

Template Synthesis

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Oriented Nanoporous Lamellar Organosilicates Templated from Topologically Unsymmetrical Dendritic-Linear Block Copolymers***Teddie Magbitang, Victor Y. Lee, Jennifer N. Cha, Hsiao-Lin Wang, W. Richard Chung, Robert D. Miller, Geraud Dubois, Willi Volksen, Ho-Cheol Kim,* and James L. Hedrick**

Microstructured porous materials have potential application in a variety of areas, including separation techniques, catalysis, sensing, coatings, microelectronics, and electroop-

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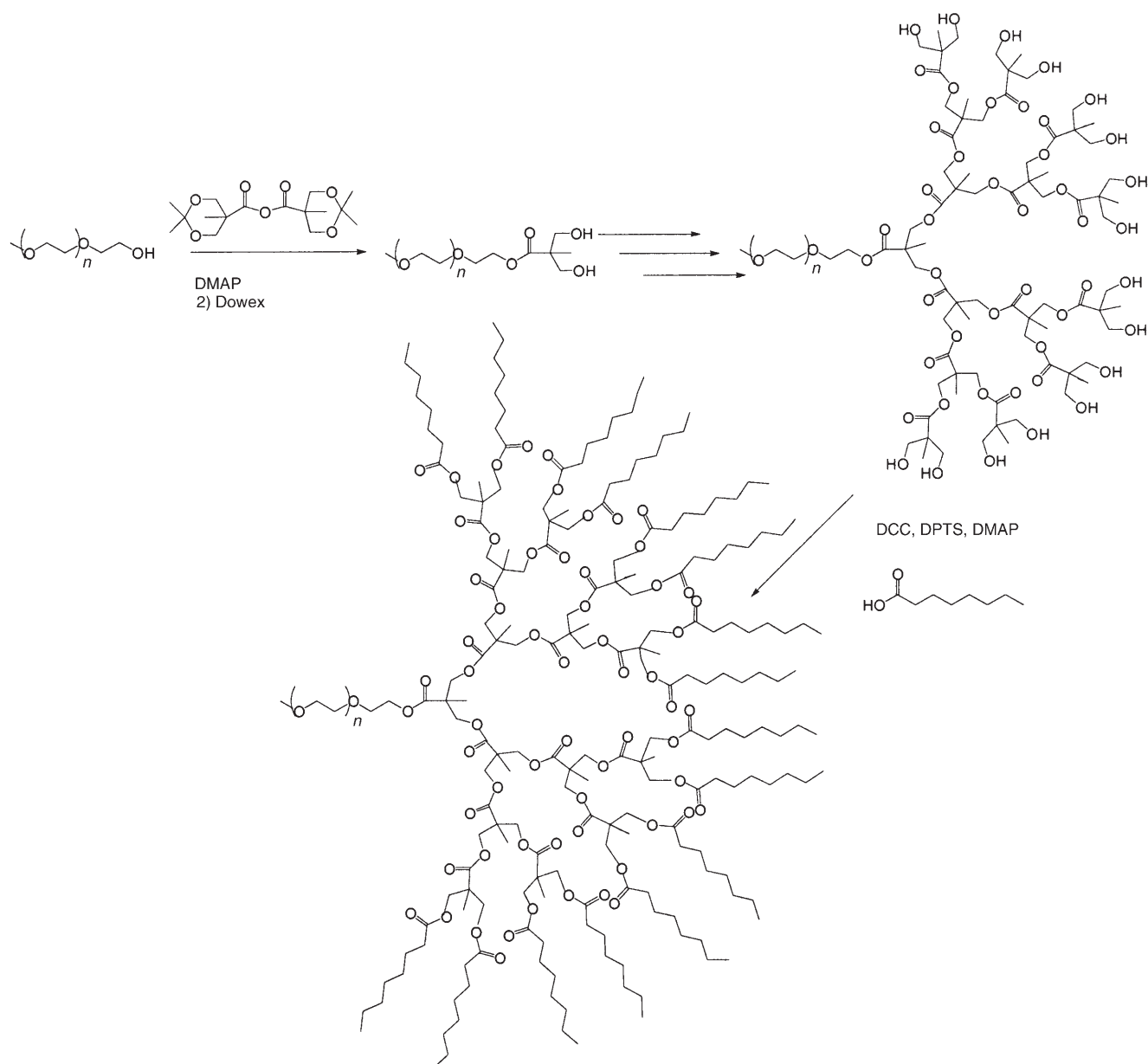
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tics.^[1] Silica-based mesoporous materials, prepared by the assembly of periodic inorganic and surfactant-based structures, have received considerable attention because of the diverse collection of possible pore sizes and shapes.^[2] More recently, this concept has been extended to include lyotropic liquid crystalline assemblies,^[3] ionic liquids,^[4] cyclodextrin-based materials,^[5] triphenylene as an electron donor (charge-transfer agents),^[6] phthalocyanine-based amphiphiles,^[7] and block copolymers^[8] as structure-directing agents. Block copolymers have the advantage of fine-tuning the polymer/solvent/silica phase behavior through variation of the monomer type, volume composition, or macromolecular architecture.^[9]

