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Simple Surfactant-Free Route to Mesoporous Organic−Inorganic Hybrid Silicas Containing Covalently Bound Cyclodextrins

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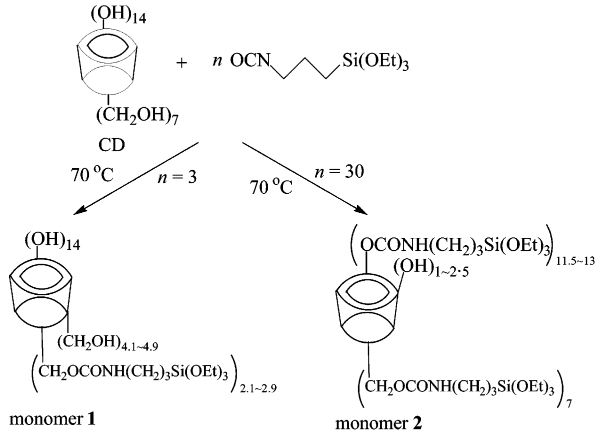
Received September 3, 2003

Abstract: Novel mesoporous organic−inorganic hybrid silicas containing covalently bound cyclodextrins have been synthesized by a simple, surfactant-free sol−gel route and are shown to have high BET surface areas and narrow pore-size distributions.

The synthesis of mesoporous inorganic materials using a structure-directing template has attracted wide attention since 1992.[1−4] To date, ionic[1] or neutral surfactants,[5,6] as well as nonsurfactants such as dibenzoyl-*l*-tartaric acid[7] or cyclodextrins (CDs),[8] have been used as structure-directing templates. Template removal by calcination or solvent extraction generates mesoporous materials with large surface areas. These purely inorganic mesoporous materials, however, are limited in applications by their lack of organic functional groups. Recently, a second generation of mesoporous hybrid silicas containing organic groups was developed in the presence of a templating surfactant.[9] Most recently, Kuroda et al. reported the direct formation of meso-structured, silica-based hybrids in the absence of surfactant templation.[10] Only a few examples with covalently bound organic groups such as CD[11,12] or cyclams[13] have provided specific cavities in addition to the mesostructures. We prepared sol−gel polymers in which CD hosts were covalently bound to polysilsesquioxane silicon.[14] These gel polymers prepared without surfactant templation were nonporous, and the only available cavities were those provided by the CD hosts. Nitrogen isotherms indicated very low BET surface areas (1.1−1.7 m^2/g).[14] Control of mesostructures in organic−inorganic hybrid silicas without the use of surfactant templation consequently has proved to be a challenge.

SCHEME 1. Synthetic Routes to CD-Containing Monomers 1 and 2



In the present work, we report the synthesis of mesoporous organic−inorganic hybrid silicas containing covalently bound CDs via a simple and environmentally friendly surfactant-free sol−gel process. These mesoporous CD-containing silica materials, produced without a structure-directing surfactant, have high surface areas and pore volumes, as well as narrow pore-size distributions, similar to those of CD-containing mesoporous materials prepared through the surfactant-templating route.[11,12] Avoidance of the surfactant template during synthesis of the CD-containing mesoporous silica materials is of significant importance for both environmental and industrial applications.

The strategy for preparing mesoporous silicas with covalently bound CD units via a surfactant-free sol−gel route involved covalently attaching triethoxysilyl groups to the CD host through urethane linkages and copolymerizing the resulting CD-containing silane monomers with tetraethoxysilane (TEOS) by the NaOH-catalyzed sol−gel reaction without using a structure-directing surfactant. Two CD-based monomers **1** and **2** with different degrees of substitution were synthesized by the reaction of purified CD with 3-isocyanatopropyltriethoxysilane in different molar ratios (Scheme 1). The IR spectra of monomers **1** and **2** show the complete disappearance of the isocyanato band at 2270 cm^{-1} and the appearance of vibration bands at 3390, 1713−1715, and 1542−1544 cm^{-1}, corresponding to N−H, C=O, and NH−CO groups, respectively. The ^{1}H NMR spectra of monomers **1** and **2** indicated that about 3 and 20 hydroxyl groups per CD molecule had been substituted by triethoxysilyl groups through urethane linkages in monomers **1** and **2**, respectively. The average degrees of substitution values of monomers **1** and **2** determined by ^{1}H NMR are in good agreement with those calculated from the respective elemental analyses of nitrogen and carbon in monomers **1** and **2**. The ^{29}Si NMR spectrum of mon-

