer 1. The clear, homogeneous solution was stirred for an additional 1 min. Stirring was then stopped, and gelation occurred to form at first a gel that occupied the same volume as the initial solution. The gel was allowed to stand in order to age at room temperature for a week. The resulting light yellow solid was crushed, washed with ethyl ether (3 × 50 mL), and dried for 48 h at room temperature under high vacuum (0.45 Torr).

CD-Based Polymer 2. In a 25-mL Schlenk flask under N_2, 1.32 g (0.5 mmol) of Monomer 2 and 2 mL of dry THF were mixed and stirred vigorously. The aqueous HCl acid catalyst (0.31 mL, 1 N) was premixed with 2 mL of dry THF and added in one portion to the flask. The aqueous acid was miscible with the THF solution of Monomer 2. The clear, homogeneous solution was stirred for an additional 0.5 min. Stirring then was stopped and gelation occurred to form at first a gel that occupied the same volume as the initial solution. The gel was allowed to stand at room temperature to age for a week. The resulting light yellow solid then was crushed, washed with ethyl ether (3 × 50 mL), and dried for 48 h at room temperature under high vacuum (0.45 Torr).

Polymethylsilsesquioxane. In a 100-mL Schlenk flask under N_2, 7.5 g (0.05 mol) of methyltrichlorosilane and 25 mL of dry THF were mixed and stirred vigorously. The aqueous HCl acid catalyst (1.35 mL, 1 N) was premixed with 25 mL of dry THF and added in one portion to the flask. The clear, homogeneous solution was stirred for 7 days. No gel formed. After concentration of the solution to a viscous oil, gelation occurred. After an additional 48 h, the white gel was crushed, washed with ethyl ether (3 × 100 mL), and dried for 48 h at room temperature under vacuum (0.45 Torr).

Silicate Polymer. In a 100-mL Schlenk flask under N_2, 7.6 g (0.05 mol) of tetramethoxysilane and 25 mL of dry THF were mixed and stirred vigorously. The aqueous HCl acid catalyst (1.8 mL, 1 N) was premixed with 25 mL of dry THF and added in one portion to the flask. The clear, homogeneous solution was stirred for 7 days. No gel formed. After concentration of the solution to a viscous oil, gelation occurred. After an additional 48 h of aging, the white gel was crushed, washed with ethyl ether (3 × 100 mL), and dried for 48 h at room temperature under vacuum (0.45 Torr).

CX-Based Polymer 3. In a 50-mL Schlenk flask under N_2, 3.78 g (3.6 mmol) of Monomer 3 and 3.6 mL of dry THF were mixed and stirred vigorously. The aqueous HCl acid catalyst (0.78 mL, 1 N) was premixed with 3.6 mL of dry THF and added in one portion to the flask. The aqueous acid was miscible with the THF solution of Monomer 3. The clear, homogeneous solution was stirred for an additional 7 min. Stirring was stopped and gelation occurred to form at first a gel that occupied the same volume as the initial solution. The gel was allowed to stand to age at room temperature for a week. The resulting light yellow gel then was crushed, washed with 50 mL of H_2O, 50 mL of CH_3OH, 50 mL of acetone, and 50 mL of ethyl ether. The solid was dried for 48 h at 50 °C under high vacuum (0.45 Torr).

CX-Based Polymer 4. In a 25-mL Schlenk flask under N_2, 1.4 g (1 mmol) of Monomer 4 and 2.5 mL of dry THF were mixed and stirred vigorously. The aqueous HCl acid catalyst (0.43 mL, 1 N) was premixed with 2.5 mL of dry THF and added in one portion to the flask. The aqueous acid was miscible with the THF solution of Monomer 4. The clear, homogeneous solution was stirred for an additional 2 h. Stirring then was stopped and gelation occurred to form at first a gel that occupied the same volume as the initial solution. The gel was allowed to stand to age at room temperature for a week. The resulting light yellow solid then was crushed, washed with H_2O, CH_3OH, and ethyl ether, and dried for 48 h at room temperature under high vacuum (0.45 Torr).

CX-Based Polymer 5. In a 25-mL Schlenk flask under N_2, 0.87 g (0.4 mmol) of Monomer 5 and 1 mL of dry THF were mixed and stirred vigorously. The aqueous HCl acid catalyst (0.17 mL, 1 N) was premixed with 1 mL of dry THF and added in one portion to the flask. The aqueous acid was miscible with the THF solution of Monomer 5. The clear, homogeneous solution was stirred for an additional 37 min. Stirring then was stopped and gelation occurred to form at first a gel that occupied the same volume as the initial solution. The polymer gel was allowed to stand to age at room temperature for a week. The resulting light yellow solid then was crushed, washed with H_2O, CH_3OH, and ethyl ether, and dried for 48 h at room temperature under high vacuum (0.45 Torr). This polymer still had calixarene units connected by silicate linkages. To free the hydroxy groups, a solution of the polymer (400 mg, 0.49 mmol) in 10 mL of THF was treated dropwise with tetrabutylammonium fluoride (1.0 M in THF, 4.5 mL, 4.5 mmol) and stirred for 36 h. The resulting mixture was filtered, and the solid Polymer 5 was washed with H_2O, CH_3OH, acetone, and diethyl ether.

Hybrid CD- and CX-Based Polymer 6. A 500-mL, round-bottomed flask containing 7.0 g (4.13 mmol) of **1′** and 2.4 g (4.13 mmol) of compound **5′**, and equipped with a reflux condenser, a magnetic stirrer, and a two-way stopcock, was evacuated and charged three times with dry N_2. The flask was charged with 150 mL of THF and 2 mL of a THF solution of Cp_2PtCl_2 (1 mg/mL). The mixture was stirred at room temperature for 30 min, and 35.4 g (0.22 mol) of triethoxysilane was added. The resulting mixture was stirred and subsequently warmed to 60 °C for 72 h. The solvent and excess triethoxysilane were removed by vacuum distillation under N_2 to form a mixture of Monomers 1 and 3. Then 21 mL of THF was added to the residue, and the mixture was stirred vigorously. The aqueous HCl acid catalyst (3.70 mL, 1 N) was premixed with 21 mL of dry THF and added in one portion to the flask. The clear, homogeneous solution was stirred for an additional 3 min. Stirring then was stopped and gelation occurred to form at first a gel that occupied the same volume as the initial solution. The gel was allowed to stand to age at room temperature for a week, and the resulting light yellow solid then was crushed, washed with H_2O, ethanol, and ethyl ether, and dried for 48 h at room temperature under high vacuum (0.45 Torr).

Hybrid CD- and CX-Based Polymer 7. In a 25-mL Schlenk flask under N_2, 1.2 g (0.5 mmol) of CD-based Monomer 2, 1.1 g (0.5 mmol) of CX-based Monomer 5, and 2.5 mL of dry THF were mixed and stirred vigorously. The aqueous HCl acid catalyst (0.18 mL, 1 N) was premixed with 2.5 mL of dry THF and added in one portion to the flask. The aqueous acid was miscible with the THF solution of monomers. The clear, homogeneous solution was stirred for an additional 2 min. Stirring then was stopped and gelation occurred to form at first a gel that occupied the same volume as the initial solution. The polymer was allowed to stand to age at room temperature for a week, and the resulting light yellow solid then was crushed, washed with H_2O, CH_3OH, and ethyl ether, and dried for 48 h at room temperature under high vacuum (0.45 Torr). This polymer still had calixarene units connected by silicate linkages. To free the hydroxy groups, a solution of the polymer (1.99 g, 0.5 mmol) in 40 mL of THF was treated dropwise with tetrabutylammonium fluoride (1.0 M in THF, 10 mL, 10 mmol) and stirred for 36 h. The resulting mixture was filtered, and the solid polymer was washed with H_2O, CH_3OH, acetone, and diethyl ether.

Extraction of 4-Nitrophenol by CD-Based Polymer 1. Polymer 1 (265 mg) was stirred with 50 mL of a buffered aqueous solution (pH 2.0) of 4-nitrophenol (8.63×10^{-5} M) at 25 °C for 18 h. The suspension was filtered, and the residual concentration of 4-nitrophenol in the filtrate was measured by UV−vis spectroscopy. The amount of 4-nitrophenol extracted into Polymer 1 was determined by subtracting the amount of 4-nitrophenol in the filtrate from that of the untreated 4-nitrophenol solution. The same procedure was used with variation of extraction time, pH, concentration of 4-nitrophenol, and the amount of polymer.

Regeneration of 4-Nitrophenol-Loaded CD-Based Polymer 1. Polymer 1 (200 mg) loaded with a known amount of 4-nitrophenol was stirred in 30 mL of pure ethanol at 25 °C for 24 h. The suspension was filtered, and the 4-nitrophenol concentration in the ethanol filtrate was measured by UV−vis spectroscopy. The amount of 4-nitrophenol removed from Polymer 1 then was determined by subtraction.

