Synthesis of Ordered Mesoporous Methacrylate Hybrid Systems: Hosts for Molecular Polymer Composites

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A functionalized, highly ordered mesoporous hybrid material based on the MCM-41 structure is synthesized through room temperature cocondensation of 3-(trimethoxysilyl)-propyl methacrylate (TMSiPMA) and tetramethyl orthosilicate (TMOS) in molar ratios of up to 1:3 in the presence of cetyltrimethylammonium chloride. Successful template removal through solvent extraction results in highly ordered mesoporous materials, as confirmed by X-ray diffraction and transmission electron microscopy. Characterization with nitrogen sorption and IR spectroscopy shows that methacrylate groups are incorporated into the host channel system. The functional groups are stable to at least 200 °C under vacuum. The C=C double bonds of the methacrylate groups are readily and completely accessible to bromination. Inorganic/organic composites coupled on the molecular level are prepared by efficient polymerization of adsorbed methyl methacrylate monomer (MMA) with the intrapore grafted methacrylate groups.

Introduction

The discovery of the M41S family of mesoporous materials[1,2] has stimulated research in the area of surfactant-templated, periodic mesoporous hosts. By overcoming the size constraints of microporous supports, new applications in catalysis, sensing or sorption involving bulkier guests are now possible. The pore sizes of these materials can be adjusted to between 15 and several hundred angstrom by choice of the templating agent and reaction conditions, using either nitrogen-containing surfactants or block copolymers.[3] While the larger size of the pores is a prerequisite for many applications, it is by itself often not sufficient when specific surface properties are desired. Specific surface sites for metal-ion binding, catalysis, or controlled sorption can be introduced through surface modifications. Three different routes have been followed in the recent past to tailor the pore walls of mesoporous supports.[4] Silane coupling agents have long been used to alter the surfaces of oxide materials by utilizing surface hydroxyl groups as anchor points, and several reports describe this approach for MCM materials.[5] The second route uses functional complexes containing some labile ligands that attach to the surface directly via reaction with hydroxyl groups.[6]

A much more intimate coupling of functional groups *into* the walls of the host can be achieved through cocondensation of organosilanes with the molecular building blocks for the mesoporous supports in the presence of the templating surfactant. Since the silane moiety is embedded in the wall, much higher stability is expected for the resulting hybrid materials. This route was pioneered by Mann et al.,[7] who added phenyl- and octyltriethoxysilane to the synthesis gel to obtain hybrid mesoporous MCM-type solids. Another phenyl-modified MCM material with 50 Å pore diameter was reported by Slade et al. in a mesitylene-assisted cocondensation.[8] Mann and co-workers extended their research to a number of functional groups including thiol, amine, epoxide, imidazole, and allylorganosiloxanes.[9] Recently, Mann et al. reported on the covalent coupling of an organic chromophore via cocondensation of tetraethoxy-

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orthosilicate (TEOS) and [3-(2,4-dinitrophenylamino)-propyl]triethoxysilane.[10] While the incorporation of all these groups was successful, in some instances template extraction resulted in lattice damage. Functionalized MCM hosts that were stable to solvent extraction were prepared by Macquarrie,[11] who used neutral templates together with aminopropyl- and cyanoethyl-functionalized silanes and TEOS to render mesoporous materials. Vinyl functions were incorporated into MCM-41 by Stein et al.[12] The products showed reactivity toward bromine after extended reaction times. Recently, Stein[13] reported the cocondensation of TEOS with (3-mercaptopropyl)-triethoxysilane and application of the template-extracted material for mercury absorption as well as oxidation to sulfonic acid groups. The high efficiency of thiol groups for mercury sorption had been demonstrated for MCM materials that were functionalized with silane coupling agents.[14]

In previous studies we reported the encapsulation of polyaniline, polyacrylonitrile,and methyl methacrylate (MMA) into micro- and mesoporous hosts.[15−17] In the latter study it was shown that adsorption of MMA and polymerization to PMMA proceeds similarly in the small cavities and channels of different zeolites as well as in the larger pores of MCM-41 (hexagonal) and MCM-48 (cubic) hosts. In this paper we describe the incorporation of methacrylate groups into the walls of highly ordered MCM-41 materials through cocondensation of TMOS (tetramethoxysilane) and 3-(trimethoxysilyl)propyl methacrylate (TMSiPMA), to result in a reactive hybrid methacrylate−MCM host (MA−MCM). The access to and the reactivity of the inner pore methacrylate groups is demonstrated by rapid addition of bromine. The utilization of functionalized MCM hybrid materials, synthesized through cocondensation, is a newly emerging field offering a range of possibilies for materials chemistry. We report the formation of a conceptually new composite through polymerization of inner pore methacrylate groups with adsorbed MMA.

Experimental Section

(a) Sample Preparation. MCM-41 was synthesized by adapting the room-temperature procedure described by Anderson et al.[18] Our standard procedure was as follows: water (64.1 g) and methanol (7.9 mL) were combined with 50 wt % aqueous NaOH (0.502 mL). The resulting pH is 12.7. Cetyltrimethylammonium chloride (C16TACl, 25% in water, Aldrich; 5.63 mL) and tetramethoxysilane (TMOS, Aldrich; 5 mL) were subsequently added with stirring. The overall molar ratio was TMOS:C16TACl:H_2O:MeOH:NaOH = 1:0.13:113:5.7:0.28. The total volume of added solvent and cosolvent is 72 mL in this receipe, containing a volume fraction of 11 vol % MeOH (in addition to the hydrolysis product of TEOS). While the sum was kept constant, the added methanol content was varied from 0 to 7.9, 15.8, or 39.6 mL representing a volume fraction of 0, 11, 22, and 55 vol %. After addition of TMOS, a thick milky solution formed within 1 min. The latter was further stirred for 15 min and kept at room temperature for 24 h, followed by filtration and prolonged washing with water. Samples were dried at room temperature.

Template removal in nonfunctionalized MCM was achieved by calcination. MCM-41 was heated in a flow of nitrogen with a temperature increase of 2 °C/min to 550 °C, where it was held for 12−15 h. The gas was then switched to air, and the sample was kept at this temperature for another 4 h.