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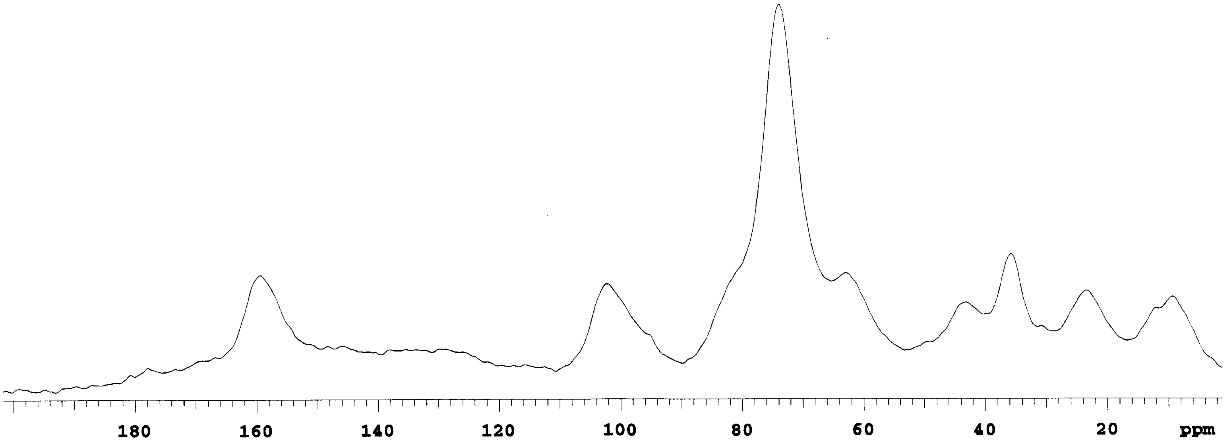
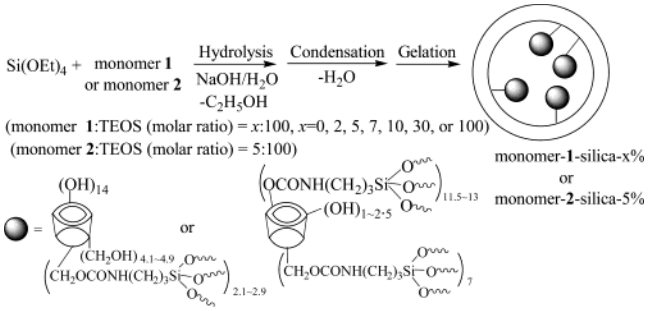


FIGURE 1. Solid-state ^{13}C NMR spectrum of mesoporous monomer−**1**−silica−5%.

SCHEME 2. Synthetic Routes to Monomer−1−Silica−*x*% and Monomer−2−silica−5% Materials



omer **1** showed a single peak at δ −46.17, and the ^{29}Si NMR spectrum of monomer **2** showed two peaks at δ −45.92 and −46.04. These ^{29}Si NMR results indicate that in monomer **1** only the primary hydroxyl groups of CD are substituted by triethoxysilyl groups through urethane linkages because of the presence of a single peak from one kind of silicon. In monomer **2**, however, the triethoxysilyl substituents are located not only on the more reactive primary oxygen atoms but also to some extent on the secondary oxygen atoms, because of the appearance of two peaks from two different kinds of silica.

Scheme 2 illustrates the synthetic procedures to form the CD-containing mesoporous monomer−**1**−silica−*x*% polymers from monomer **1** and monomer−**2**−silica−5% polymer from monomer **2**. Monomer **1** or **2** was co-condensed with TEOS via a sol−gel process in the presence of NaOH as the catalyst and without surfactants as the template. The ratio of monomer **1** to TEOS was varied to produce a series of monomer−**1**−silica−*x*% polymers. The ratio of monomer **2** to TEOS was 0.05/1 to produce insoluble monomer−**2**−silica−5% polymer. It was found that insoluble gel polymers formed when the ratio of monomer **1** to TEOS was higher than 0.02/1. No insoluble gel polymer monomer−**1**−silica−0% or monomer−**1**−silica−2%, however, was formed when the ratio was 0/1 or 0.02/1. Moreover, when CD-based monomer **1** was replaced with bis(2-hydroxyethyl)-3-aminopropyltriethoxysilane (BHEAPTES) monomer with two OH groups for the co-condensation reaction with TEOS, no insoluble gel polymer BHEAPTES−silica−*x*% could be obtained even when the BHEAPTES-to-TEOS ratio reached 0.1/1. These results suggest that CD-based monomer **1** with a suitable molar ratio not only acts as the polymerizable silane monomer but also plays a critical structure-directing template role for the formation of an insoluble cross-linked network silica structure.