Extraction of Metal Cations by CX-Based Polymer 3. Polymer 3 (100 mg) was stirred with 50 mL of a buffered aqueous solution (pH 5.0) containing Fe^{3+}, Cu^{2+}, Co^{2+}, and Cr^{3+} (1.0×10^{-4} M for each metal cation) at 25 °C for 18 h. The suspension was filtered, and the residual metal cation concentrations in the filtrate were measured by ICP-AE spectroscopy. The amounts of Fe^{3+}, Cu^{2+}, Co^{2+}, and Cr^{3+} extracted by Polymer 3 were determined by subtracting the respective amounts of the ions in the filtrate from those of the untreated metal cation solution. The experiment was repeated with a higher concentration of the same ions (1.0×10^{-3} M for each metal cation) and with other metal cations. Similar experiments were carried out in which Polymers 4, 5, 6, and 7 were used to extract metal ions.

Simultaneous Extraction of 4-Nitrophenol and Metal Cations by Hybrid CD- and CX-based Polymer 6. Polymer 6 (355 mg) was stirred with 50 mL of buffered aqueous solution (pH 5.0) containing 4-nitrophenol (8.63×10^{-5} M) and Fe^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, and Cr^{3+} (1.0×10^{-4} M for each metal cation) at 25 °C for 18 h. The suspension was filtered, and the residual concentrations of 4-nitrophenol and metal cations in the filtrate were measured respectively by UV−vis spectroscopy and ICP-AE spectroscopy. The amount of 4-nitrophenol extracted by Polymer 6 was determined by subtracting the amount of 4-nitrophenol in the filtrate from that of the untreated solution. The amounts of Fe^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+}, and Cr^{3+} extracted by Polymer 6 were determined by subtracting the amounts in the filtrate from those in the untreated solution.

Results

Synthesis. The strategy to link organic hosts to silsesquioxane frameworks involved covalently attaching an allyl group to the host, hydrosilylating the allyl double bond, and polymerizing the resulting silane by the sol−gel technique. Scheme 1 illustrates the procedure for preparing two silylated CD monomers. These processes began with commercially available β-cyclodextrin, the toroidal, cyclic heptamer of glucose. Allyl groups were placed on the 2 and 6 positions of all seven glucose units.[13] The objective in having two allyl groups per glucose was to enable polymers to grow from both the upper and lower faces of the CD torus and therefore to provide extensive cross-linking. Two distinct monomers were produced (Scheme 1) by either methylating the still remaining 3-hydroxy groups or leaving them free in order to modulate hydrogen-bonding properties of later polymers. Hydrosilylation of the allyl groups with trialkoxysilanes and dicyclopentadienylplatinum(II) chloride (Cp_2PtCl_2) as catalyst[14] produced Monomer 1 (with seven free 3-hydroxy groups per cyclodextrin

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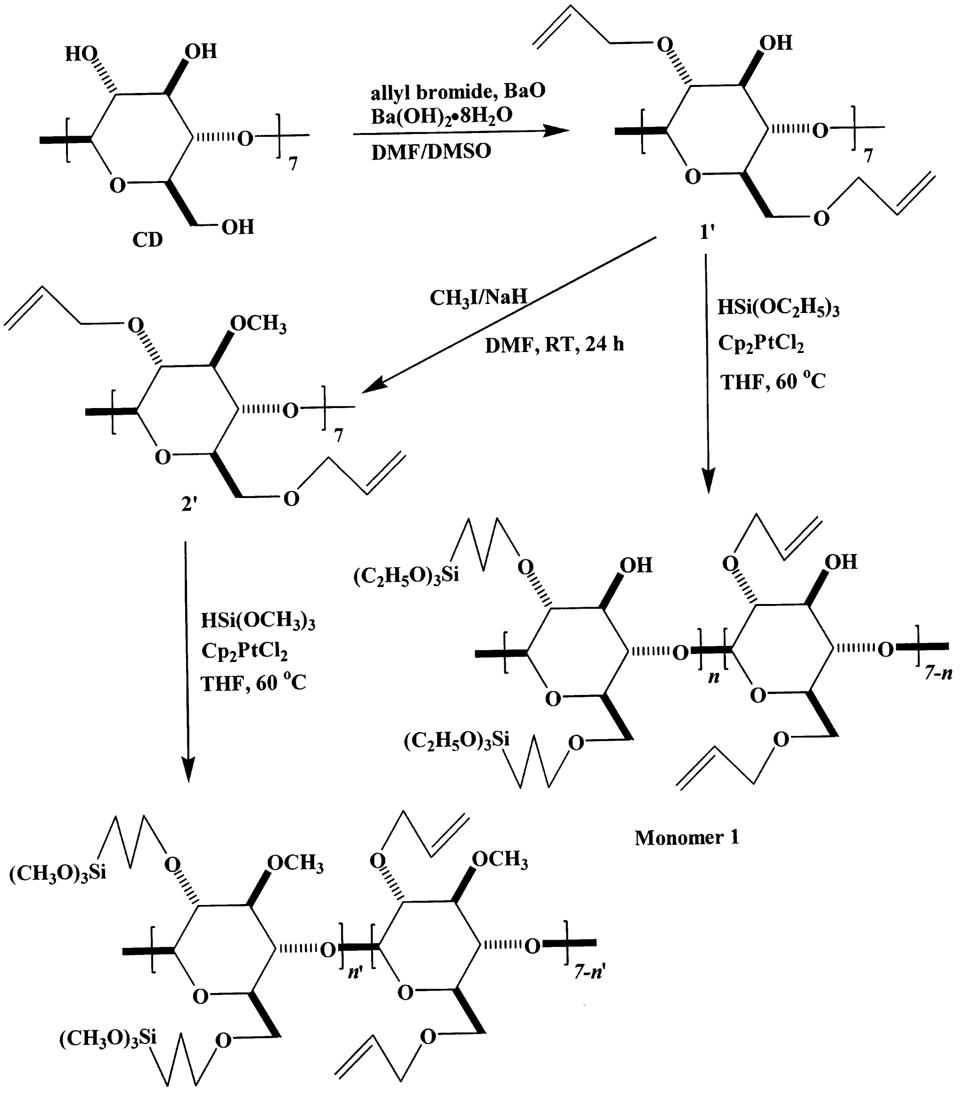
(13) Bergeron, R. J.; Meeley, M. P. *Bioorg. Chem.* **1976**, *5*, 197−202.

Scheme 1



Monomer 1

Monomer 2

unit) or Monomer 2 (with the 3 position fully methylated). It was estimated from the ^1H NMR spectra that about 90% of the allyl groups had been silylated. Scheme 1 represents the incomplete hydrosilylation process by including both fully silylated glucose units ($n/7$ or $n'/7$ ~0.9) and completely unsilylated glucose units (~0.1). Monosilylated units naturally are present but are excluded pictorially for simplicity.

Scheme 2 shows the procedure for preparing silylated CX monomers. The tetrameric calixarene was prepared by literature procedures.[15] The *tert*-butyl groups were removed from all four phenols (**3′**),[16] and the phenolic hydroxyls were allylated (**4′**).[17] Double Claisen rearrangements reconfigured the four allyl groups from the oxygens to the para carbons, as both ortho positions were blocked.[18] The *C*-allylated phenols (**5′**) then provided a starting point for several CX monomers. The allyl groups may be hydrosilylated[14] directly to give Monomer 3 with free phenolic hydroxyls. The *C*-allylated system may be *O*-allylated again (**6′**) and then hydrosilylated to give Monomer 4. Whereas Monomer 3 can polymerize from only one face, Monomer 4 was constructed in order to allow polymerization to take place from both the top and bottom faces of the CX.

An alternative double CX structure was constructed as follows. The *C*-allylated phenolic system **5′** was dimerized through a silicate linkage by treatment with sodium hydride and tetrachlorosilane (**7′**),[19] and the dimer was hydrosilylated in the usual fashion to produce Monomer 5.[14] The silicate linkages in Monomer 5 can be hydrolyzed in a later step to create free hydroxyl groups. Monomers 3−5 have four silyl groups per CX, all on a single face, and Monomer 4 has eight silyl groups per CX, emanating from opposite faces. The ^1H NMR spectra indicated that nearly all the allyl groups had been silylated for all three CX monomers.

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(14) Apfel, M. A.; Finkelman, H.; Janini, G. M.; Laub, R. J.; Luhmann, B.-H.; Price, A.; Roberts, W. L.; Shaw, T. J.; Smith, C. A. *Anal. Chem.* **1985**, *57*, 651−658.

(15) Gutsche, C. D.; Iqbal, M.; Stewart, D. *J. Org. Chem.* **1986**, *51*, 742−745.

