Communications

A New Family of Copolymers: Multifunctional Periodic Mesoporous Organosilicas

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Periodic mesoporous organosilicas (PMOs) are organic−inorganic polymers with highly ordered pore networks and large internal surface areas.[1−6] In addition, recent results have demonstrated that PMOs have better hydrothermal and mechanical stability than ordered mesoporous silicas.[7] Although a variety of ordered nanoporous organosilicas containing single functional organic bridging groups have been reported,[8−10] there have not been any reported with two or more groups. We have recently reported the synthesis and characterization of ordered PMOs prepared with the alkylethylene oxide surfactant $C_{18}H_{37}(OCH_2OCH_2)_{10}OH$ (Brij 76) in acidic media.[11] These findings led us to attempt the synthesis of ordered PMO copolymers containing more than a single organic functional group in the pore walls (Figure 1) using this versatile technique. Our primary incentive for creating multifunctional PMOs is to gain the ability to tailor the large surfaces of the periodic mesoporous materials for sorbents, sensors, and catalysts with superior performance. Herein, we report our first synthesis of a new class of ordered multifunctional PMO copolymers prepared with the phenylene- and ethylene-bridged organosilica precursors.

The copolymers were prepared using our Brij 76 templating method with the two precursors at various ratios while keeping the total number of moles constant. The Brij 76 surfactant (4.0 g) was added to a 200-mL mixture of HCl (13.1 mL, 12.2 M) and deionized water (186.9 mL) while stirring. The covered mixture was heated at 50 °C for 12 h before adding the premixed precursors into the clear solution. The reactant molar ratio of Brij 76/H_2O/HCl/organosilanes was 0.11:222:3.20:0.56. The mixture was covered and stirred at 50 °C for 12 h and then heated at 90 °C for 24 h under static conditions. The recovered precipitates were refluxed in deionized water for 24 h. Surfactant template removal was accomplished by three template extraction cycles with acidified ethanol (rather than calcinations, in order to keep the C−Si linkages intact) to produce the mesoporous copolymers. The powder X-ray diffraction patterns of the copolymers made with 3:1, 1:1, and 1:3 molar ratios of phenylene to ethylene (denoted P3E1, P1E1, and P1E3, respectively) are shown in Figure 2. All exhibit a high degree of ordering with clear (100), (110), and (200) Bragg reflections consistent with *p*6*mm* pore structures, with hexagonally packed arrays of circular cylinders making up the pores surrounded by the solid copolymer matrix. Nitrogen sorption measurements performed on the PMO copolymers showed classical type IV isotherms with large nitrogen capacities of 0.9−1.1 cm^3/g (STP). The isotherms were dominated by a large step in the mesoporous range and then flatten out, indicating the lack of any macropores. The pore size distribution is very narrow and centered at 4 nm. The physicochemical properties derived from XRD and N_2 sorption measurements of the PMO copolymers, pure PMOs, and pure silica synthesized with the same protocol using TMOS as the precursor are listed in Table 1. Although there is a trend in pore size based on precursor ratio, the pore sizes of the copolymers do not differ by very much.

Solid-state ^{13}C CP/MAS NMR spectra of the pure and copolymer PMOs are shown in Figure 3. The ^{13}C chemical shifts of all the samples show only a single carbon peak assigned to the ethylene and phenylene groups (ca. 5 and 134 ppm, respectively) covalently linked to Si. This shows that the carbon moieties and the C−Si bonds were stable during the synthesis of the PMO copolymers. Resonances associated with trace amounts of ethanol (ca ∼16 and ∼58 ppm), used in the extraction of the surfactant, were observed in the ethylene-bridged PMO and the copolymers. The methoxy and ethoxy group resonances of precursors were undetectable indicating a high degree of hydrolysis achieved during synthesis. The absence of any Brij 76 surfactant peaks (ca. 72.9, 70.9, 61.7, 32.7, 30.5, 26.9 ppm) indicates the efficiency of extraction.

