428 *Chem. Mater.* **2010,** *22,* 428–434
DOI:10.1021/cm9029903

CHEMISTRY OF
MATERIALS
Article

Mesoporous Melamine Resins by Soft Templating of Block-co-Polymer Mesophases

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Received September 28, 2009. Revised Manuscript Received November 16, 2009

Mesoporous melamine resins have been prepared using hexamethoxymethyl melamine (HMMM) as monomer and block-co-polymer Pluronic F127 as template. At acidic conditions, HMMM condenses into melamine resins, replicating the mesophases formed by the block-co-polymer template. The template can be removed by solvent extraction, yielding mesoporous melamine resins with surface areas of up to 258 m^2/g and pore diameters of 7.8 nm. At a HMMM/F127 weight ratio of 1:1 an ordered mesoporous melamine resin is observed exhibiting a 2d hexagonal arrangement of cylindrical pores. The simplicity of the synthesis of these mesoporous films allows the large scale production of the materials, for example, in the form of free-standing films.

Introduction

Porous polymers are an emerging class of materials, as they promise to complement porous inorganic materials in a number of applications.[1−3] Although microporous polymers and organic frameworks with pore diameters < 2 nm were recently synthesized by scaffolding or self-assembly approaches,[4−16] polymers with pores in the mesoporous regime, that is, with pore diameters > 2 nm, were mainly prepared using templating methods,[17,18] analogous to their inorganic counterparts. Mesophases formed from surfactants or amphiphilic block-co-polymers have been used as templates for the generation of a series of mesoporous inorganic materials, including mainly silica and metal oxides.[19−21] However, for organic materials, it seemed that such organic templates are not applicable as especially the compatibility between the template and the polymer precursor has to be carefully adjusted so that mesophase formation of the template can occur. Also, the removal of the organic template from the organic replica can cause severe problems. Therefore, mostly hard templating procedures using inorganic templates have been often applied for the preparation of mesoporous organic or carbon materials.[18,22] Just in rare cases have mesostructured organic materials been prepared by polymerization of monomers in the presence of micellar systems or lyotropic mesophases,[23,24] yielding, however, mainly unordered materials, with broad pore size distributions and sometimes lower surface areas. Nevertheless, in a series of recent papers, it was shown that the preparation of ordered mesoporous polymers can be carried out using such an organic−organic self-assembly. Zhao et al. reported that Pluronic surfactants can be

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used in the synthesis of highly ordered mesoporous phenolic resins.[25,26] with high surface areas ($S_{\mathrm{BET}} \approx 550-650$ m^2 g^{-1}). At the same time, Ikkala et al. showed that the self-assembly of functional block copolymers, i.e., poly(styrene)-block-poly(4-vinylpyridine), could also be used for the synthesis of mesoporous phenolic resins.[27,28] Removal of the template was accomplished in both cases by thermal decomposition of the template polymer. Further heating even transferred the ordered mesoporous phenolic resin into mesoporous carbon. These ordered mesoporous phenolic resins and the mesoporous carbons derived therefrom have attracted much interest and recently a variety of new structures and morphologies of these materials have been prepared.[29−31] Furthermore, composite structures were prepared using additional inorganic precursors in the synthesis.[32] Consequently, some applications from adsorption and purification materials to catalyst supports have already been suggested.[32,33]

However, so far, the organic−organic self-assemblies have just successfully been applied for phenolic resins and no other polymer composition with a comparable mesostructure has been reported. In this paper, the extension of the organic−organic self-assembly approach to the synthesis of mesoporous melamine resins is presented. Melamine resins are a large-scale product in the chemical industry and used as cross-linker in organic coatings and plastics. If high surface areas and porosity can be introduced in such networks, interesting applications might furthermore arise due to the abundance of amine groups on the pore walls. Indeed, porous materials with amine functionalities on the pore walls have recently attracted great interest, as they could find applications for example in catalysis,[34−36] proton conducting membranes[37] or for the selective adsorption and storage of carbon dioxide.[38−41] Recently, silica-templated melamine resins have also been used as adsorbents for CO_2 capture.[42] Nitrogen-rich mesoporous materials have also found application as "reactive templates", for the preparation of mesoporous, or in general nanostructured metal nitrides via nanocasting.[43−46]