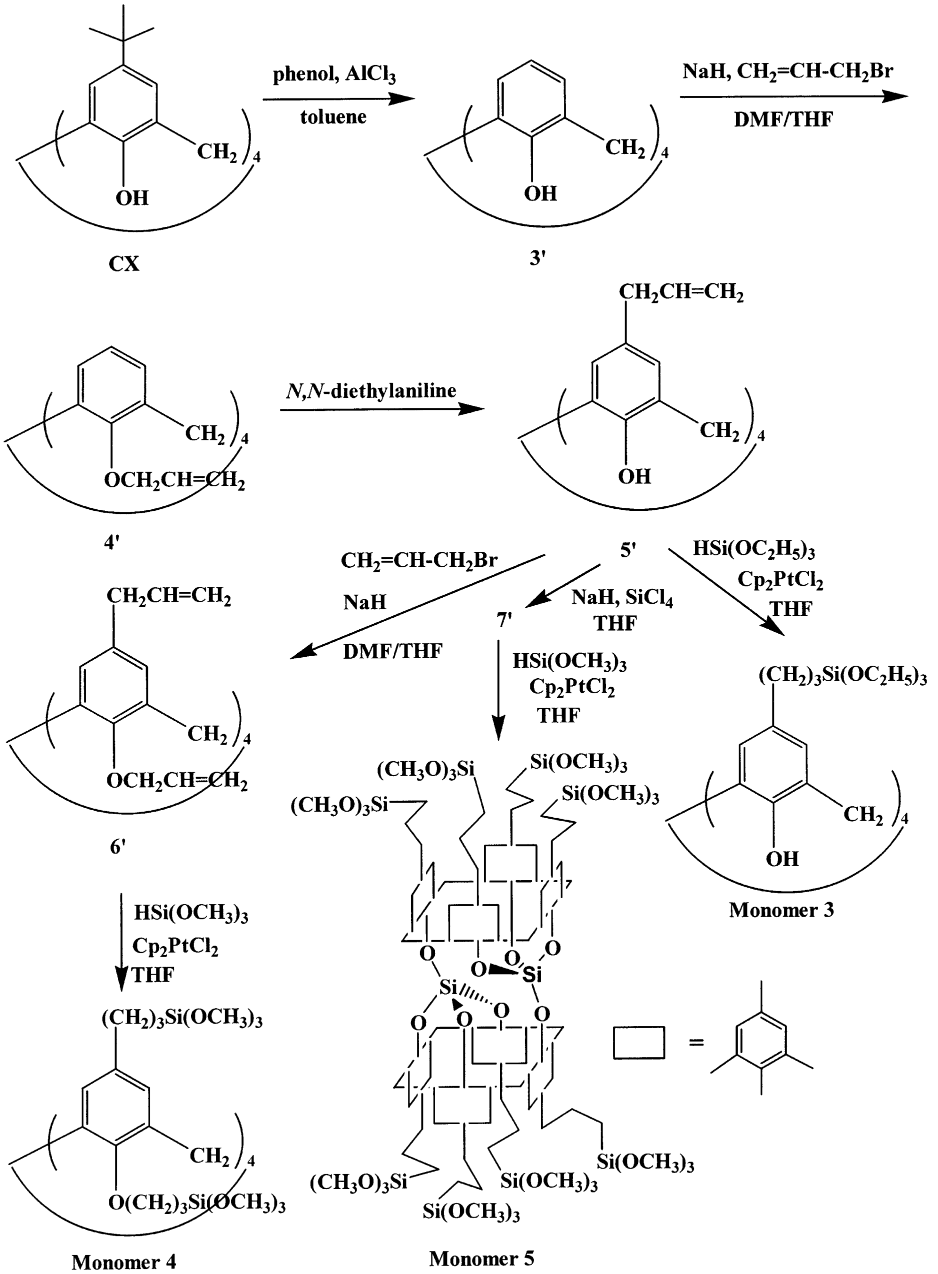
(16) Gutsche, C. D.; Lin, L. G. *Tetrahedron* **1986**, *42*, 1633−1640.

(17) Gutsche, C. D.; Dhawan, B.; Levine, J. A.; Kwang, H. N.; Bauer, L. J. *Tetrahedron* **1983**, *39*, 409−426.

(18) Gutsche, C. D.; Levine, J. A.; Sujeeth, P. K. *J. Org. Chem.* **1985**, *50*, 5802−5806.

(19) Hajek, F.; Hosseini, M. W.; Graf, E.; Cian, A. D.; Fischer, J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1760−1762.

Scheme 2



Polymerization of these monomers either singly or as mixtures was carried out by the sol–gel method in anhydrous tetrahydrofuran (THF) with aqueous hydrochloric acid as the catalyst.[20] Trialkoxysilyl groups (Si–O–R) are hydrolyzed to generate siloxane (Si–O–Si) bonds via intermediate silanols (Si–O–H). Because each silicon atom offers three potential sites of siloxane formation, and each monomer has anywhere from four (CX) to fourteen (CD) silyl groups, hydrolysis leads to a growing, highly cross-linked polysilsesquioxane polymer. Branching and cross-linking continues in solution until the network is sufficiently large for the gel transition to occur. The resulting gel then consists of a solid polymer network interspersed with solvent (THF) and containing the covalently bound hosts. Removal of the supporting solvent collapses the network to afford the host-containing polysilsesquioxane gel.

Processing Monomers 1–5 in this fashion produced Polymers 1–5, respectively (Schemes 3 and 4). Polymer 5 differs from Polymer 3 in that two CX units offer their hydroxylated ends to a single region in space within the rigid polymer. Hybrid polymers containing both CD and CX units were constructed by polymerizing mixtures of monomers. Polymer 6 (Scheme 5) was constructed from Monomer 1 (with 3 hydroxy groups) and Monomer 3 (with phenolic hydroxy groups). Polymer 7 was constructed from Monomer 2 (with the 3 positions methylated) and Monomer 5 (the dimeric structure). After gelation and isolation of the polymers from Monomer 5 and from the mixture of Monomers 2 and 5, the silicate linkages were hydrolyzed to produce free hydroxyl groups on the CX units (Schemes 4 and 5).

Schemes 3–5 are intended to provide only a crude illustration of the resulting cross-linked polymer struc-

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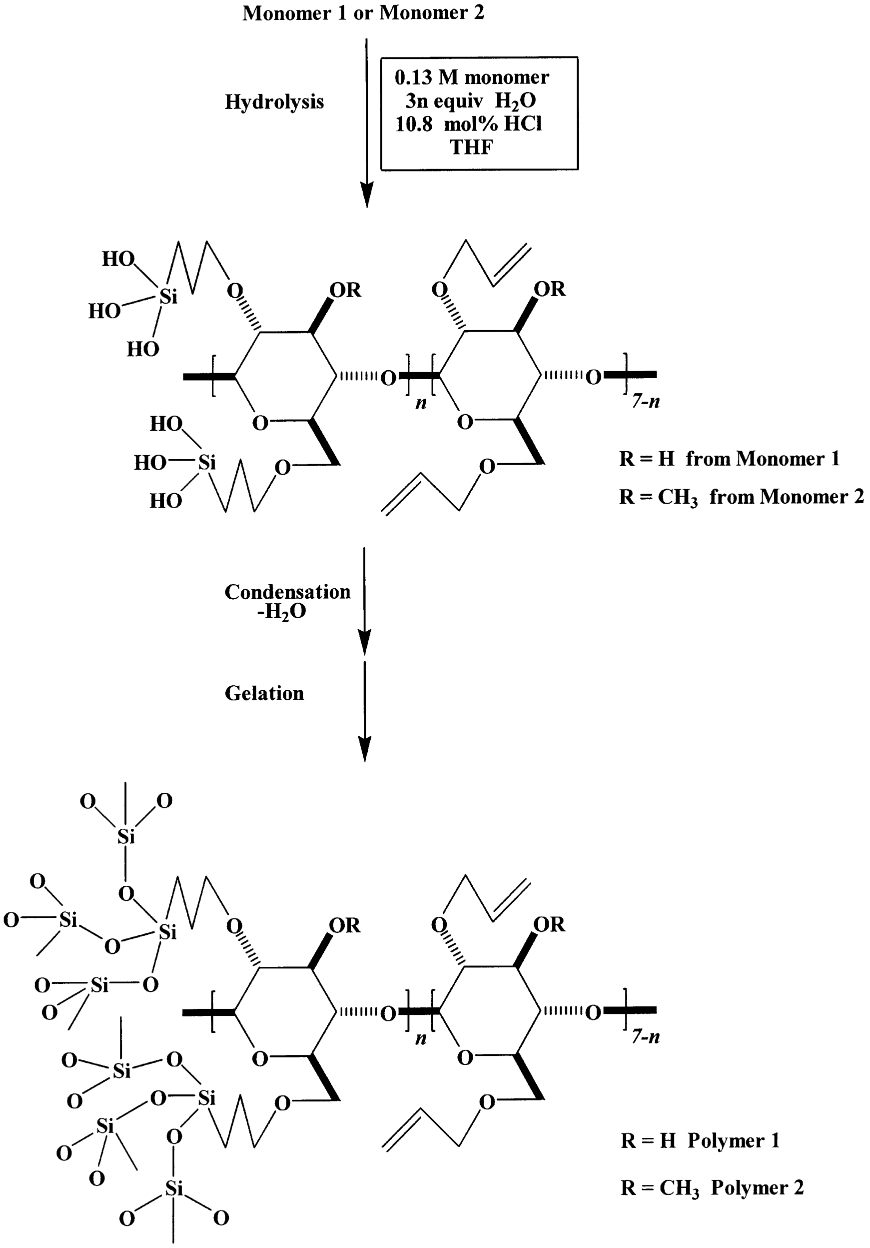
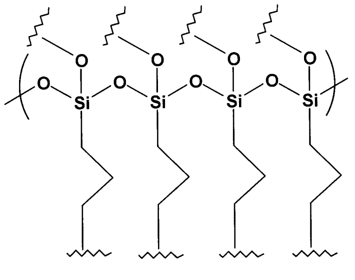
[20] (a) Shea, K. J.; Loy, D. A.; Webster, O. *J. Am. Chem. Soc.* **1992**, *114*, 6700–6710. (b) Oviatt, H. W., Jr.; Shea, K. J.; Small, J. H. *Chem. Mater.* **1993**, *5*, 943–950.