The standard procedure for the synthesis of MCM-41 was varied for the inclusion of 3-(trimethoxysilyl)propyl methacrylate (TMSiPMA) in the following way:

Stoichiometric amounts of TMOS were replaced by TMSiPMA, ranging from molar ratios of 1:7, 1:5, and 1:3 to 1:1 TMSiPMA:TMOS. TMOS and TMSiPMA were simultaneously added by syringe to the stirred aqueous solution. After 24 h the MA−MCM samples were washed with water, dried at room temprature, and conditioned at 75 °C in air for 1−3 days. Template removal was performed by four different ways of solvent extraction, as described in the text.

It should be noted that we also attempted to perform the cocondensation at elevated temperature (100 or 75 °C). However, only minute amounts of the acrylate groups were incorporated at 75 °C after washing, and none was found in the MCM materials when heated at 100 °C.

Methacrylate groups were further attached to previously calcined MCM-41 powder through silane-coupling chemistry, using weighed amounts of TMSiPMA corresponding to the methacrylate content incorporated during cocondensation. Dry MCM samples (1 g) were combined with a solution of TMSiPMA in dry methanol (0.79 mL in ca. 50 mL methanol) under exclusion of air. The resulting suspension was stirred in nitrogen atmosphere under reflux at 70 °C for 15 h, filtered, washed with methanol, and dried at room temperature.

(b) Reactivity of Incorporated Methacrylate Functionality. Bromination was performed with a 0.1 M Br_2/CH_2Cl_2 solution that was diluted to either stoichiometric amounts with respect to the amount of incorporated methacrylate groups or was offered in 4-fold excess. A 400 mg sample of functionalized or unfunctionalized (for reference purposes) MCM was stirred in 40 mL bromine solution at room temperature under exclusion of light. The decrease in bromine concentration was followed by UV spectroscopy at 409 nm. Reference solutions of the same bromine concentration without the MCM powder were measured at similar time intervals. The samples were filtered and washed with dichloromethane and water, and the bromine content in the MCM powders was determined by quantitative elemental analysis.

For intrachannel polymerization, methyl methacrylate (MMA) was adsorbed into methacrylate hybrid MCM materials following the procedure described previously.[17] Template-extracted MA−MCM samples were evacuated at 120 °C for 2 h to a dynamic vacuum of at least 3×10^{-4} Torr prior to MMA exposure. Degassed MMA was introduced to the powder via gas-phase transfer at room temperature with stirring for 1−2 h. Benzoyl peroxide (BPO; ca. 0.1 wt %) initiator was admixed to the MMA-loaded MCM and the sample was heated at 75 °C for 15 h under static nitrogen atmosphere. Additional heating at 120 °C and evacuation for 1 h at this temperature resulted in the final composite.

(c) Sample Characterization. FTIR spectra (Mattson Instruments, Polaris; DTGS detector, 128 scans, 4 cm^{-1} resolution) were taken at every step of the synthesis or after template removal and bromination. Usually, dry powders were spread between KBr plates under nitrogen in a glovebox, and the plates were sealed with vacuum grease at their periphery.

Surface areas were determined from nitrogen adsorption/desorption isotherms collected at 77 K with a Coulter Omnisorp 100 instrument under static-sampling conditions. Prior to measurements, samples were dehydrated for 12 h at 150 °C (or at 120 °C for polymer composites). BET surface areas

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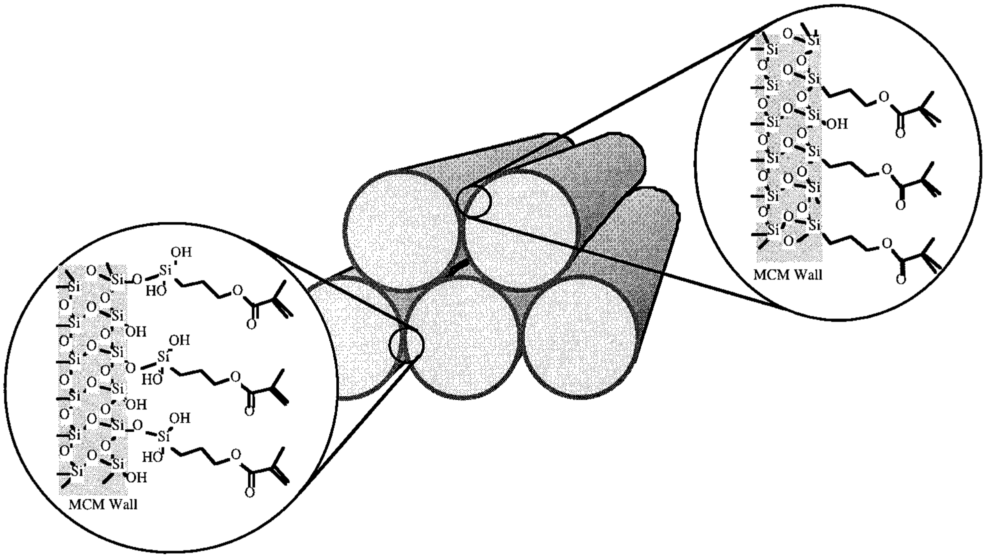
Scheme 1. Sketch of Methacrylate Inclusion into MCM-41 by Silane-Coupling Reaction (left) and Cocondensation (right)



were determined within a range of relative pressure, $p/p_0 = 0.01-0.1$, and pore volumes were extracted from T-plots (film thickness 6−8 Å). Thermogravimetric measurements were performed on a DuPont TGA 951 analyzer operated with a TA Instrument 2000 interface. Sample amounts of about 10 mg were heated at 10 °C/min to 700 °C (except where noted) under either air or nitrogen atmosphere. A Scintag XDS 2000 instrument equipped with a liquid nitrogen cooled germanium detector was used for X-ray diffraction measurements.

Transmission electron micrographs were taken with a JEOL FX-2000 microscope operated at 200 kV, and scanning electron micrographs were taken on a Philips ElectroScan Environmental SEM System 2020, with specimens sonicated in ethanol and dispensed onto a holey carbon grid (TEM) or carbon studs (SEM).

Results and Discussion

Synthesis. Methacrylate MCM hybrids can be synthesized by the two different approaches displayed in Scheme 1. In the left part, the traditional silane-coupling mechanism is shown: the MCM host is prepared by known procedures, the template removed by calcination, and the dry host is subsequently reacted with 3-(trimethoxysilyl)propyl methacrylate. Attachment is achieved via at least one silanol bridge to the MCM support and residual methoxysilyl groups can cross-link, depending on the humidity and sterics at the interface. This partial attachment mode can render the grafted groups unstable against hydrolysis reactions. In contrast, true incorporation of the silyl groups into the channel wall can result from the cocondensation of TMOS and TMSiPMA during MCM synthesis (right part in Scheme 1). This latter method is expected to result in more stable hybrid materials because the Si−O bonds are more deeply buried in the wall. Compared to the after-synthesis grafting methods, these bonds are expected to be less susceptible to hydrolysis. We have focused our effort on the synthesis and characterization of the true hybrid MA−MCM materials, but we have included silane-coupled MCM hosts for comparison.