TABLE 1. Properties of Monomer−1−Silica−*x*% and Monomer−2−silica−5%

sample	BET surface area (m^2/g)	total pore volume (V_p, cm^3/g)	mesopore diameter (nm)[a]
monomer−**1**−silica−0%			
monomer−**1**−silica−2%			
monomer−**1**−silica−5%	386	0.35	3.7
monomer−**1**−silica−7%	351	0.36	3.9
monomer−**1**−silica−10%	89	0.11	3.7
monomer−**1**−silica−30%	32		
monomer−**1**−silica−100%	8		
monomer−**1**−silica−5%	164	0.60	18.7

[a] Calculated from the desorption branches by the BJH method.

Figure 1 contains the solid-state ^{13}C NMR spectrum of monomer−**1**−silica−5%. The carbon in the urethane connector (O**C**ONH) is found at δ 159, and the carbons in the CD are found in the region δ 60−110, indicating that the covalently bound CD units are intact after the sol−gel process. The carbons in the connector (OCONH**C**H$_2$**C**H$_2$**C**H$_2$Si) are found in the region δ 9−50. Thus, all peaks in the ^{13}C spectrum are readily accounted for, and the polymerization process has in no way degraded the CD structure. The solid-state ^{29}Si NMR spectrum of monomer−**1**−silica−5% shows two signals at δ −62.2 and −65.1, attributed to T^2 ($CSi(OH)O_2$) and T^3 ($CSiO_3$) substructures, respectively, as well as one strong signal at δ −110.6 attributed to the Q^4 (SiO_4) substructure.

The BET surface areas and pore volumes, as well as the pore-size distributions, of monomer−**1**−silica−*x*% and monomer−**2**−silica−5% samples were obtained by nitrogen adsorption−desorption isotherm measurements (Table 1 and Figure 2). It can be seen from Table 1 that monomer−**1**−silica−5% and monomer−**1**−silica−7% materials with respective percentages of CD units of 5 and 7% have BET surface areas of 386 and 351 m^2/g.

Monomer−**1**−silica−10%, monomer−**1**−silica−30%, and monomer−**1**−silica−100% materials with percentages of CD units equal to or higher than 10% have BET surface areas lower than 100 m^2/g. The monomer−**1**−silica−5% and monomer−**1**−silica−7% samples exhibit type IV isotherms with type H2 hysteresis loops (Figures 2a and 2b).[15−17] Such H2 hysteresis loops are similar to those observed for many mesoporous inorganic oxides[7,16] and are attributed to pore connectivity effects, which are a

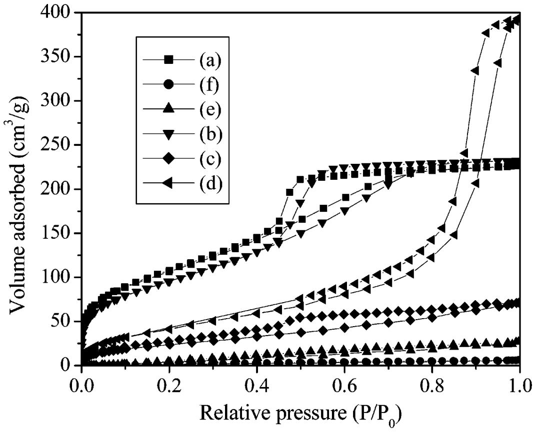


FIGURE 2. Nitrogen adsorption—desorption isotherms of (a) monomer—**1**—silica—5%, (b) monomer—**1**—silica—7%, (c) monomer—**1**—silica—10%, (d) monomer—**2**—silica—5%, (e) monomer—**1**—silica—30%, and (f) monomer—**1**—silica—100%.