Scheme 3



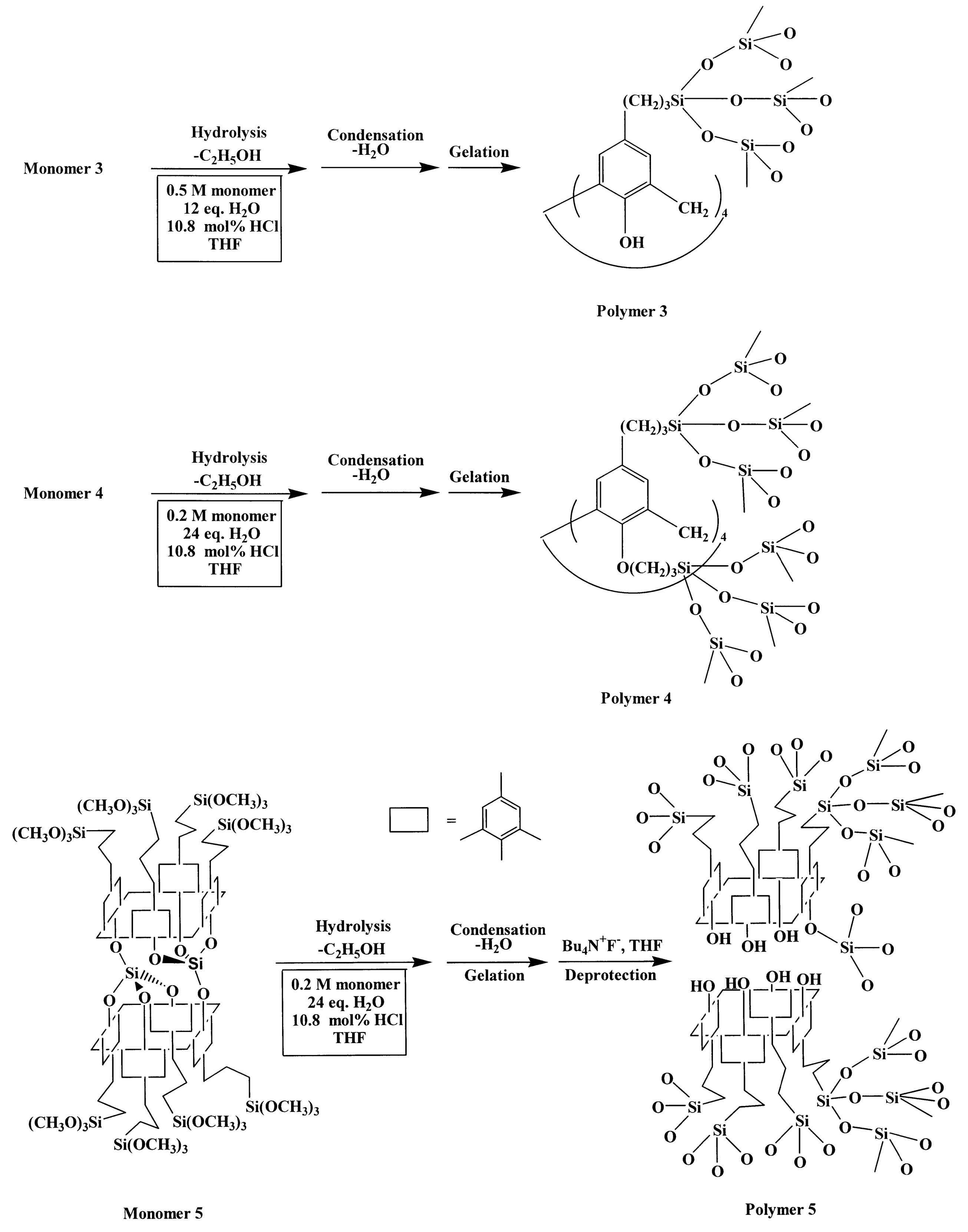
tures. For example, in Polymer 1 (Scheme 3), each of the seven glucose units in each CD unit (only one is shown) can possess up to six siloxane connections, for 42 siloxanes per CD. Each of the 42 siloxane oxygens can be attached to another silicon atom (to complete the siloxane group), and each of these is connected to two more oxygens and one carbon from other CD units; thus each CD is directly attached potentially to 42 other CD units, and through additional siloxane linkages to another 84, for a total of 126 in the next layer of connections. Successive polymerization then multiplies up the factor. If only 90% of the allyl groups had been hydrosilylated and 90% of the silanol units successfully formed siloxane connections, there would still be many cross-links per CD. Steric effects would limit realization of all such connections, but clearly a very highly branched, cross-linked structure is obtained. It should be kept in mind that all of the polymers have structures based on the linear form **1**, in which each side chain oxygen is cross-linked to another silicon to form a fully three-dimensional polymer.



1

Table 1 contains the gelation times for the sol−gel polymerization of CD and CX monomers, both separately and as mixtures, and for several controls. Methyltrichlorosilane and tetramethoxysilane failed to polymerize to gels either at 1.0 M monomer concentration

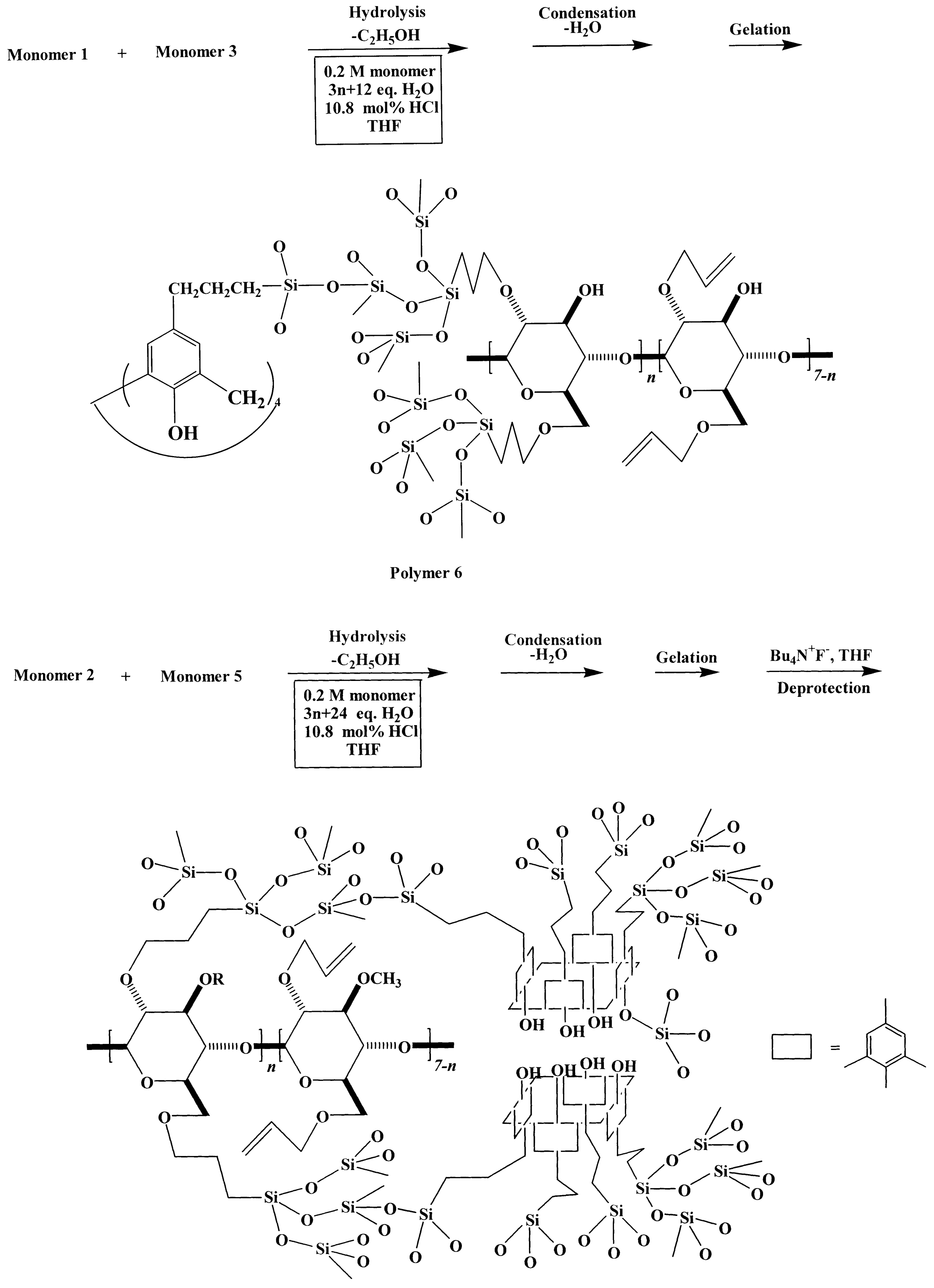
Scheme 4



or concentrations above 5.0 M. In contrast, the CD- and CX-containing monomers polymerized readily at quite low concentrations. The monomer concentration is important in this process. The CD-based Monomers 1 and 2 formed gels within one minute at concentrations as low as 0.13 M. Monomer 3 failed to gel at this concentration, but did gel within 7 min at 0.5 M. Monomers 4 and 5 and the mixtures of CD and CX monomers formed gels at concentrations as low as 0.2 M.