During hybrid synthesis, stoichiometric amounts of TMOS were replaced by TMSiPMA with increasing molar ratio from 1:7 TMSiPMA:TMOS up to 1:1. The presence of the methacrylate functional group in the MCM material directly after synthesis is visible in the FTIR spectrum in Figure 1. We compare an MCM-41 sample without methacrylate groups and an MA−MCM with a 1:7 molar ratio before template removal. Strong and characteristic vibrations of C16TACl are detected at 2923, 2854, and 1489 cm^{-1} in both samples. The hybrid, however, shows additional bands due to the C=O carbonyl stretch vibration at 1717 cm^{-1}, the C=C double bond at 1637 cm^{-1}, and additional CH bending modes at 1404 and 1321 cm^{-1}. The covalent linkage of the propyl methacrylate residue to the silica framework is also indicated through a Si−C stretch at 1165−1170 cm^{-1} (upper trace). Mann et al. observed this bond at similar wavenumbers (1140 cm^{-1}) after cocondensation of octyltriethoxysilane with TEOS[7] and at 1150 cm^{-1} upon inclusion of the above-mentioned chromophore.[10]

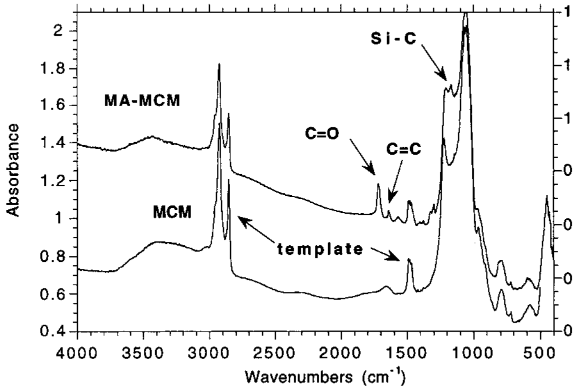


Figure 1. FTIR spectra of siliceous MCM-41 (bottom) and MA−MCM after cocondensation with 1:7 TMSiPMA:TMOS (top; offset) before template extraction. Spectra are normalized to the intensity of the SiO_2 band at 1086 cm^{-1}.

We studied the influence of the silane coupling agent as well as the methanol content on the crystallinity, pore size, and stability of the MCM materials. Results are compiled in Table 1 for samples before template removal. Figure 2 illustrates the influence of TMSiPMA concentration in the gel on the d-values in the X-ray diffraction patterns (with 11 vol % methanol added as

Table 1. X-ray Diffraction Data ($d_{(100)}$-Values) of MCM-41 Materials before Template Extraction with Different Amounts of Methanol Cosolvent and Varying Molar Ratios of TMSiPMA:TMOS in the Synthesis Gel[a]

added MeOH, vol %	d-values for differing TMSiPMA:TMOS molar ratios 0	1:7	1:5	1:3	1:1
55	36.6			36.2	gel
22	39.0			36.4	31.8
11	40.1	39.3	38.6	36.4	
0	40	39.7		39	

[a] Samples were dried at room temperature.

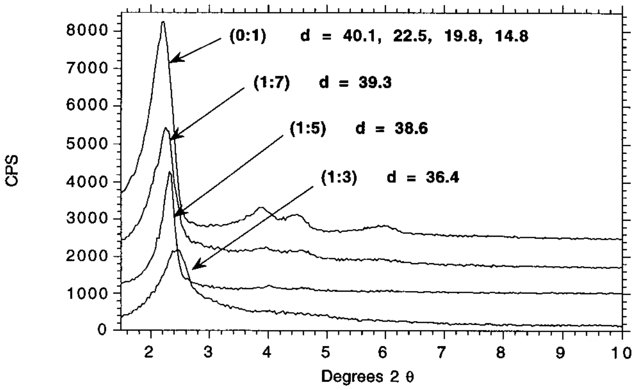


Figure 2. X-ray diffractograms of MA−MCM with an increasing molar ratio of TMSiPMA:TMOS in the synthesis gel before template extraction. The synthesis was performed with 11 vol % added methanol. Spectra are offset for clarity.

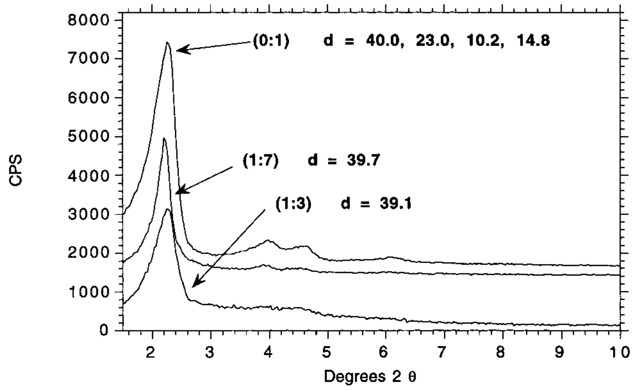


Figure 3. X-ray diffractograms of MA−MCM with increasing molar ratios of TMSiPMA:TMOS without methanol in the synthesis gel. Spectra are offset for clarity.

a cosolvent). The typical XRD patterns for hexagonal MCM-41 are obtained; however, a steady decrease in the $d_{(100)}$ value is observed upon cocondensation with increasing silyl methacrylate content. At a high content, the inclusion of the methacrylate groups results in increased disorder. The number and intensity of peaks additional to the (100) reflection decreases from 3 (molar ratio 1:7) to 2 (1:5) and only one broad peak in samples with a 1:3 ratio. These trends persist with methanol contents of 22 and 55 vol %. Without alcohol, the contraction of the unit cell is less pronounced; d values of the 1:7 and 1:3 samples are very similar (d = 39.7 and 39.1 Å, respectively) and are close to those of the pure MCM-41 (d = 40 Å), but peak broadening and loss of outer reflexes with an increasing amount of TMSiPMA is still observed (see Figure 3). Our standard synthesis was performed with 11 vol % methanol, because results were better reproduced under these conditions.