Melamine resins belong to the class of amino resins or amino plastics, which are closely related to their phenolic analogs both in synthesis and application.[47] Indeed, some approaches toward porous melamine resins have been carried out using templating strategies. For example, porous melamine resins have been prepared using microemulsions as a structural template. In this way, porosities of 86 vol % were achieved with 65 nm pore sizes.[48] The same approach has been used applying different ionic and nonionic surfactants, yielding melamine−formaldehyde resins with porosities of up to 89 vol % and 156 m^2/g with pores in the range of 100 nm.[49] Microporous nitrogen containing carbons were synthesized by heating mixtures of anionic surfactants with melamine resins to 800 °C.[50] Pore size analysis of the resulting N-doped carbons revealed a significant influence of the surfactants, thus materials with surface areas of up to 539 m^2/g have been obtained.

The so far reported methods for preparing porous melamine resins were using melamine and formaldehyde as monomers, which were condensed under acidic or basic pH in presence of the template. The polymerization of melamine with formaldehyde yields various methylolmelamines as well as a mixture of higher oligomers in the first step. However, the relative amounts of these various components are dependent on the reaction conditions (pH, catalyst, and resin stoichiometry),[51,52] which can make the optimization of parameters toward templated, porous melamine resins a labor-intensive task. Beside the usage of melamine and formaldehyde, other precursors for melamine resins were developed.

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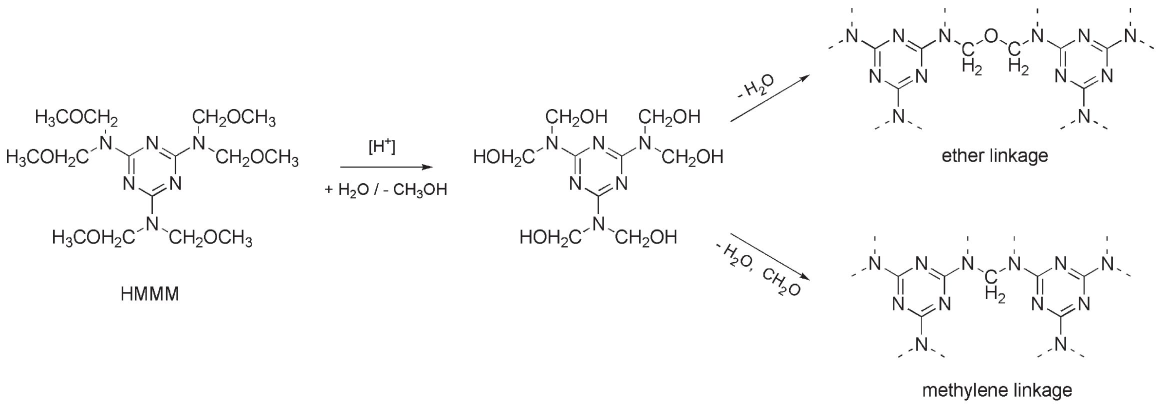
Scheme 1. Simplified Condensation Pathway of HMMM toward Melamine Resin; Possible Connection Patterns Are Shown in Form of Ether and Methylene Linkages



Hexamethoxymethylmelamine (HMMM) has been often used to avoid the uncontrolled self-condensation properties when used as cross-linking agents.[53−56] HMMM can be condensed into melamine resins by acid catalysis, forming networks analogous to the one observed from the reaction of melamine and formaldehyde. Recently, HMMM has been used for the fabrication of melamine resin nanoparticles and lamellar mesoscopic gels.[57] For the here shown templating procedure, the usage of HMMM has the striking advantage that it can be used analogous to sol−gel precursors in well-known procedures toward mesoporous inorganic materials. Indeed, HMMM and F127 are the only components needed for the preparation of the mesoporous melamine resins, beside the appropriate solvent and acid.

Experimental Section

Materials. Hexamethoxymethyl melamine (HMMM) was purchased from ABCR. F127 was purchased from Aldrich. All chemicals were used as received.