Characterization. All polymers were characterized by solid state ^{13}C and ^{29}Si NMR spectroscopy, FTIR, powder X-ray, SEM, TEM, and nitrogen adsorption

Scheme 5



Polymer 6

Polymer 7

porosimetry. These results are presented in the Discussion section.

The pH stability of the Polymers 1 and 3 was tested by stirring samples in solutions buffered to pH 2, 7, or

Table 1. Gelation Times for the Sol−Gel Polymerization of CD- and CX-Based Silane Monomers to Nanoporous Polysilsesquioxanes

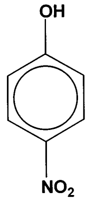
monomer	monomer conc. (M)	amount of H_2O (eq. monomer)[a]	gelation time (min)
1	0.13	3n	1
2	0.13	3n	<1
3	0.13	12	no gel
3	0.5	12	7
4	0.2	24	120
5	0.2	24	37
1 + **3**	0.2	3n + 12	3
2 + **5**	0.2	3n + 24	2
CH_3SiCl_3	1.0	3	no gel
$Si(OCH_3)_4$	1.0	4	no gel
CH_3SiCl_3	>5.0	3	no gel
$Si(OCH_3)_4$	>5.0	4	no gel

[a] n represents the extent of hydrosilylation in Schemes 1, 3, and 5.

11 for 2 days. The polymers were recovered and examined by solid-state NMR and FTIR.

Molecular weights were not measured for these insoluble polymers, as has normally been the case for insoluble sol−gel polysilicates.[20]

Association Properties of Organic Guests. 4-Nitrophenol (**2**) was selected as the substrate for extensive association studies because it is soluble in water and is UV active. A standard aqueous solution of **2** was prepared with known concentration. The powdered polymer was placed in the solution, and the mixture was stirred vigorously at room temperature (25 °C). The polymer was removed after a period of time, and the concentration of **2** remaining in the aqueous filtrate was measured by UV−vis spectroscopy. The treated polymer was washed with water and soaked in ethanol to remove the associated **2**. The concentration of released **2** was measured in the ethanol solution in order to determine the renewability of the polymer.



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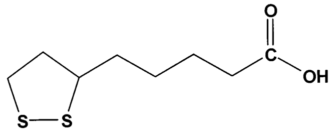

3

The degree of association depends on the structure of the polymer, the structure of the guest, the reaction time, the pH, the concentration of the guest in solution, and the loading level (defined as the weight of the guest in grams divided by the weight of the host in grams, converted to percentage). Figure 1 illustrates the effect of loading level for Polymer 1 with 4-nitrophenol for a series of association experiments over the same amount of time and with the same concentration of the organic substrate. Thus, only the amount of the insoluble polymer is varied. Figure 2 illustrates the effect of reaction time for the same materials at constant loading level and concentration of **2**. The experiments were carried out for loading levels of 0.2 and 5.0%. Figure 3 illustrates the effect of substrate concentration, and Figure 4 shows the effect of pH.

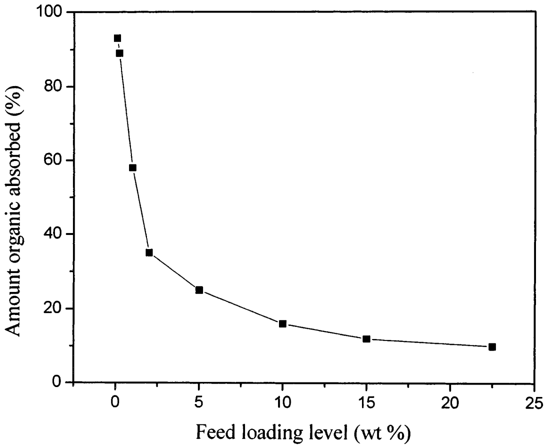

Figure 1. Effect of loading level of Polymer 1 on the absorption of 4-nitrophenol (8.63×10^{-5} M in water).

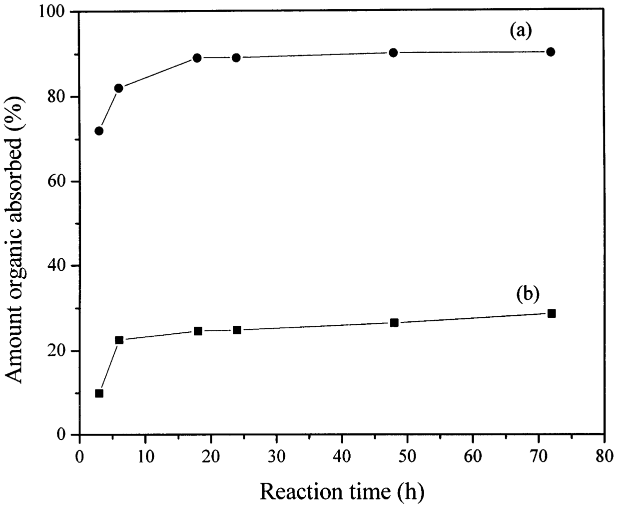

Figure 2. Effect of reaction time on the absorption by Polymer 1 of 4-nitrophenol (8.63×10^{-5} M in water) for two loading levels: (a) 0.2%, (b) 5%.

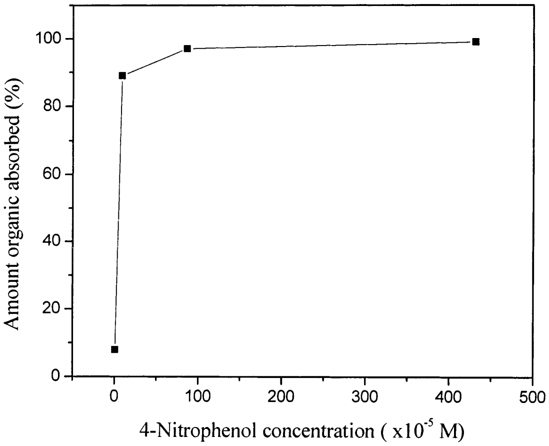

Figure 3. Effect of solute concentration on the absorption of 4-nitrophenol by Polymer 1 (loading level 0.2%) in water.

Additional association experiments were carried out on D,L-6,8-thioctic acid (**3**) with Polymer 1. At pH 7, 94% of **3** was absorbed at a 1% loading level and 44% was absorbed at a 5% loading level.

Association experiments were carried out on 4-nitrophenol with the other six polymers. For a loading level of 0.2%, reaction time of 18 h, and substrate concentra-

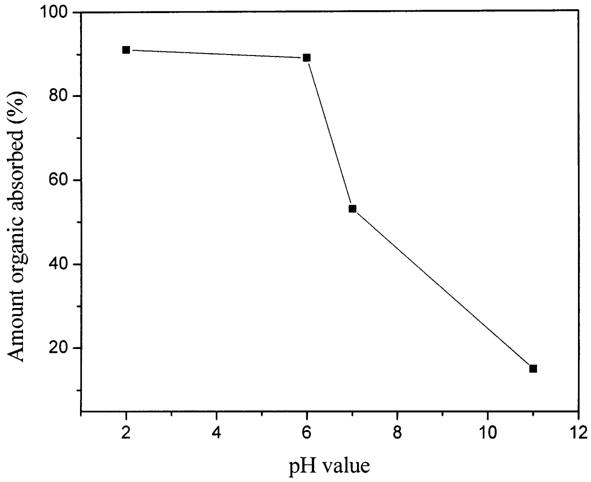

Figure 4. Effect of pH on the absorption of 4-nitrophenol (8.63 × 10^{-5} M in water) by Polymer 1 (loading level 0.2%).

Table 2. Percentage Extraction of Metal Cations in Water[a]

metal cation	Polymer 4	Polymer 3	Polymer 5	Polymer 6	Polymer 7
Fe^{3+}	<1.0	24.8	26.2	35.2	33.8
K^+	<1.0	6.5	6.9	7.9	7.2
Cu^{2+}	<1.0	3.4	3.2	4.2	3.5
Co^{2+}	<1.0	<1.0	<1.0	<1.0	<1.0
Ni^{2+}	<1.0	<1.0	<1.0	<1.0	<1.0
Cr^{3+}	<1.0	<1.0	<1.0	<1.0	<1.0

[a] Aqueous phase [metal nitrate = 1.0 × 10^{-4} M]; reaction time, 18 h; reaction temperature, 25 °C.

tion in water of 8.63 × 10^{-5} M, the percentage absorption was 86% for Polymer 2, 63% for Polymer 3, 46% for Polymer 4, 68% for Polymer 5, 92% for Polymer 6, and 87% for Polymer 7.