Even without coupling agent present in the synthesis mixture, we find a unit cell contraction (decreasing $d_{(100)}$ value) with increasing methanol concentration. Comparable results were reported by Anderson et al.[18,19] It appears that micelle formation and assembly into the hexagonal liquid crystal system is disturbed by the interaction of the polar constituents at the micelle interface.

Template Removal. Calcination, the common method for template removal, must be substituted with other extraction methods for functionalized MCM materials in order to retain the chemical integrity of the organic groups in the lattice. As described below, the properties of the final material are dramatically affected by different methods of template removal.

(a) Soxhlet Extraction. About 500 mg of as-synthesized MA−MCM was filled into a Soxhlet thimble and extracted with ethanol under reflux from 2 h to 3 days. Only about one-third of the template could be extracted after 2 h, and further extractions did not improve upon this result.

(b) Ethanol/NaCl Extraction. Following the method by Tuel et al.,[20] samples were subjected to several subsequent extractions with a 20/80 vol % H_2O/EtOH mixture that contained 1 g of NaCl in 100 mL solution. Up to about 95% of the template could be removed after two or three extractions at room temperature for 24 h; however, an increasing shift of the d-value to lower values and the disappearance of outer peaks indicated a loss in structural order. This was confirmed with BET measurements that showed an almost complete loss of porosity in these samples.

(c) Removal with Azeotropic Mixtures. To shorten the duration of the extraction procedure and possibly to avoid the collapse of the mesoporous host, we adapted the method described by Schmidt et al. for siliceous MCM-41.[21] An acidic azeotropic mixture of heptane and ethanol (52/48 wt %, 0.15 M in HNO_3) was used. Two grams of sample was immersed in 30 mL of this solution and stirred at either room temperature, 50 °C, or 80 °C (oil bath temperature) under reflux for about 20 h. This procedure was performed on the siliceous and the MA−MCM samples. The results are very similar for both materials. Most of the template is removed after the first extraction, as confirmed with FTIR and TGA data (a remainder of ca. 7 wt % is still detected). This amount is similar at all extraction temperatures. The crystallinity is best retained in samples refluxed at higher temperatures: pure MCM-41 before extraction with a d-value of 40 Å (showing three additional peaks) has its d-value reduced to 38.9 Å (and one additional peak) when extracted at room temperature. An extraction at 50 °C results in a d-value of 38 Å (and three additional peaks). At 80 °C, a d-value of 40 Å is obtained and outer peaks stay intact. Extraction at 80 °C was applied to the hybrid sample and is shown in Figure 4 (TMSiPMA:

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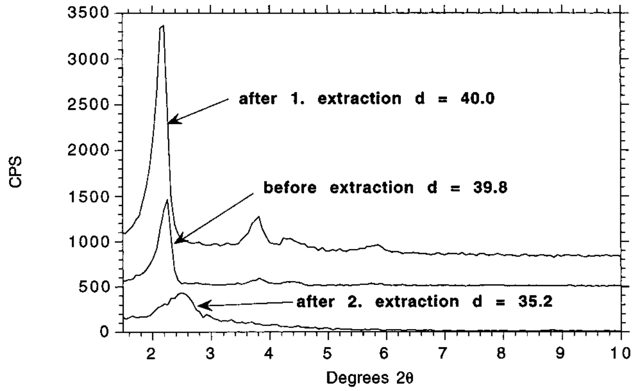

Figure 4. Evolution of crystallinity in the X-ray diffractogram of MA−MCM (TMSiPMA:TMOS = 1:7) after template extraction with azeotropic mixtures of heptane/ethanol. Spectra are offset for clarity.

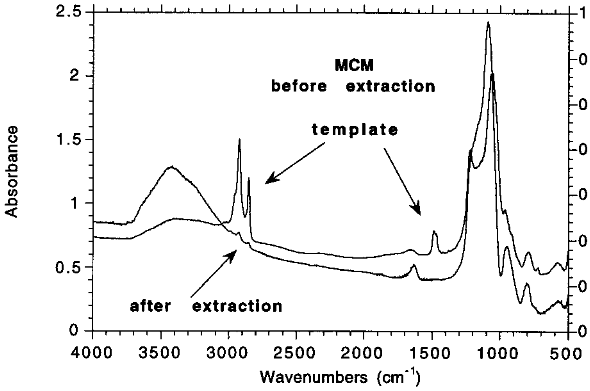

Figure 5. FTIR spectra of siliceous MCM-41 before (left scale) and after template removal with an ethanol/HCl mixture.

TMOS = 1:7). The first extraction cycle removes large parts of the template and therefore results in samples showing stronger X-ray diffraction peaks than the untreated samples. However, complete removal is only possible after a second extraction, lasting 2−4 h. At this point all samples show only the main (100) diffraction peak in the X-ray diffractogram with strongly reduced intensity. Nitrogen sorption shows retention of high surface areas (ca. 600 m^2/g), but the well-defined adsorption step indicative for cappillary condensation is lost.

(d) Extraction in Ethanol/HCl. Finally, an extraction method reported by Davis et al.[22] that uses acidified ethanol under reflux was adapted. In our samples a nearly complete extraction of the template required stirring of 1 g of sample in a mixture of 92 mL of ethanol and 8.3 mL of concentrated HCl under reflux for only 2 h. This is shown in the FTIR spectra in Figure 5 for pure MCM-41. The strong template C−H stretch vibrations at 2923 cm^{-1} and 2852 cm^{-1} are almost completely removed, as is the 1478 cm^{-1} vibration, and the residual peaks account for only about 1 wt % as determined from TGA. This extraction procedure is capable of removing the template also in our functionalized MA−MCM hosts. As seen in Figure 6c, the strong template vibrations have disappeared in this sample and small new bands at 2975, 2931, 2899, and 2862 cm^{-1}, as well as 1456 cm^{-1}, are visible after extraction. These vibrations are associated with propyl methacrylate groups and not with the template: when TMSiPMA was coupled to the surface of previously calcined MCM-41, an almost identical spectrum was obtained (see Figure 6b). The characteristic C=O and C=C bands of the methacrylate groups are visible at 1701 and 1638 cm^{-1} in both samples. Interestingly, the C=O stretch frequency is shifted down (from 1718 cm^{-1} before extraction) in the cocondensed sample after template removal, which seems to correspond to changes in the polarity of the environment. Related effects have been observed for the C=O modes when MMA was adsorbed into dry NaY zeolites; they were interpreted as an interaction of the C=O group with the sodium cations located in the supercages.[17,23]