Methods. The NMR measurements in solution were conducted using a Bruker DPX-400 spectrometer operating at 400.1 MHz. The solid-state NMR $^{13}C\{^{1}H\}$ CPMAS (cross-polarization magic angle spinning) measurements were carried out using a Bruker Avance 400 spectrometer operating at 100.6 MHz for ^{13}C using a Bruker 4 mm double resonance probe-head operating at a spinning rate of 10 kHz. 1H composite pulse decoupling was applied during the acquisition. ^{13}C chemical shifts were referenced externally to TMS (tetramethylsilane) using adamantane as a secondary reference. Nitrogen sorption experiments were conducted at 77 K using an Autosorb-1 from Quantachrome Instruments. Before sorption measurements, the samples were degassed in vacuum overnight at 80 °C. The surface area was calculated from multipoint BET plot, and the pore volume was determined by the BJH method. Elemental analysis was performed on a Vario Micro setup. The IR spectra were collected with a BIORAD FTS 6000 FTIR spectrometer, equipped with an attenuated total reflection (ATR) setup. Thermogravimetric analyses have been carried out using a NETZSCH TG209. The heating rate was 10 K/min. The measurements were carried out under ambient atmosphere. Transmission electron microscopy (TEM) images of microtomed samples were taken with a Zeiss EM 912Ω at acceleration voltage of 120 kV.

Synthesis of Mesoporous Melamine Resins. In a typical synthesis, 1 g of HMMM was dissolved in ethanol (2.5 g) containing HCl (37 wt %, 0.1 mL) by heating at 373 K for 20 min under reflux. A solution of Pluronic F127 (0.25−1.5 g) dissolved in ethanol (2.5 g) was poured into the above solution and then heated to 373 K for additional 4 h under reflux. After cooling down, the resulting clear solution was poured and dried on a petridish to evaporate the ethanol and subsequently cured at 423 K for 12 h. Note that fast evaporation of the ethanol was ensured by casting thin films, which are transparent after solvent removal, condensation, and aging. When thicker films are produced, the polymer membranes become turbid and lose some of their structural order and surface area. The template block copolymer was removed by solvent extraction (~0.15 g of the sample in 120 mL of ethanol and stirring) at 60 °C for 3 h. The samples were dried in an oven at 50 °C overnight.

Results and Discussion

For the synthesis of the mesoporous melamine resins (MMR), HMMM and the template Pluronic F127 are dissolved in ethanol under acidic conditions and heated to 100 °C for 4 h. Throughout the reaction a transparent colorless solution is observed. After evaporation of the solvent in Petri dishes the samples were cured at 150 °C for 12 h, yielding transparent, yellow-brown films. With lower template content, the films are rather brittle, but they become more flexible with increasing template content. When carefully handled, they can be taken off from the dish to obtain free-standing films (see Figure S1 in the Supporting Information). For template removal the films are washed in ethanol at 60 °C for 3 h. Solid-state NMR measurements (see below) indicate that 3 h of washing are sufficient to ensure complete extraction of the surfactant polymers. Longer washing times on the other hand yield in partial pore collapse especially when higher template/HMMM ratios were used (see Figure S2 in the Supporting Information). Different F127:HMMM weight ratios have been applied ranging from 1:4 (MMR-0.25) to 1.5:1 (MMR-1.5). The chemical structure of the melamine resins after extraction of the Pluronic template was

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analyzed using elemental analysis, IR spectroscopy and ^{13}C{^{1}H} CPMAS solid-state NMR measurements. The cross-linking reaction of HMMM starts with the splitting of the ether groups when water and an acid is present leading to methylol groups. These methylol groups can cross-link and two principle linkages are possible during condensation, namely an ether linkage ($-N-CH_2-O-CH_2-N-$) or a methylene linkage ($-N-CH_2-N-$) (Scheme 1).[51,52,58]