Renewability was determined for the removal of **2** from six of the polymers. Expressed as the percentage of 4-nitrophenol released, the renewabilities were 74% for Polymer 1, 71% for Polymer 2, 54% for Polymer 3, 46% for Polymer 5, 42% for Polymer 6, and 41% for Polymer 7.

Finally, the ability of Polymer 1 to extract 4-nitrophenol from aqueous solution was compared with that of several other materials. For a loading level of 0.2%, 18 h reaction time, and substrate concentration of 8.63 × 10^{-5} M, Polymer 1 absorbed 89% of **2**, activated charcoal absorbed 83%, Ma and Li's CD-polyurethane polymer[7] absorbed 30%, polymethylsilsesquioxane absorbed 7%, and pure silicate formed from tetramethoxylsilane absorbed 2%.

Association Properties of Inorganic Cations. Aqueous solutions were prepared containing several inorganic cations (either separately or as mixtures) at known concentrations. These solutions were stirred at 25 °C for 18 h, and the residual metal cation concentrations were measured by inductively coupled plasma (ICP) spectrophotometry. Tables 2−4 contain the percentages of extracted metals for several of the polymers at various concentrations of metal. The effect of pH on extraction abilities was examined (Table 5) for metal ion concentration of 1.0 × 10^{-4} M and 18 h.

Simultaneous Association of Organic Molecules and Inorganic Cations. A solution containing 4-nitrophenol at 8.63 × 10^{-5} M and various inorganic ions at 1.0 × 10^{-4} M was stirred for 18 h at 25 °C with the hybrid Polymers 6 or 7. The percentages of extracted materials are given in Table 6.

Table 3. Percentage Extraction of Metal Cations in Water[a]

metal cation	Polymer 4	Polymer 3	Polymer 5	Polymer 6	Polymer 7
Fe^{3+}	<1.0	20.4	20.7	23.5	22.9
K^+	<1.0	11.1	13.4	23.3	16.4
Cu^{2+}	<1.0	5.2	5.3	5.9	5.7
Co^{2+}	<1.0	<1.0	<1.0	<1.0	<1.0
Ni^{2+}	<1.0	<1.0	<1.0	<1.0	<1.0
Cr^{3+}	<1.0	<1.0	<1.0	<1.0	<1.0

[a] Aqueous phase [metal nitrate = 1.0 × 10^{-3} M]; reaction time, 18 h; reaction temperature, 25 °C.

Table 4. Percentage Extraction of Metal Cations in Water[a]

metal cation	Polymer 3	Polymer 4	Polymer 6
Eu^{3+}	6.9	<1.0	8.3
Ba^{2+}	3.3	<1.0	2.3
Sr^{2+}	<1.0	<1.0	<1.0
Ca^{2+}	<1.0	<1.0	<1.0
Mg^{2+}	<1.0	<1.0	<1.0
Na^+	<1.0	<1.0	<1.0

[a] Aqueous phase [metal nitrate = 1.0 × 10^{-3} M]; reaction time, 18 h; reaction temperature, 25 °C.

Table 5. Effect of pH on the Percentage Extraction of Metal Cations in Water[a]

	metal cations extracted (%)				
polymer	Fe^{3+}	Cu^{2+}	Co^{2+}	Cr^{3+}	pH
3	2.1	1.3	<1.0	<1.0	2
3	11.2	2.1	<1.0	<1.0	3
3	28.1	3.4	<1.0	<1.0	4
3	34.8	5.2	<1.0	<1.0	5
6	4.0	1.6	<1.0	<1.0	2
6	22.4	3.2	<1.0	<1.0	3
6	35.8	4.1	<1.0	<1.0	4
6	40.4	6.3	<1.0	<1.0	5

[a] Aqueous phase [metal nitrate = 1.0 × 10^{-4} M]; reaction time, 18 h; reaction temperature, 25 °C.

Table 6. Percentage Absorption of Metal Cations and 4-Nitrophenol in Water[a]

solute	Polymer 6	Polymer 7
4-nitrophenol	90	86
Fe^{3+}	33.3	30.9
Cu^{2+}	4.8	2.3
Co^{2+}	<1.0	<1.0
Ni^{2+}	<1.0	<1.0
Cr^{3+}	<1.0	<1.0

[a] Aqueous phase [metal nitrate = 1.0 × 10^{-4} M, 4-nitrophenol = 8.63 × 10^{-5} M]; reaction time, 18 h; reaction temperature, 25 °C.

Discussion

Gelation Times and Mechanism. The CD-based Monomers 1 and 2 can form monolithic gels within one minute (Table 1) at concentrations as low as 0.13 M. In contrast, methyltrichlorosilane and tetramethoxysilane (TMOS) failed to polymerize to gels at concentrations of 1.0 M or higher. Monomer 2 differs from TMOS by only a single substituent on each silicon atom. The greater mass and volume of the fourth substituent (the CD host) must provide the critical difference in the ability to polymerize to gels.

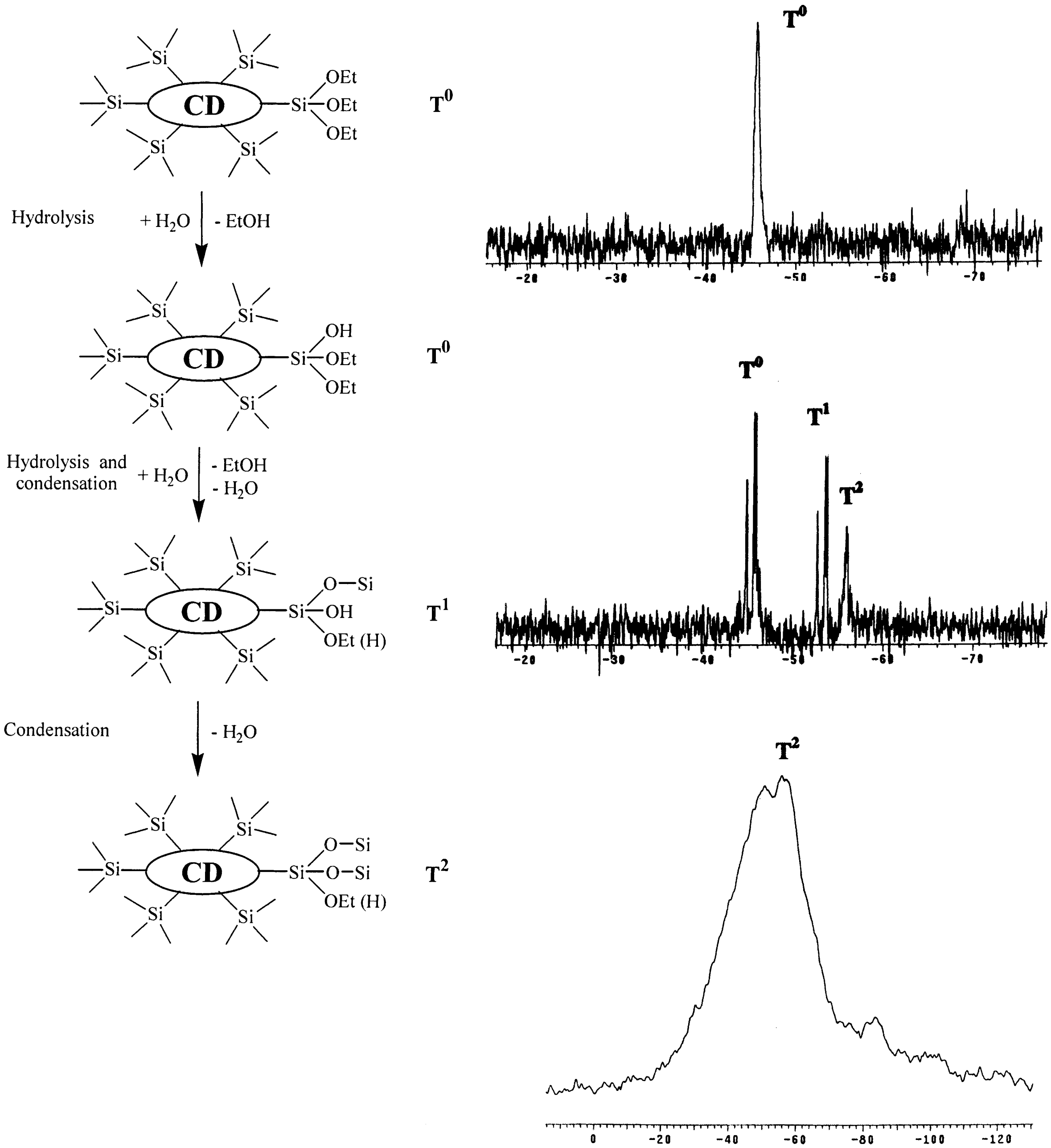

Figure 5. Right: ^{29}Si NMR spectrum of (top) Monomer 1 in $CDCl_3$, (middle) the sol–gel solution in $CDCl_3$ under acidic conditions after the addition of 9 equiv of water, and (bottom) the solid Polymer 1 with magic angle spinning. Left: Diagrams of the progress of hydrolysis and condensation from the starting material at the top to the polymer at the bottom.