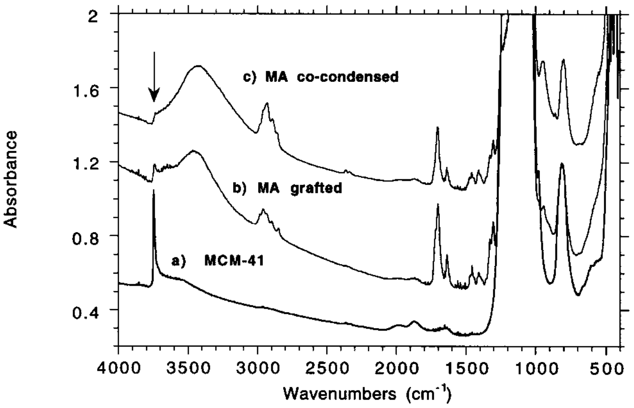

Figure 6. FTIR spectra of (a) calcined MCM-41, (b) calcined MCM-41 after grafting with TMSiPMA, (c) cocondensed MA−MCM-41 (with TMSiPMA:TMOS = 1:7) after template removal with an ethanol/HCl mixture (offset). Spectra are normalized to the intensity of the SiO$_2$ band at 1086 cm^{-1}.

The condensation of TMSiPMA into the MCM framework is now also visible after removal of the template: the strong hydroxyl band, present in dry MCM-41 as seen in Figure 6a, has nearly vanished in the dry MA−MCM sample (Figure 6c) through consumption of the silanols by cocondensation. Postsynthesis grafting of TMSiPMA, however, leaves more hydroxyls unreacted (Figure 6b).

The crystallinity of the samples is completely retained on using extraction method d, in contrast to the other extraction methods described above. The high quality of the MCM-41 material obtained using this template extraction method is seen in the X-ray diffraction pattern in Figure 7: all *d*-values remain essentially unchanged upon template removal, and the intensity of the diffraction peaks increases dramatically. Similar results are obtained with MA−MCM samples, as seen in Figure 8: the $d_{(100)}$ remains largely unchanged. If the same samples are calcined, however, they do experience the typical decrease in *d*-values (see also Table 2). Scanning electron microscopy was performed on the pure MCM-41 (Figure 9a) as well as on the 1:7 hybrid (Figure 9b) after template removal by solvent extraction. Both samples have a similar morphology consisting of thin, irregularly shaped plates. Transmission electron micrographs of both samples show the usual crystalline

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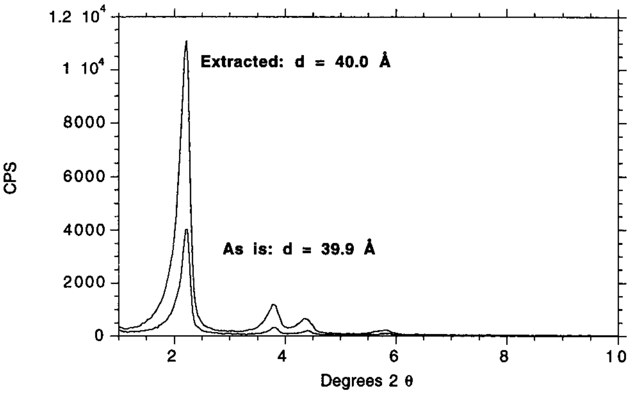

Figure 7. X-ray-diffraction patterns of MCM-41 before (bottom) and after (top) template removal with ethanol/HCl mixtures.

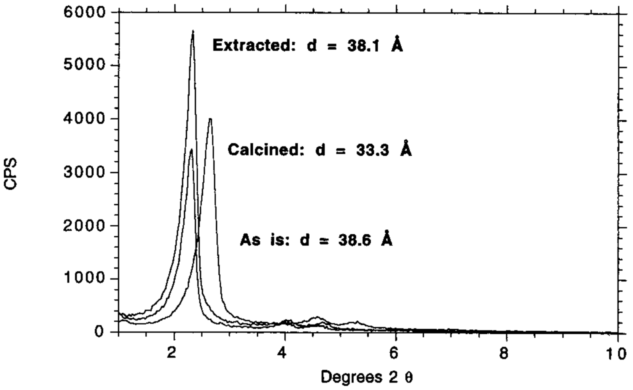

Figure 8. X-ray-diffraction patterns of MA–MCM (with TMSiPMA:TMOS = 1:7) before (bottom) and after (top) template removal with an ethanol/HCl mixture and after calcination.

hexagonal patterns of MCM-41 (Figure 10). Examination of these micrographs suggests a reduced pore size in the template extracted MA-MCM compared to the calcined MCM-41.

Thermogravimetry. The amount of template or included acrylate in the MCM hosts was determined with thermogravimetry. Samples containing the template were usually heated in a nitrogen atmosphere with a heating rate of 10 °C/min, since oxygen or air would sometimes result in sudden exothermal events on the balance. This procedure allowed us to resolve the decomposition of residual template from that of the methacrylate functional groups. On heating in air, both components are consumed at the same temperature and are thus unresolved under those conditions. Under nitrogen, the template is usually removed at temperatures between 150 and 300 °C, with two maxima at about 210 and 260 °C. The template amounts to about 0.72 g/g dry mass of MCM when no TMSiPMA is present. Upon inclusion of TMSiPMA, the template is released in a broad peak around 250 °C. However, a new peak between 400 and 460 °C indicates the presence of the functional group. The amount of this fragment increases with increasing molar ratio of TMSiPMA:TMOS offered during the synthesis, from 0.15 g/g MCM over 0.19 to 0.20 g/g MCM for the ratios 1:7, 1:5 and 1:3, respectively. A weight loss at a similar temperature was observed for the grafted samples under nitrogen.

Quantitative determinations of the functional group contents after template extraction were performed with thermogravimetry in air. Under these conditions, samples containing a molar ratio of 1:7 acrylate to TMOS in the synthesis gel desorb about 0.23 g/g of dry mass of MCM at 296 °C. A loss of 0.26 g/g of MCM (1 mol of PMA/8 mol of SiO_2) is expected for these samples, if all methacrylate in the gel had been condensed into the lattice during synthesis. These values agree well with results from elemental analysis (C: expected 13.8 wt %, measured 12.5 wt %). With a molar ratio of 1:5, a weight loss of 0.28 g/g of MCM is measured (expected: 0.35 g/g of MCM). In contrast, for samples prepared via silane-coupling reactions with presynthesized MCM hosts (molar ratio offered: 1:5), the maximum weight loss in the TGA amounts to 0.16 g/g of MCM and is observed at higher temperatures between 330 and 380 °C. This incomplete coupling reaction is confirmed by the presence of remaining hydroxyl groups in the FTIR.