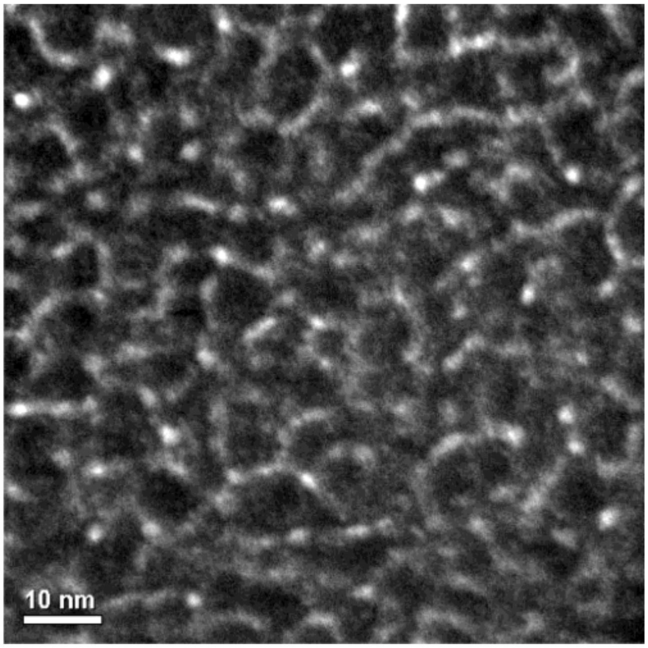


FIGURE 3. TEM image of monomer—**1**—silica—5% material.

result of the presence of relatively uniform channel-like pores.[15,16] From the transmission electron microscopy image of monomer—**1**—silica—5% material (Figure 3), we can see that the porous material has many disordered uniform channel-like mesopores, in good agreement with the nitrogen adsorption—desorption results. The BJH pore-size distributions of monomer—**1**—silica—5% and monomer—**1**—silica—7% samples calculated from the desorption branches of the isotherms (Figures 4a and 4b) further confirm that both of these samples have a narrow BJH pore-size distribution centered at 3.7 and 3.9 nm, respectively, which is comparable to that observed for neutral surfactant-templated mesoporous CD-containing silica material.[11]

These results demonstrate the formation of mesopores with uniform pore-size distributions in monomer—**1**—silica—5% and monomer—**1**—silica—7% materials prepared without the use of the surfactant template. Although it has been reported in the literature that even without surfactant templation, alkylene- or arylene-bridged polysilsesquioxanes can be mesoporous and have high surface areas,[18,19] most of these materials have broad pore-size distributions, and the pores are produced in the presence of short, stiff organic bridges such as 1,4- or 1,3,5-benzene. To our knowledge, this is the first time that mesoporous silica materials containing covalently bound, rather large terminal CD units and with narrow pore-size distributions have been prepared without using a structure-directing surfactant. It is worth noting that insoluble gel material could not be obtained from the sol—gel reaction of pure TEOS or a mixture of monomer **1** and TEOS with a molar ratio of ≤0.02/1. Additionally, mesoporous materials with BET surface areas higher than 100 m^2/g and narrow pore-size distributions were not obtained when the molar ratio of monomer **1** to TEOS was equal to or higher than 0.1/1 (Figure 2). These results suggest that the presence of a suitable molar ratio of substituted CD monomer **1** plays a critical role in the formation of uniform meso-structured CD-based silicas. Moreover, it is evident from Figure 5 that such mesoporous structures with a narrow pore-size distribution cannot be formed in monomer—**2**—silica—5% material, in

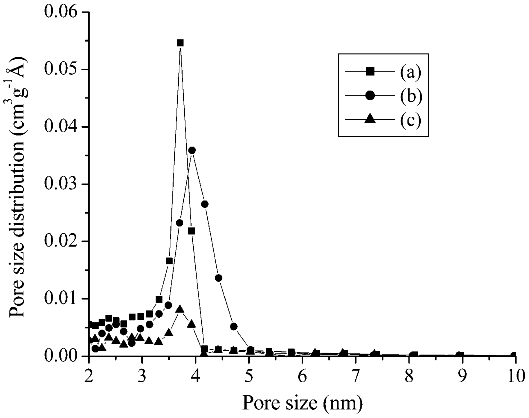


FIGURE 4. BJH pore-size distributions of (a) monomer—**1**—silica—5%, (b) monomer—**1**—silica—7%, and (c) monomer—**1**—silica—10%.

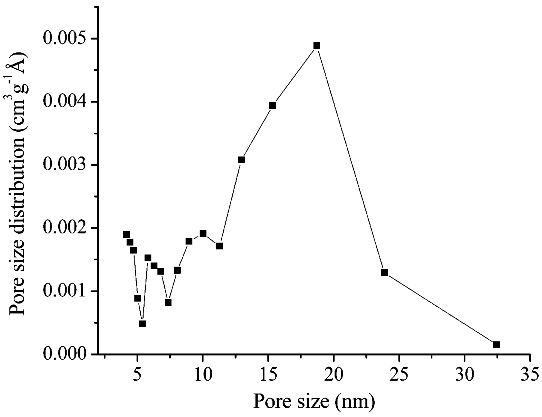


FIGURE 5. BJH pore-size distribution of monomer—**2**—silica—5%.