The CX-based monomers were somewhat slower in the gelation process. Although Monomer 3 failed to polymerize to a gel at a monomer concentration of 0.13 M, it did form a monolithic gel within seven minutes at only slightly higher concentrations of 0.5 M. In contrast, Monomers 4 and 5 polymerized to gels at 0.2 M, although the process was slower. Monomer 3 is unique among the five distinct monomers in that it polymerizes from only a single face (see Schemes 1 and 2).

Shea and Loy have described three broad classes of alkoxysilyl monomers on the basis of their gelation behavior under acidic conditions: rapid gelation even at low concentration, slow gelation, and no gelation. Monomers 1 and 2 appear to belong to the first class and Monomers 3–5 belong to the second class. Shea and Loy have correlated the rate of gelation with the mechanism. In the fast processes, the monomer (Si–O–C) dimerizes and trimerizes (through Si–O–H to Si–O–Si) initially, and polymerization then follows rapidly. The slower processes begin with intramolecular reactions in which the Si–O–Si bonds form within the same molecule (cyclization) rather than with neighbors. These materials then polymerize slowly.

The initial stages of polymerization may be followed, after Shea,[21] by using substoichiometric quantities of water in the sol–gel polymerization reaction. There is insufficient water to complete hydrolysis of all the Si–O–C groups. Gelation then is inhibited, and the initial intermediates remain in solution and may be examined by solution-phase ^{29}Si NMR spectroscopy. With excess water, the product gels out into a solid phase that is unavailable for solution NMR techniques. Figure 5

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[21] Shea, K. J.; Loy, D. A. *Acc. Chem. Res*, **2001**, *34*, 707–716.

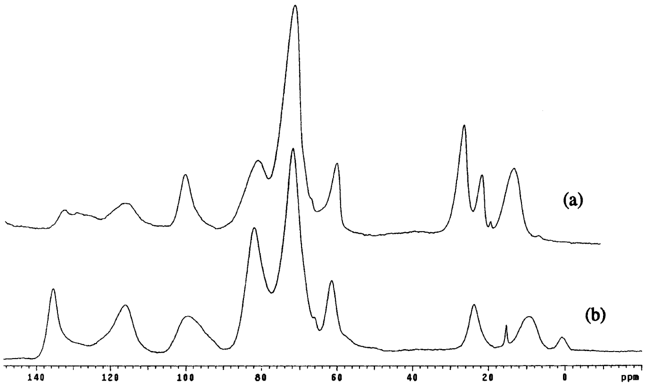

Figure 6. Solid state ^{13}C spectra of Polymers 1 (a) and 2 (b) with magic angle spinning and cross polarization.

shows the results of such an experiment with Monomer 1. The spectrum of the starting material at the top on the right exhibits a single ^{29}Si peak at δ −45.7, a position associated with the T^0 structure (Si bonded through three oxygens to zero other silicons). The upper left of Figure 5 schematically illustrates the initial monomer. Hydrolysis of the Si−O−C groups to Si−O−H groups initially generates a variety of T^0 peaks, depending on the number of hydrolyzed organic groups (see the second diagram from the top on the left). Dimerization then begins to create Si−O−Si bonds, first of the T^1 type (Si bonded through three oxygens to one other silicon) and then of the T^2 type (Si bonded through three oxygens to two other silicons) (see the third and fourth diagrams on the left). Complete condensation eventually would lead to T^3 structures, the maximum permitted in these silsesquioxanes in which all the silicons are bonded to a single carbon.

The middle spectrum in Figure 5 on the right was obtained with the conditions of substoichiometric water. The soluble intermediate species exhibits several T^0 peaks, several T^1 peaks, and at least one T^2 peak. As intramolecular bridging would lead to only a single T^1 species and no higher structures, these observations are consistent with the rapid mechanism described by Shea and Loy.[21] The solid state ^{29}Si spectrum of the final polymer at the bottom of Figure 5 on the right is dominated by the T^2 species at δ −55 (and the background peak from the rotor).

Characterization. Further characterization of the structures of the final Polymers 1 and 2 was obtained from solid state ^{13}C NMR spectroscopy (Figure 6). The presence of at least two large peaks in the region δ 65−90 is consistent with the O-bonded carbons in the glucose ring, and the peak at δ 100 corresponds to the anomeric carbon O−C−O. The Si−C−C−**C**−O resonance from the linkage also should appear in the region δ 65−90. These results confirm that the glucose rings are intact and not hydrolyzed. The peak at δ ca. 60 is from unhydrolyzed Si−O−C carbons in both spectra. The spectrum of Polymer 1 (a) contains a peak at δ 23 from unhydrolyzed Si−O−C-**C** groups (Polymer 1 contained ethoxy groups, whereas Polymer 2 contained methoxy groups; see Scheme 1). These peaks decreased in intensity during the tests for the stability of the polymer to acidic and basic conditions. The two large peaks at δ ca. 10 and 25 are respectively from the Si−**C**−C−C−O and Si−C−**C**−C−O carbons in the linkage between CD and silicon. Unsilylated alkenic carbons appear in the region δ 110−140. The amount is quite small for Monomer 1 but significant for Monomer 2.

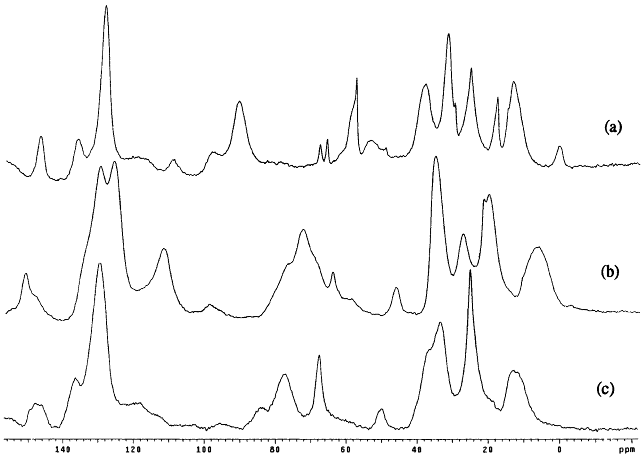

Figure 7. Solid state ^{13}C NMR spectra of Polymers 3 (a), 4 (b), and 5 (c) with magic angle spinning and cross polarization.

Figure 7 contains the solid state ^{13}C spectra for the CX-based Polymers 3−5. The Si−**C**−C−C and Si−C−**C**−C peaks at δ 13 and 25 indicate the presence of the grouping that links CX to silicon. The benzylic carbons are found at δ ca. 30 and the doubly benzylic linkage between the CX aryl groups are found at δ ca. 40. Polymer 4 in addition has O−C carbons at δ ca. 70. The aromatic carbons of the CX unit concentrate around δ 130 (the quaternary aromatic peaks either are small or are invisible due to poor cross polarization). Hydrosilylation was very effective in Polymers 3 and 5 but less so in Polymer 4 (which required two hydrosilylation reactions per aromatic ring), as witnessed by the peaks at δ 110 and 135 (cf. Figure 7b).

The solid state ^{13}C NMR spectra for the mixed Polymers 6 and 7 showed intact glucose rings and CX groupings, as well as all other expected peaks.

The ^{13}C NMR spectra support high levels of hydrosilylation in most cases, intact glucose rings in all CD polymers, intact CX groupings, and the presence of the Si−C−C−C linkages in all cases.

The solid state ^{29}Si NMR spectrum of the CD-based Polymer 1 (Figure 5) has already been seen to contain a peak at δ −55 from T^2 species, in which silicon has two siloxy linkages, **Si**(OSi)$_2$. The ^{29}Si NMR spectrum of the CX-based Polymer 3 is dominated by this δ −55 peak, but in addition has a smaller peak at δ −64 from T^3 species, in which silicon has three siloxy linkages, **Si**(OSi)$_3$.

The infrared spectra of all the polymers contained the Si−O−Si stretching vibration at 1050−1100 cm^{-1}. The absence of sharp peaks in the powder X-ray pattern of Polymer 1 indicated that there are no highly ordered micropores. Similar patterns were observed for the other polymers.

The SEM images of all the polymers indicated no welordered arrays as in zeolites, but rather a random network exhibiting some porosity. TEM images of Polymers 1 and 3 confirmed this conclusion and indicated that the pore diameter is 1.5−8 nm for CD-based polymers. The CX-based polymers revealed no pore structure. Although the pores in the CD-based polymers could come from either the cyclodextrins or the silsesquioxane network, the absence of pores in the CX-based polymers suggests that the observed pores are likely to be from the cyclodextrin cavity. Apparently the calixarene cavity is too small for the resolution of the TEM experiment.

Nitrogen adsorption porosimetry indicated that all polymers have low BET surface areas of 1.1−1.7 m^2/g, similar to the values observed by Ma and Li.[7] These values are much lower than that of activated charcoal (ca. 600 m^2/g). The strong association of organic molecules with our polymers therefore does not result from surface adsorption. Nonetheless, CD units at or near the surface may provide the primary binding sites. Our evidence does not address this issue.