The ^{29}Si CP/MAS NMR spectra of the pure phenylene- and ethylene-bridged PMOs and the 1:1 copolymer (Figure 4) provide valuable information about the stability of the Si−C and Si−O bonds. Each spectrum shows only one major region of ^{29}Si peaks, centered

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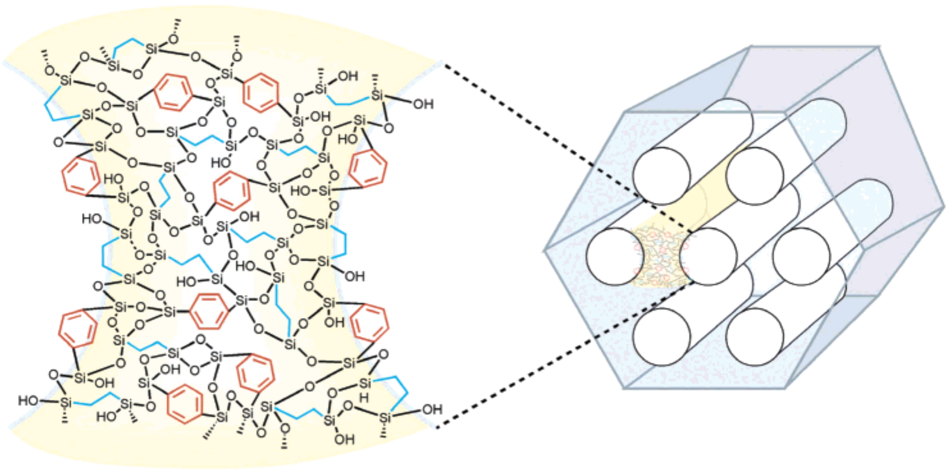

Figure 1. Schematic of PMO copolymer.

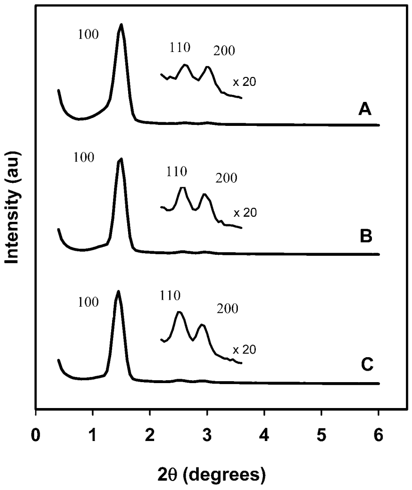

Figure 2. Powder X-ray diffraction patterns of phenylene/ethylene copolymers: (A) P3E1, (B) P1E1, and (C) P1E3.

Table 1. Physicochemical Properties of Mesoporous Organosilicas

sample	d^a (Å)	BET surface area (m^2/g)	total pore volume (cm^3/g)	pore size^b (Å)	wall thickness^c (Å)
phenylene PMO	59	940	0.70	35	33
P3E1 copolymer	59	940	0.90	36	26
P1E1 copolymer	59	1070	1.00	40	25
P1E3 copolymer	61	1050	1.10	39	25
ethylene PMO	61	1070	1.10	44	26
pure silica	61	990	1.40	46	24

[a] $d(100)$ spacing of the extracted products (±2 Å). [b] Calculated from adsorption branch. [c] Estimated from a_0 pore size; where $a_0 = (2\sqrt{3}/3)*d(100)$.

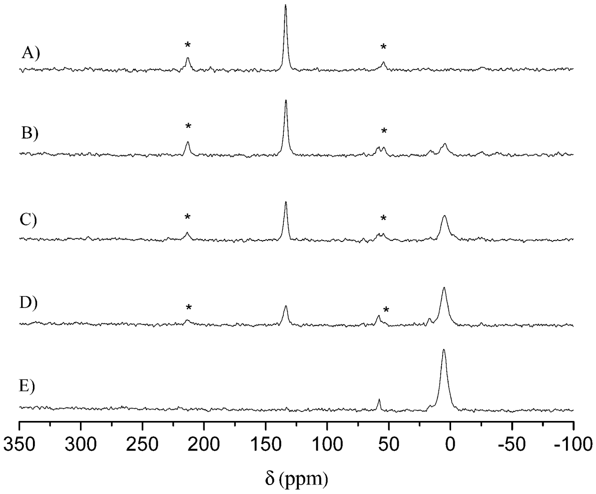

Figure 3. ^{13}C CP/MAS NMR spectra of the PMOs: (A) 100% phenylene-bridged, (B) P3E1, (C) P1E1, (D) P1E3, and (E) 100% ethylene-bridged PMO.