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which the CD units have a much higher degree of substitution than those in monomer−**1**−silica−5% material, suggesting the importance of the degree of substitution in CD-based monomers with self-organizing ability. Thus, it is plausible that the meso-structured CD-based hybrid silicas with uniform mesopores are formed by the self-assembly of the CD-based siloxane species, which is the result of hydrogen bonding among OH groups of the substituted CD units. The process can be termed *self-templation*.

The small-angle powder X-ray diffraction (XRD) patterns of the mesoporous monomer−**1**−silica−5% and monomer−**1**−silica−7% materials showed no apparent peak in the small-angle region, but their wide-angle powder XRD patterns revealed a typical amorphous silica halo at a 2θ value of ~21°, indicating the amorphous nature of the mesoporous CD-based organic−inorganic hybrid silicas.

In conclusion, novel mesoporous silica materials containing nanoporous cavities provided by covalently bound CDs have been synthesized directly from a mixture of CD-based silane and TEOS monomers via a simple, surfactant-free sol−gel route that probably involves a self-templating mechanism. The organic and silicon structures were supported by solid-state NMR spectroscopy. The ^{13}C and ^{29}Si spectra provided evidence for intact covalently attached CD units. The mesoporosity was characterized by the nitrogen adsorption−desorption isotherms and transmission electron microscopy. Preparation of mesoporous CD-containing silica materials with narrow pore-size distributions via a surfactant-free sol−gel reaction extends the possibilities of producing new organic−inorganic hybrid mesoporous materials. These mesoporous hybrid CD-containing silicas are potentially useful for a wide variety of applications such as removal of organic contaminants from wastewater and chromatographic separation.

Experimental Section

Cycloheptaamylose (β-CD) was purified by recrystallization from H_2O three times and dried at 110 °C for 12 h. 3-Isocyanatopropyltriethoxysilane and bis(2-hydroxyethyl)-3-aminopropyltriethoxysilane (BHEAPTES) were purchased from Gelest and used without purification.

Characterization Methods. FTIR spectra were obtained on KBr pellets using a Nicolet Magna IR TM spectrophotometer 550. A Varian Mercury 400 spectrometer operating at 400.2 MHz (^{1}H) and 100.6 MHz was used to record ^{1}H and ^{13}C NMR spectra. ^{29}Si NMR spectra were obtained with a Varian Chemagnetics Infinity Plus 500 spectrometer operating at 99.3 MHz. Chemical shifts are expressed in parts per million (δ). High-resolution ^{13}C and ^{29}Si MAS NMR spectra were run at 75.5 and 59.6 MHz, respectively, on a Varian VXR300 spectrometer with a ZrO_2 rotor and two Teflon caps. The spinning speed ranged between 4 and 6 kHz. The experiments were carried out with high-powered proton decoupling. Elemental analyses for C and N were obtained on a CHN CE440 analyzer (Exeter Analytical, Inc.). The XRD patterns were obtained with a Rigaku D-MAXA diffractometer using Cu Kα radiation. The BET surface areas of all the materials were determined by N_2 adsorption at liquid N_2 temperature using an Autosorb-1 volumetric sorption analyzer. All samples were degassed at 100 °C until the test of outgas pressure increase was passed by 10 μHg/min prior to their analysis. TEM images were recorded on a Hitachi HF-2000 transmission electron microscope.

Preparation of CD-Based Monomer 1. To a stirred solution of purified β-CD (5.74 g, 5.0 mmol) in 70 mL of dried DMF (or dried pyridine) was added 3.70 g (15.0 mmol) of 3-isocyanatopropyltriethoxysilane. The solution was stirred at 70 °C under N_2 for 48 h. The solvent was removed under reduced pressure under N_2. The product monomer **1** was obtained in 97% yield as a light yellow solid: IR (KBr) 3390 (N−H), 1713 (C=O), 1542 (NH−CO); ^{1}H NMR (DMF) δ 0.62 (m), 1.15 (t), 1.58 (m), 3.06 (m), 3.47 (m), 3.80 (m), 3.97−4.82 (m), 4.95 (m), 5.76−5.93 (m); ^{13}C NMR (DMF) δ 7.3, 18.3, 23.0, 43.3, 57.8, 60.0, 69.8, 72.2, 73.0, 81.6, 101.6, 102.0, 155.8; ^{29}Si NMR (DMF) δ −46.17. Elemental analyses for $C_{42}H_{70}O_{35}(C_{10}H_{21}O_4NSi)_x$, Found: C, 45.75; N, 2.21 (x = 2.1 calculated from % C, and x = 2.9 calculated from % N).