The MA–MCM hybrids prove to be stable to at least 200 °C. Heating under vacuum for 15 h at this temperature does not change the FTIR pattern of the methacrylate groups, nor does the TGA indicate significant losses of the functional groups after this treatment.

Pore Volumes. Nitrogen sorption experiments were performed to study the remaining pore volumes after inclusion of methacrylate into the lattice as well as the effect of template removal. In Figure 11 we show the adsorption isotherm of MCM-41 (X-ray diffractogram shown in Figure 7) after solvent extraction following method d. This process of template removal results in materials with high surface areas (1175 m^2/g), large pore volumes (0.91 mL/g), and pore diameters of 26–28 Å (width of distribution 2–3 Å at FWHM; BJH method). Figure 12 shows nitrogen sorption isotherms of MA–MCM samples with molar ratios of 1:7 TMSiPMA:TMOS. The top isotherm is taken of this sample following calcination under nitrogen/air atmosphere at 550 °C such that neither the acrylate nor the template remains. Very high surface areas around 1200 m^2/g and pore volumes of 0.77 mL/g (pore diameter 22–24 Å) are achieved that are comparable to ordinary siliceous MCM-41 after calcination. The bottom isotherm results from the same sample after template extraction with ethanol/HCl mixtures, with the functional groups still attached. The pore size is significantly smaller, 18 Å, and the pore volume is reduced to 0.41 mL/g. The overall surface area is now reduced to about 820 m^2/g. These results are explained with the internal lining of the mesopores with methacrylate residues, effectively reducing the pore size and volume. A compilation of surface areas and pore volumes of a series of samples is given in Table 2, together with the development of lattice parameters after different treatments. Ranges are shown for the pure MCM-41 phases, and representative examples of cocondensed and grafted samples are includud. As stated before and seen in Figure 8, *d*-values vary only slightly between template-containing and solvent-extracted samples. In contrast, significant lattice contractions (*d*-value changes from 38.6 to 33.3 Å) are seen after calcination. When BET surface areas are compared for acrylate cocondensed samples and samples treated by silanation, very similar results are obtained. Usually, surface areas of about 700–800 m^2/g are observed. Pore volumes and sizes are reduced to a similar degree in cocondensed and grafted samples.

Table 2. Development of *d*-Values and BET Surface Areas of MCM-41 Materials (11 vol % MeOH)[a]

		d(100)			extracted		calcined	
	mol ratio[b]	with template	solvent extracted	calcined	BET surface, m^2/g	BET pore vol, mL/g	BET surface, m^2/g	BET pore vol, mL/g
cocondensation	1:7	38.6	38.1	33.3	822	0.41	1200	0.77
cocondensation	1:5	37.6	37.2	33.5	876	0.49	1160	0.66
Si− coupled	1:5			33.3[c]	722[d]	0.30[d]	990[c]	0.69[c]
no TMSiPMA	0	39.0−38.6	40.0−38.6	36.6−33.0	1200−1176	0.91−0.87	1150−990	0.79−0.69

[a] Samples were dried at 75 °C. [b] TMSiPMA:TMOS. [c] Before coupling. [d] After coupling

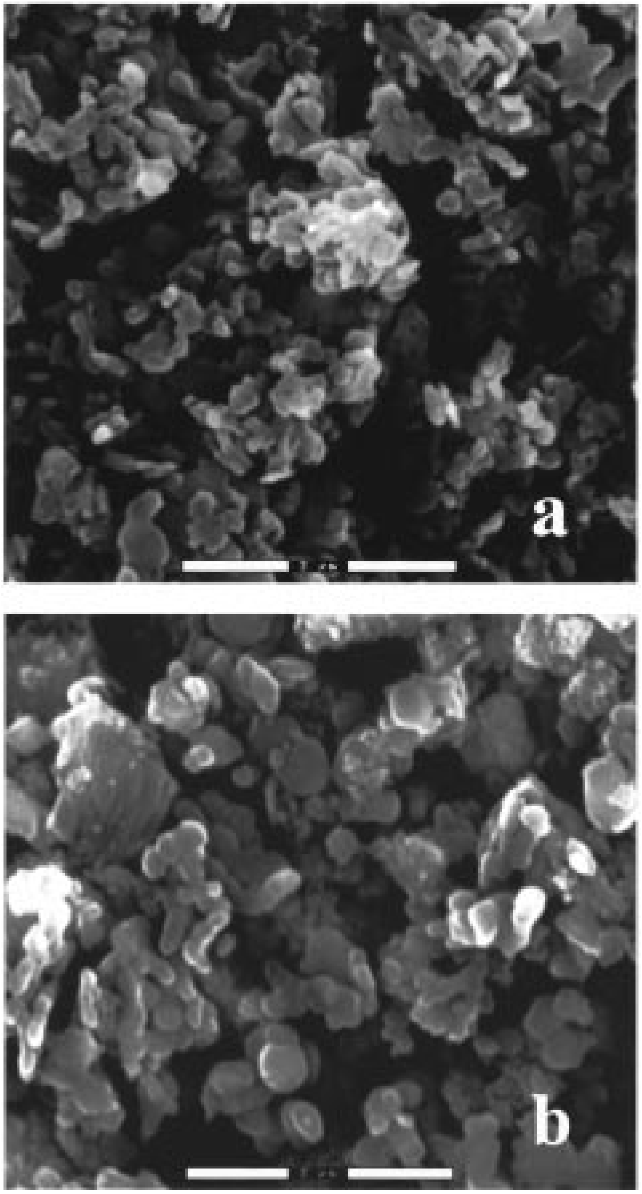

Figure 9. Scanning electron micrographs of (a) siliceous MCM-41 and (b) a 1:7 methacrylate hybrid after template removal through solvent extraction with an ethanol/HCl mixture.