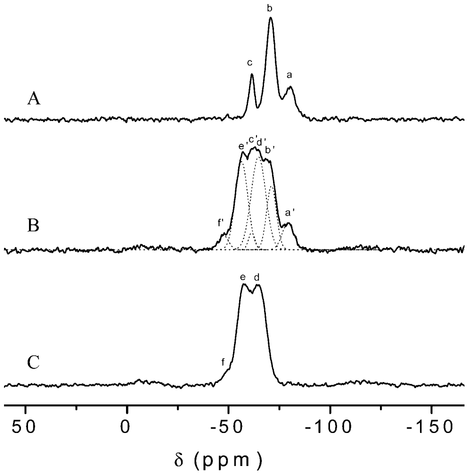

Figure 4. ^{29}Si CP/MAS NMR spectra of the PMOs: (A) 100% phenylene-bridged, (B) P1E1 copolymer, (C) 100% ethylene-bridged. Peaks a, b, and c, and d, e, and f are the $-RSi(OSi)_n(OH)_{3-n}$ units where $n = 3$, 2, and 1, respectively, for phenylene- and ethylene-bridged PMOs, and the prime letters are the respective units in the copolymer.

around −75 ppm for phenylene-bridged silica, −60 ppm for ethylene-bridged silica, and −65 ppm for the copolymer. These regions represent the $-RSi(OSi)_n(OH)_{3-n}$ or T_n structural units of the individual PMOs where R is either a phenylene ($-C_6H_4-$) or ethylene ($-CH_2CH_2-$) group. The phenylene-bridged spectrum (Figure 4A) displays three resolved peaks at −80, −70, and −61 ppm assigned to $n = 3$, 2, and 1, respectively (peaks a, b, and c). The ethylene-bridged silica spectrum (Figure 4C) displays peaks at −64, −57, and −50 ppm for $n = 3$, 2, and 1 respectively (peaks d, e, and f). The deconvoluted silica spectrum of the P1E1 copolymer (Figure 4B) displays six resolved peaks which can be assigned to the T_n structural units of the two equivalent R groups of the individual polymers within the matrix of the copolymer (a′, b′, and c′ for $R = -C_6H_4-$ and d′, e′, and

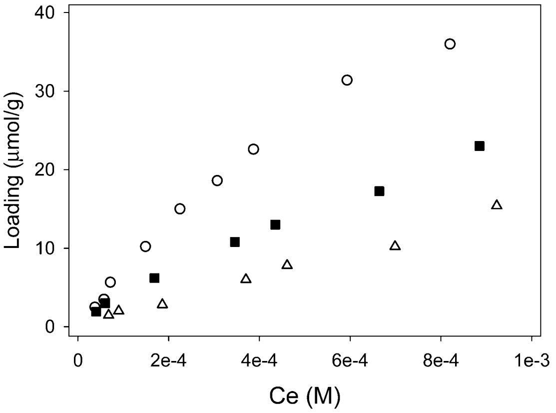

Figure 5. Adsorption isotherms of 4-chlorophenol on the ethylene-bridged PMO (△), phenylene-bridged PMO (■), and on the P1E1 copolymer (○).

f' for R = $-CH_2CH_2-$ when $n = 3$, 2, and 1, respectively). The copolymerized PMO did not show any significant changes in the chemical shifts or the line half widths of the T_n signals related to the two individual PMOs. The absence of any $Si(OSi)_n(OH)_{4-n}$ peaks centered around −105 ppm confirms that the C−Si bonds of the precursors did not cleave during synthesis.

Quantitative determination of monomer incorporation into the copolymers made by carbon elemental analysis showed that the molar ratio of phenylene to ethylene monomer was high in the PMO copolymers. This indicates that hydrolysis and condensation of the phenylene monomer is more efficient than the ethylene monomer under these experimental conditions.

We recently reported the high adsorption capacity of a diethylphenylene-bridged organosilica for phenolic compounds.[12] This material, however, is amorphous, which is most likely due to the nonrigid nature of the bridging group. The newly synthesized 1:1 PMO copolymer synthesized from more rigid phenylene and ethylene-bridged precursors not only has a higher adsorption capacity than the two individual PMOs (Figure 5) but also has an ordered structure. This shows that the phenylene/ethylene combination of functional groups results in a material with improved performance over that of the single functional group PMOs.

Although we report only the phenylene/ethylene PMO copolymer here, we have successfully synthesized and characterized more than 10 of these novel materials in our laboratory from different combinations of methylene-, ethylene-, ethenylene-, and phenylene-bridged precursors with up to four precursors per copolymer (see Supporting Information). This also clearly illustrates the versatility of our synthetic protocol and may indicate its potential use for the synthesis of bimetallic oxides and sol−gel materials where discrepancies in hydrolysis and condensation rates of the precursors has led to phase separation and inhomogeneous products. PMO copolymers represent a new and exciting way to introduce multiple functionality into pore walls of ordered mesoporous materials and can potentially lead to sorbents, sensors, and catalysts with superior performance.

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Supporting Information Available: Additional experimental details and figures (structures, nitrogen gas sorption, powder X-ray diffraction, DRIFTS of copolymers) and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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