Because melamine has six substitution sites, it is apparent that most melamine resins are quite complex mixtures of these bonding patterns, making the elucidation and description of the chemical structure rather difficult. Elemental analysis of the melamine resins after template removal gives a C/N molar ratio of 1.65, close to the calculated value of 1.5 for a fully condensed network with ether linkages. Compared to a ratio of 2.50 for the HMMM monomer, the C/N ratio thus confirms a high amount of cleavage and removal of methoxy groups, before or during cross-linking of the networks. The significant residual mass of the C,H,N-elemental analysis (~27 wt %) points to a high amount of oxygen in the networks, thus indicating a higher amount of ether linkages. However, as even a fully condensed network exclusively composed out of ether linkages should not exceed an oxygen content of 19.3% the residual mass also has to be assigned to some amount of physisorbed water.

IR measurements (Figure S3) of the melamine resins confirm the existence of triazine rings in the pore wall shown by the characteristic triazine vibration at 1566 cm^{-1}. A broad peak at ~3400 cm^{-1} points to free hydroxy groups in the networks, but physisorbed water can also not be excluded to be responsible for this peak. Solid-state ^{13}C{^{1}H} CPMAS NMR measurements show two signals at 155 and significantly more intense at 165 ppm indicative of the triazine rings, a narrow peak at 70 ppm and a broader peak 53 ppm (Figure 1c). The signal at 70 ppm is assigned to the methylene groups in ether linkages, whereas the 53 ppm resonance is associated with methylene linkages (or unreacted methoxygroups).[59] From the spectra, it can be concluded that the melamine resins are composed of triazine rings connected by a mixture of both linkages, whereas the NMR together with the reported condensation mechanism of HMMM at stronger acidic conditions indicate a major amount of ether linkages. The melamine resins, even though highly cross-linked, still feature rather flexible structural units, which will have some influence on the synthesis, processing, and structure of the resulting porous resins.

From the NMR spectra, it can be furthermore concluded that after 3 h extraction time almost the entire Pluronic template has been removed from the melamine resin, as just a very weak signal appeared at 15 ppm indicative for the methyl groups in the PPO chain of F127.

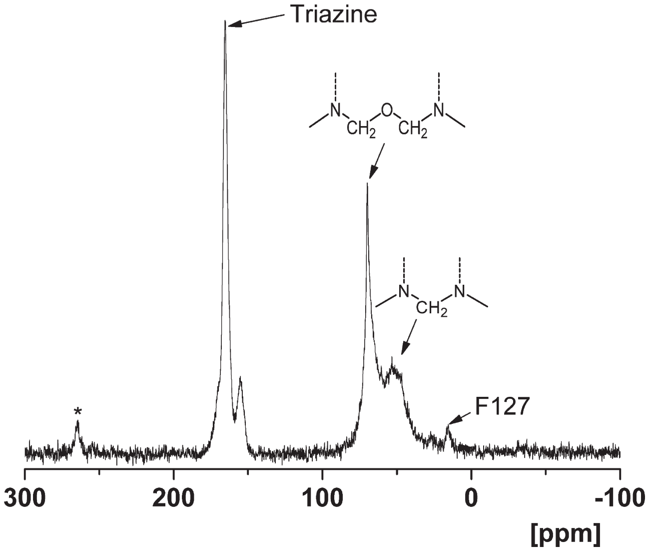

Figure 1. ^{13}C{^{1}H} CPMAS-NMR spectra of melamine resin MMR-1.0 after template removal, characteristic peaks are assigned. The asterisk marks a rotational sideband.

The mesostructure of the resins prepared with different F127:HMMM ratios have been assessed by nitrogen sorption, electron microscopy, and XRD measurements.