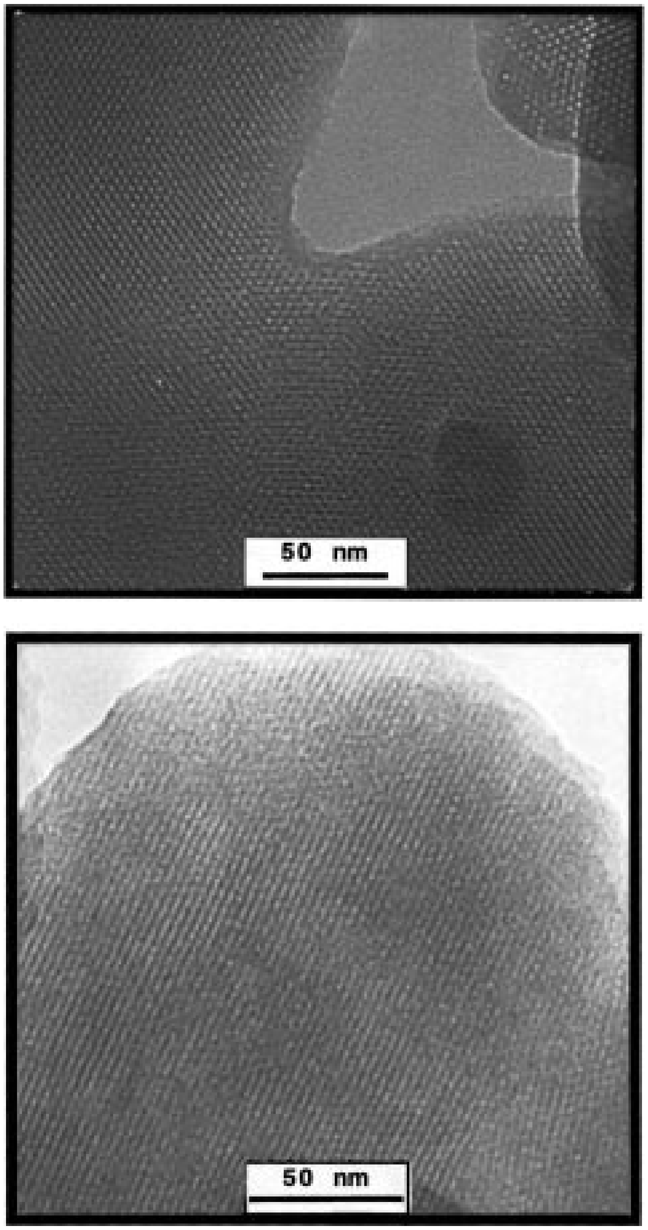

Figure 10. Transmission electron micrographs of (a) MCM-41 and (b) of MA−MCM (7:1) after template extraction.

However, calcination of the hybrids recovers high pore volumes and high surface areas through the removal of the methacrylate groups from the pore walls. These results demonstrate that the functional residues in our newly synthesized MCM hybrids are situated at the pore wall surface and are not buried within the walls. Furthermore, the functional groups are not associated with a separate phase.

Chemical Reactivity of Cocondensed Methacrylate Groups in MCM Hosts. To probe the access to and the reactivity of the methacrylate group in the pores, we studied two different reactions aiming at the reactivity of the C═C double bonds. To illustrate molecular access, we used a bromination reaction, as previously described by Stein et al.[12] A 0.1 M bromine solution in CH_2Cl_2 was diluted with CH_2Cl_2 to give stoichiometric amounts with respect to the experimentally determined methacrylate concentration in the sample. The change of the bromine concentration was followed by UV spectroscopy after addition to the MCM

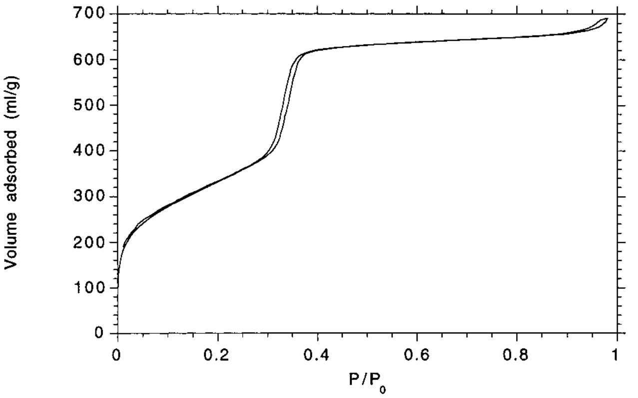

Figure 11. Nitrogen adsorption/desorption isotherms of siliceous MCM-41 after template removal with an ethanol/HCl mixture. BET surface area, 1175 m^2/g.

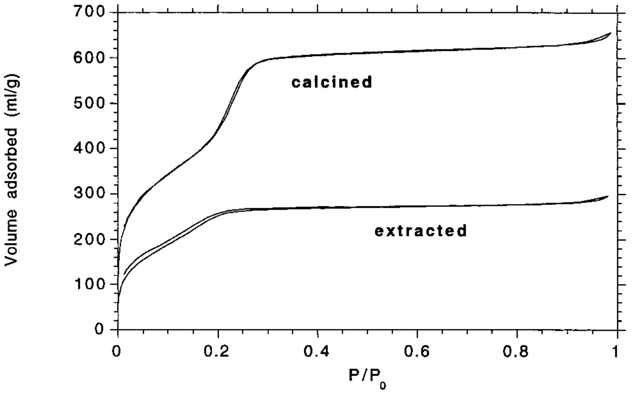

Figure 12. Nitrogen adsorption/desorption isotherms of an MA–MCM sample (TMSiPMA:TMOS = 1:7) after template removal with an ethanol/HCl mixture (bottom; BET surface area, 822 m^2/g) and after calcination of template and acrylate groups (top; BET surface area, 1200 m^2/g).

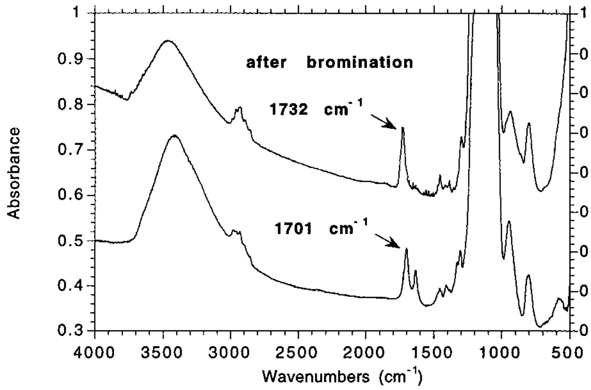

Figure 13. FTIR spectra of a dry 1:7 MA–MCM after template removal (bottom; left scale) and after bromination (top; offset). Spectra are normalized to the intensity of the SiO_2 band at 1086 cm^{-1}.