Preparation of CD-Based Monomer 2. To a stirred solution of purified β-CD (5.74 g, 5.0 mmol) in 70 mL of dried pyridine was added 45.0 g (0.15 mol) of 3-isocyanatopropyltriethoxysilane. The solution was stirred at 70 °C under N_2 for 48 h. The solvent and residual 3-isocyanatopropyltriethoxysilane were removed under reduced pressure of N_2. The product monomer **2** was obtained in 92% yield as a sticky, yellow solid: IR (KBr) 3390 (N−H), 1715 (C=O), 1544 (NH−CO); ^{1}H NMR ($CDCl_3$) δ 0.62 (m), 1.16 (m), 1.56 (m), 3.11 (m), 3.2−5.0 (m); ^{29}Si NMR ($CDCl_3$) δ −45.92 and −46.04. Elemental analyses for $C_{42}H_{70}O_{35}(C_{10}H_{21}O_4NSi)_y$, Found: C, 47.76; N, 4.61 (y = 18.5 calculated from % C, and y = 20.0 calculated from % N).

Preparation of Monomer−1−Silica−*x*% Materials. Tetraethoxysilane (TEOS) and monomer **1** were used as the Si sources. The mole ratio of Si:H_2O:NaOH was 1:223:1.2. Samples were prepared with monomer **1**:TEOS molar ratios of 0:1 (monomer−**1**−silica−0%), 0.02:1 (monomer−**1**−silica−2%), 0.05:1 (monomer−**1**−silica−5%), 0.07:1 (monomer−**1**−silica−7%), 0.1:1 (monomer−**1**−silica−10%), 0.3:1 (monomer−**1**−silica−30%), and 1:0 (monomer−**1**−silica−100%). For example, for the synthesis of monomer−**1**−silica−5% material, to 1.13 g of monomer **1**, dissolved in 3.3 g of anhydrous DMF, was added 2.53 g of TEOS to form a homogeneous solution. This solution was added dropwise to a NaOH aqueous solution containing 0.67 g of NaOH and 56 g of H_2O under vigorous stirring at room temperature. The clear, homogeneous sol solution was stirred for 30 min at room temperature after the addition, and no gel formed. The solution was then put into an oven and cured for 2 days at 80 °C. The light yellow gel product was filtered, washed thoroughly with H_2O, acetone, THF, and diethyl ether, and dried at 80 °C in vacuo for 24 h.

Preparation of Monomer−2−Silica−5% Materials. To 0.96 g of monomer **2**, dissolved in 3.0 g of anhydrous DMF, was added 0.65 g of TEOS to form a homogeneous solution. This solution was added dropwise to a NaOH aqueous solution containing 0.31 g of NaOH and 26 g of H_2O under vigorous stirring at room temperature. The solution was stirred for 30 min at room temperature after the addition and then put into an oven and cured for 2 days at 80 °C. The light yellow gel product was filtered, washed thoroughly with H_2O, acetone, THF, and diethyl ether, and dried at 80 °C in vacuo for 24 h.

Preparation of BHEAPTES−Silica−*x*% Materials. Tetraethoxysilane (TEOS) and BHEAPTES were used as the Si sources. The mole ratio of Si:H_2O:NaOH is 1:223:1.2. Samples were prepared with BHEAPTES:TEOS molar ratios of 0.05:1 (BHEAPTES−silica−5%) and 0.1:1 (BHEAPTES−silica−10%). For example, for the synthesis of BHEAPTES−silica−5% material, to 0.20 g of BHEAPTES, dissolved in 0.5 g of anhydrous DMF, was added 2.76 g of TEOS to form a homogeneous solution. This solution was added dropwise to a NaOH aqueous solution containing 0.67 g of NaOH and 56 g of H_2O under vigorous stirring at room temperature. The clear, homogeneous sol solution was stirred for 30 min at room temperature after the addition, and no gel formed. The solution was then put into an oven and cured for 2 days at 80 °C, and still no gel formed.

Acknowledgment. The authors thank the National Science Foundation (Grant CHE-0091162) for support of this work.

JO0352979