Nitrogen sorption measurements on the resins confirm the open pore structure and accessible high surface areas (Figure 2, Table 1). All isotherms show a type IV characteristic with a steep increase in the adsorption branch at higher relative pressures indicative of mesoporous systems. As expected, the porosity and surface area of the resins increase with increasing template content, that is from sample MMR-0.5 to MMR-1.0. On the other hand, a further increase in the F127/HMMM ratio yields a decrease in porosity and surface area and finally for MMR-1.5 no defined mesoporosity can be observed, shown in the broad hysteresis of the nitrogen sorption isotherm and the low surface area. The fact that the values of porosity and surface area of the materials are going through a maximum confirms that the framework consists of a rather flexible polymer; at a certain thinness of the wall, the polymer cannot withstand the high capillary pressure, leading to pore collapse. It is further noticeable that for the first framework in which this effect is observed (MMR-1.25), no change in the pore size is found, showing that pore collapse is due to the involved capillary pressures, a critical phenomenon, and the pores either vanish completely or stay open. A comparable effect was observed for slightly cross-linked mesoporous polybenzimidazole templated with silica spheres.[60] A further decrease in wall thickness then results in a collapse of nearly all the pores shown by an isotherm, indicating a broad pore size distribution as observed for sample MMR-1.5

The mesoporous structure of the resins was also confirmed by TEM measurements (Figure 3, Figure S4 in the

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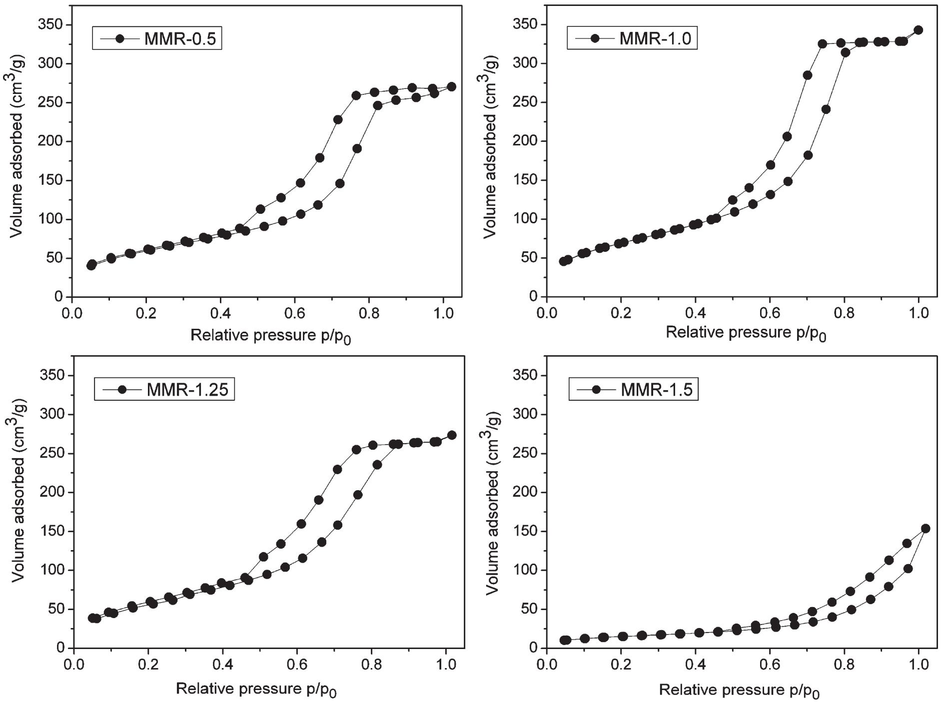

Figure 2. Nitrogen sorption isotherms of mesoporous melamine resins prepared with different F127/HMMM ratios.

Table 1. Porous Characteristics of Mesoporous Melamine Resins

sample	S_{BET} (m^2/g)	V_{p} (cm^3/g)	d_{pore} (nm)
MMR-0.25			
MMR-0.5	224	0.42	7.8
MMR-1.0	258	0.53	7.8
MMR-1.25	214	0.42	7.7
MMR-1.5	56	0.24	12.4 (broad)

Supporting Information). From the TEM pictures a transition of the pore structure can be observed. While spherical pores are observed in sample MMR-0.25, MMR-0.5 exhibits a nonordered wormlike structure. Higher concentrations of the polymer then yield cylindrical micelles arranged in a 2D hexagonal packing. At a HMMM/F127 ratio of 1:1 cylindrical pores are observed that are arranged in well-ordered hexagonal arrays, comparable to the pore structures found in SBA-15 or the corresponding phenolic resins, FDU-15.