Stability of the polymers to high and low pH was monitored by infrared spectroscopy and solid-state NMR spectroscopy. The OH vibrations at 3440 and 1383 cm^{-1} from Si−O−H groups became smaller. The ^{13}C spectra indicated that the CD and CX units remained intact during these experiments. The disappearance of the ethyl peaks at δ 55.5 and 14.2 ($SiO\mathbf{C}H_2\mathbf{C}H_3$) indicated hydrolysis possibly with further polymerization. The ^{29}Si spectrum indicated an increase in the T^3 resonance at δ ca. 64 and the appearance of Q-type resonances from SiO_4 units from hydrolysis of C−Si bonds. The Q peaks, however, are quite small in comparison with the T peaks. Although there is some alteration in the siloxane matrix at high and low pH, it is important that the embedded CD hosts are not impaired.

Association Properties of Organics. 4-Nitrophenol served as the standard organic guest because of its aqueous solubility and its ultraviolet absorption. Polymer 1 was the subject of experiments exploring variation of a number of factors. The loading level is the term we use to describe the amount of the solid polymer present in relation to the amount of dissolved organic (grams guest per grams host in percentage). We use weight rather than moles because the solid polymer does not permit calculation of molar ratios. It should provide many sites of nanometer dimension (hence, *nanopockets*) appropriate in size to absorb the organics. As demonstrated by Figure 1, the affinity of the polymer is highest and close to quantitative at low loading levels (<0.2%), whereas it drops rapidly to less than 20% organic absorbed at loading levels above 5%. On a g/g basis, the polymer exhibits saturation as the amount of guest increases. This observation may result because surface sites are most effective, because only some interior nanopockets are accessible, or because all sites are filled.

The process of absorption shows relatively little time dependence (Figure 2). After a very brief delay, absorption rises quickly and achieves the 90% level in about 20 h. At high loading levels, when absorption is low, the process still is complete in under 10 h. Stirring for extremely long times (18 h) does not result in a significant increase in the amount of organic absorbed.

The percentage of organic absorbed shows some dependence on the concentration of the organic (Figure 3). At extremely low levels ($<10^{-5}$ M), the percentage of absorbed material drops rapidly. Above this threshold level, it is extremely high (>90%). In this particular experiment, we did not follow the effect to even higher concentrations ($>10^{-2}$ M), but we expect absorption to start to decrease again as the effect of the loading level catches up to the effect of solute concentration.

The ability of Polymer 1 to absorb 4-nitrophenol is highest under acidic conditions and falls off at high alkalinity (Figure 4). This effect may result from the acidity of the phenol. At high pH, the anionic form begins to predominate, and it would be more highly solvated by water and hence less available for absorption by the polymer. Cyclodextrins have been found in general to absorb neutral, polar organics most efficiently.[6] We expect Polymers 1 and 2 to be generally effective in absorbing neutral organics. Our own experiments were limited only by the experimental design that required ultraviolet absorption for measurement of substrate concentrations. We also tested absorption of a larger, more functional molecule, D,L-6,8-thioctic acid (**3**). Like 4-nitrophenol, **3** was efficiently removed (94%) at low loading levels (1%), but removal decreased to 44% at a loading level of 5%. Thus, the affinity of carboxylic acids to our polymers is similar to that of phenols.

The remaining polymers also were tested for the ability to absorb 4-nitrophenol (**2**). We found that all the CD-based polymers absorbed ca. 90% of **2** at a loading level of 0.2%. The CX-based polymers, however, exhibited lower affinity for this material, absorbing 46−68% under the same conditions. Thus, cyclodextrins are very effective in all formulations. Even the calixarenes showed very good abilities to absorb this neutral organic.

If these polymers are to have practical utility, ideally they should be renewable. Activated charcoal, for example, is nonrenewable. It must be discarded after use. We found that all of our polymers were renewable to some extent. The CD-based polymers released >70% of absorbed 4-nitrophenol, and the CX-based polymers released >40%. Thus, cyclodextrins release the organic somewhat more effectively than the calixarenes.

We also compared Polymer 1 with various other materials in terms of ability to remove 4-nitrophenol from aqueous solution. We found that Polymer 1 was superior to all other materials tested. Under a common set of conditions, Polymer 1 removed 89%, whereas activated charcoal removed 83%. Although this difference is not great, Polymer 1 is at least as good as activated charcoal and is largely renewable. The CD-containing urethane polymer synthesized by Ma and Li, which provided the conceptual basis for nanopockets, absorbs only about 30% of **2** under these conditions. In the polymer of Ma and Li, CD units are doubly connected to chains of the form $-O(CO)NH(CH_2)_6NH(CO)O-$. Thus, there is an important difference between CD embedded in polysilsesquioxanes and those embedded in polyurethanes. The two polymers may differ in the number of cyclodextrin sites that are available, either because fewer CD units were incorporated into urethane or because fewer are accessible. Alternatively, the silsesquioxane superstructure may offer a synergistic effect. We tested the latter hypothesis by examining the abilities of polymethylsilsesquioxane from methyltrichlorosilane and of silicate from tetramethoxysilane to absorb **2**. Although both materials exhibited poor abilities (respectively 7% and 2%), they were not negligible. The 7% absorption by polymethylsilsesquioxane, however, could not explain the entire difference between the silicate and urethane polymers. Consequently, we believe that the primary effect is better availability of the CD nanopockets in the polysilsesquioxane matrix, although synergism may enhance the effect slightly. It also should be noted that the sugar and silicon constituents of Polymer 1 should exhibit very low degrees of toxicity, whereas the toxicity of urethanes would have to be tested in this context.

Association Properties of Inorganic Cations. We examined the abilities of the CX-based polymers to remove inorganic cations from aqueous solution. At present we have examined only the tetrameric calixarenes. Many other varieties exist, in which the number of phenolic units varies (e.g., six or eight) or in which phenol is replaced by another organic entity. These materials will be the subjects of future experiments. Our CX-based Polymers 3 and 5 and the hybrid Polymers 6 and 7 proved to be effective and selective for removal of iron cations (Tables 2−4). These experiments were carried out with several inorganic ions present in solution (either singly or as mixtures). Their percentages were measured before and after treatment with the polymers. There is a small dependence on concentration, with slightly higher percentages of Fe^{3+} extracted at 10^{-4} M than at 10^{-3} M. Polymers 3 and 5−7 showed small affinities for potassium, copper, europium, and barium cations. The ability of Polymers 3 and 6 to absorb iron is pH dependent (Table 5). Within the pH range 2−5, the ability decreased with increasing acidity. Polymer 4 was ineffective at removing any inorganic cation. Of the CX-based polymers, it is the only one lacking hydroxyl groups. Polymers 3, 5, 6, and 7 all have a crown of hydroxyl groups, which must be critical in binding with metal cations.

We examined the abilities of the hybrid Polymers 6 and 7 to absorb 4-nitrophenol and metal cations simultaneously (Table 6). These two processes occurred quite independently. Both polymers absorbed about 90% of **2**, 30% of Fe^{3+}, and 2−4% of Cu^{2+} in a single experiment, comparable to the experiments in which the polymers were treated separately with organics or inorganic cations. Clearly, the sites available for organics and for inorganic cations are entirely distinct.

Conclusions

Hosts from the cyclodextrin (CD) and calixarene (CX) families may be bound covalently to trialkoxysilanes, which may be hydrolyzed and condensed by the sol−gel process into polymers that physically resemble silica gel. These gel polymers formed in high yield usually in minutes. NMR spectra indicated that the CD or CX units were still intact. Tests at high and low pH demonstrated good stability of these materials to hydrolysis. Cyclodextrin provides a nanometer-scale pocket inside the polysilsesquioxane matrix suitable for encapsulation of organics, and calixarene provides a binding site for inorganic cations. SEM and TEM images revealed that the polymers pack in a random network rather than in a well-ordered array, and BET measurements indicated relatively low surface area (1.1−1.7 m^2/g).

Association experiments with 4-nitrophenol, in which the organic was in aqueous solution and the polymer was present as a solid, resulted in removal of >90% of the organic from solution by the CD-based polymers. The association process was examined as a function of amount of polymer, concentration of solute, pH, and time of contact. Once the polymer had been charged with the organic, it could be renewed by treatment with ethanol, which dissolved out the guest. The CD-based polymers were slightly better than activated charcoal, which is not renewable, in terms of extent of encapsulation of the organic, and considerably better than CD bound to a urethane polymer.[7]

The CX-based polymers selectively removed iron cations from aqueous solution, in the presence of numerous other inorganic cations. Hybrid polymers containing both CD nanopockets and CX unit successfully removed both 4-nitrophenol and iron cations.

These polymers have a number of advantages. (1) They are easily prepared in high yield from inexpensive, readily available starting materials. (2) They can be designed to contain a wide variety of organic hosts when prepared according to our synthetic procedure. (3) They remove organics effectively and iron and other metal cations selectively, depending on the nature of the host. (4) They are largely renewable. Our current experiments involve incorporation of other members of the cyclodextrin and calixarene families into the polysilsesquioxane matrix. For example, variation of the size of the cavity through change in the respective number of glucose or phenol units should alter the selectivity of the materials. Other classes of hosts with different binding properties also will be examined.

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