samples. After about 1.5–2 h the relative decrease in intensity of the 409 nm absorption band with respect to the reference solution had ceased, indicating the end of conversion. When the samples were filtered, washed with CH_2Cl_2 and water and were reevaluated with thermogravimetry in nitrogen, a new weight loss at 360 °C was detected. A shoulder within this new peak at 422 °C corresponds to the desorption of the functional group, as was observed before bromination. The total weight loss was 27.6 wt % in air. A weight loss of ca. 37 wt % is expected if all the previously determined methacrylate groups were brominated with 1 mol of bromine/mol of methacrylate and were released during the measurement. Quantitative elemental analysis of a sample vigorously washed in water detected 8.4 wt % bromine. This is only about half the amount of 19.4 wt % expected, assuming dibromination of the double bond. Dibromination is usually achieved with alkenes under similar reaction conditions. However, in the presence of a competing nucleophile, such as residual water, monobromination is possible.[24] Residual water in the pores of the functionalized MCM materials might have induced the addition of Br–OH to the double bond under release of HBr. Excess bromine in the reaction solution results in near complete dibromination. In any case, bromine addition (as opposed to physical adsorption) has obviously occurred in the hybrid materials. This was confirmed by FTIR spectroscopy, as seen in Figure 13. The C=C double bonds at 1635 cm^{-1} are clearly visible in dry samples before exposure to bromine solution, but they are consumed completely after bromination. Furthermore, the C=O stretch vibration is shifted significantly, from 1701 to 1732 cm^{-1}. A carbonyl stretch position at 1740 cm^{-1} is commonly observed in the synthesis of mono- or dibrominated methacrylates.[25] This shift upon bromine addition can be explained with a loss of delocalization between the C=C and the C=O double bonds. Similar shifts to higher energy are observed upon polymerization of the methacrylate goups (see below).

The fast bromination of the intra-MCM double bonds demonstrates that they are accessible in the pores and promises other possible applications of methacrylate-functionalized MCM hybrids. In a previous study,[17] we showed that inorganic/organic composites can be formed through polymerization of preadsorbed methyl methacrylate within the pores of microporous zeolites or mesoporous MCM-41 and -48. Here, the polymer filaments encapsulated within the pores are intimately entangled with the host. With lattice-incorporated methacrylate groups now available in MA–MCM, strongly coupled composites can be created through a covalent linkage on the molecular level. To prepare a PMMA/MA–MCM molecular composite, the dehydrated functionalized MA–MCM was exposed to MMA vapor at ambient temperature. The presence of the adsorbed MMA is visible in the FTIR spectrum in Figure 14 (lower trace). The signature of the methacrylate groups strongly increases in intensity after MMA adsorption, as compared to that of the hybrid before adsorption (see Figure 13). Polymerization is initiated with benzoyl peroxide under nitrogen, and the polymerization is performed for 12 h at 70 °C and 1 h at 120 °C, followed by evacuation for 1 h at 120 °C. The FTIR spectrum of the molecular composite is shown in Figure 14 (upper trace). Clearly, all double bonds have been consumed in anchoring the polymer to the MCM walls. The polymerization is further indicated by the shift of the epoxy

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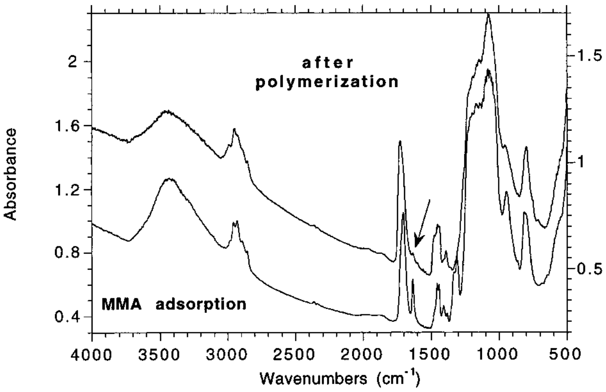

Figure 14. FTIR spectra of a dry 1:7 MA−MCM host after methyl methacrylate adsorption (bottom; left scale) and after polymerization with the adsorbed methyl methacrylate (top; offset). Spectra are normalized to the intensity of the SiO_2 band at 1086 cm^{-1}.

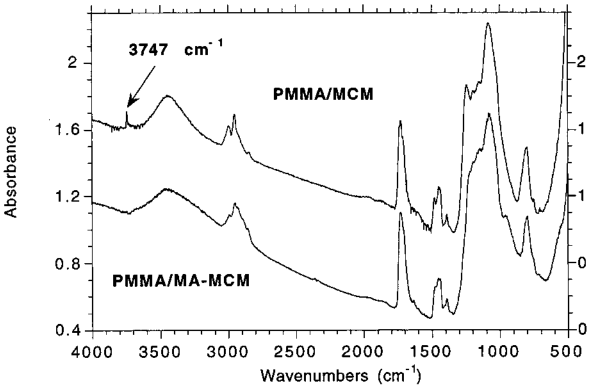

Figure 15. FTIR spectra of a dry 1:7 MA−MCM host (bottom; left scale) and a siliceous MCM-41 host (top; offset) after polymerization of adsorbed MMA. Spectra are normalized to the intensity of the SiO_2 band at 1086 cm^{-1}.

carbonyl frequency from 1701 to 1729 cm^{-1}. When MMA polymerization is performed in pure siliceous MCM-41 hosts, a similar amount of PMMA is incorporated into the pore system, as seen in a comparison in Figure 15. However, in the latter case, hydroxyl groups at 3747 cm^{-1} reappear in the FTIR spectrum after polymerization. This is not observed in the hybrid MCM, where the silanols had been replaced with the propyl methacrylate functional groups. Sorption isotherms show that both composite samples are essentially nonporous, having their pores completely filled with polymer.

Summary. In conclusion, we have demonstrated that incorporation of predetermined quantities of acrylate groups into the MCM walls is possible through cocondensation of TMOS with 3-(trimethoxysilyl)propyl methacrylate at room temperature. Efficient solvent extraction results in highly ordered MA−MCM hybrid materials with large pore volumes, stable to at least 200 °C. The encapsulated methacrylate groups are easily accessible, as demonstrated through fast bromine addition. Furthermore, covalently coupled inorganic/organic composites were prepared through polymerization of additional adsorbed MMA with the functional groups. We are currently extending the scope of the coupling reactions and applications of hybrid mesoporous MCM materials in new areas of catalysis and materials science.

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