It is noticeable that nitrogen sorption measurements show no surface area and porosity for sample MMR-0.25. This is in stark contrast to the TEM results, where spherical pores are clearly visible and homogeneously distributed throughout the sample (Figure 3a, Figure S4 in the Supporting Information). However, this contradiction is readily explained by the fact, that these pores are separated by large pore walls and the missing interconnection between the pores in the dry state inhibits the availability of the pores for nitrogen sorption. Still, as mesopores are visible in the TEM pictures, the template polymer was clearly removed during solvent extraction, which seems hardly possible when the pores are permanently isolated from each other. One explanation could be that through the soft and flexible pore walls, the framework can swell to some extent during solvent extraction, opening diffusion pathways for the template polymers and allowing their extraction from the melamine resin. In the dry samples, however, the mesostructures and pore walls are rigid enough to prevent nitrogen from entering the pores. A comparable effect has been recently observed for mesoporous polystyrene.[61]

The transition from an unordered porous structure into an ordered one is supported by XRD measurements (Figure 4). Although no reflection peak is found in XRD at lower concentration of the block-co-polymer (MMR-0.25), a weak shoulder is observed for materials with increasing template content (MMR-0.5). The materials prepared from a template content of weight ratio 1:1 (MMR-1.0) exhibit a narrow peak at lower angles (0.71°), which can be attributed to the (10) reflection of hexagonally arranged cylindrical pores observed in the TEM pictures. The intense peak reflects a *d*-spacing of 12.4 nm, corresponding to a unit cell parameter of $a_0 = 14.3$ nm.

It is noticeable that these values are comparable to the recently described phenolic resin FDU-15, which exhibit quite similar values.[25] As FDU-15 is furthermore prepared from a similar precursor/F127 weight ratio of 1:1 (there resol precursor, here HMMM) it can be concluded that the approach introduced here should be expandable to various other porous structures as shown for mesoporous phenolic resins. In contrast to these phenolic resins, where calcination can lead to mesoporous carbons, calcination in this case does not yield any porous structures, even though two distinct steps for the decomposition of the F127 template (280 °C) and the melamine resin (659 °C) can be distinguished from the TGA measurements of the composites (see Figure S5 in the Supporting Information). Again this is explainable by the rather flexible pore walls of the melamine resins. It should be noted,

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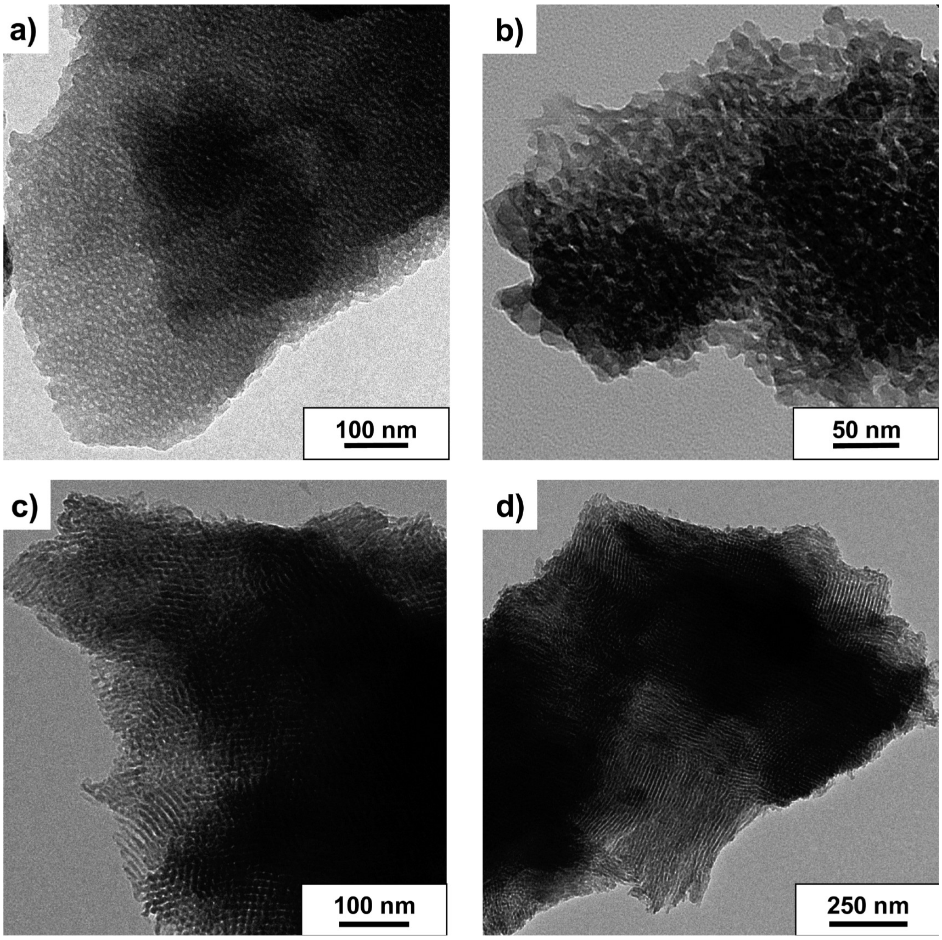

Figure 3. TEM micrographs of mesoporous melamine resins: (a) MMR-0.25, (b) MMR-0.5, (c, d) MMR-1.0 in higher and lower magnification.

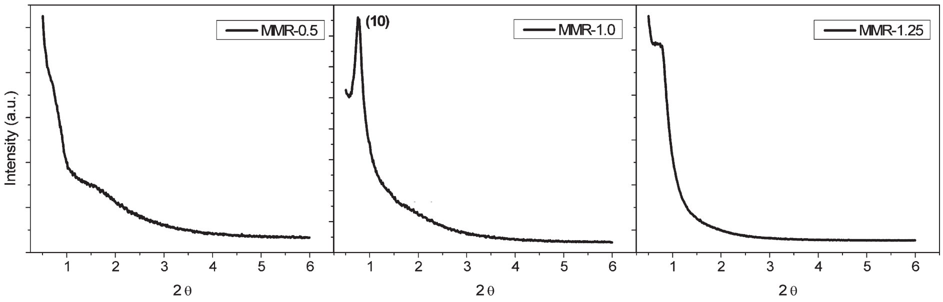

Figure 4. XRD measurements on melamine resins with different monomer-template ratios.

however, that variation in the preparation conditions (e.g., pH) could yield in the formation of stronger pore walls by introducing a higher amount of methylene linkages, which consequently is one of the major tasks of our ongoing work.

Conclusion

In conclusion, mesoporous melamine resins were prepared via replication of mesophases formed from the block-co-polymer Pluronic F127. Materials with pore sizes of 7.8 nm and surface areas of up to 258 m^2/g have been prepared. At a F127/HMMM weight ratio of 1:1, an ordered mesoporous resin is formed, exhibiting cylindrical pores arranged in a 2-dimensional fashion with a unit cell parameter of a_0 = 14.3 nm. These new materials are promising candidates for several applications, especially because of the high amount of chemical functionalities in form of amine groups on the pore walls. Thus MMRs will be tested for sorption and purification applications. The materials might also be used as reactive templates for the generation of nanostructured metal nitrides, via backfilling of the melamine resins with metal precursors and subsequent heat treatment. Furthermore, as HMMM is often used as cross-linking agent, a variety of protocols for the formation of polymer/melamine composites are described, which principally can also be applied for the here shown templating approach, yielding tailorable chemical structures of the pore walls.

Acknowledgment. Financial support by the BMBF (Grant number 01RC0901F), the Genome-based Integrated Bioprocess Project of the Ministry of Science and Technology of Korea, and Brain Korea 21 (BK21) is gratefully acknowledged. We are grateful to Dr. Astrid Jürgensen for help with XRD measurements. We thank Prof. Markus Antonietti and the Max Planck Institute of Colloids and Interfaces for the TGA and TEM measurements.

Supporting Information Available: Picture of a MMR-1.0 film. BET results of MMR-1.0 after different extraction times. IR spectrum and TGA of MMR-1.0; Additional TEM pictures of melamine resins (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.