We have recently described the generation of nanoporous organosilicates by using block copolymers that exhibit unimolecular self-organization within a vitrifying organosilicate matrix. This process requires an environmentally responsive, star-shaped macromolecule that organizes the organosilicate vitrificate into nanostructures through a matrix-mediated collapse of the interior core of the core-corona polymeric structure. The insoluble core is rendered compatible in the thermosetting matrix and dispersed through the outer corona designed to be miscible with the matrix.^[8c,g] The unimolecular nature of the amphiphile eliminates the complex dynamic assembly that characterizes most amphiphiles, and the curvature constraints of this architecture generate non-interconnected spherical pores up to high volume fractions (approximately 50%) upon porogen burn out. Herein, the synthesis of amphiphiles that are between conventional surfactants and block copolymers, with the shape of the former and the size of the latter, is described with the objective of templating a wide variety of porous morphologies through an amphiphile, organosilicate self-assembly process. Amphiphilic dendrons as described by Percec et al.^[10] are an example of a system that self-assembles into a variety of nanostructures. Alternatively, dendritic linear hybrid AB amphiphilic block copolymers are also likely candidates, as Frechet, Meijer, Stupp, Hawker, and others^[11] have shown that such architectures respond to changes in their environment through changes in the type and shape of micelles formed. In addition, these copolymers assemble into well-defined Langmuir–Blodgett monolayers that are capable of the formation of nanostructured materials with unusual properties and morphologies.^[12] Wiesner and co-workers used such amphiphilic dendrimers as structure-directing agents for aluminosilicate-based materials and generated hybrids with a wide variety of nanostructured morphologies.^[13] As the shape of low-molecular-weight surfactants has a pronounced effect on the type of aggregate structure formed in silica-surfactant self-assembly, we felt that a dendritic linear amphiphilic copolymer provides an excellent platform from which to tailor the size and shape of the copolymer. Herein, the responsiveness to change in the environment of the copolymer can be tuned by the type, surface functionality, and dendrimer generation together with the structure and molecular weight of the linear component.^[14] Herein, we describe the use of amphiphilic dendritic linear copolymers, based on poly(ethylene oxide) (PEO) and a dendron derived from 2,2'-bis(hydroxymethyl)propionic acid (bis(MPA)),^[15] as struc-

ture-directing agents for organosilicates to generate a unique, oriented perforated porous lamellar morphology.

PEO hydroxy-functionalized oligomers ($M_w = 4800$ and 9800 g mol^{-1} ; polydispersity indices (PDI) = 1.03 and 1.05, respectively) were chosen as the linear component of the copolymer, as PEO has been shown to be miscible with the methyl silsequioxane (MSSQ) prepolymer over wide compositional and molecular-weight ranges.^[8c,g] Dendrons derived from bis(MPA) were chosen as they decomposed cleanly and quantitatively upon thermolysis,^[16] furthermore, they can be prepared by both divergent and convergent methods and provide exquisite NMR spectroscopic handles to follow the various chemical transformations.^[17] Frechet and co-workers showed that hydroxy-terminated PEO is an excellent scaffold for the divergent growth of dendrons using acetal-protected anhydride derivatives of bis(MPA) and also importantly demonstrated that the PEO facilitates product purification through precipitation.^[18] This divergent-growth approach was employed using acetonide-protected bis(MPA) anhydride, prepared from the self-condensation of the acetonide-protected bis(MPA) using *N,N'*-dicyclohexylcarbodiimide (DCC), in the presence of dimethylaminopyridine (DMAP; 0.25 mol % with respect to the anhydride) in a solvent mixture of CH_2Cl_2 /pyridine (90:10). An approximate 2–4-fold excess of anhydride was used to insure quantitative conversion of the terminal hydroxy groups, and the reaction was performed at room temperature (approximately 15–18 h) under nitrogen (Scheme 1). Upon completion, the excess anhydride was treated with methanol to facilitate purification as the by-products generated are soluble in diethyl ether and the PEO copolymers do not allow polymer precipitation. Deprotection of the acetonide groups was accomplished by using Dowex 50W-X2 acidic ion-exchange resin in methanol at 54°C for 5 h. This general procedure was repeated for each generation and for both poly(ethylene) glycol (PEG) molecular weights surveyed, thus ultimately producing up to six generations of bis(MPA) dendron “block length” in the copolymers. These transformations were followed using ^{13}C NMR spectroscopy, as the quaternary carbon atom of bis(MPA) is sensitive to the substitution of the neighboring hydroxy groups, and the spectra associated with dendritic, linear, and terminal substitution have been identified by model-compound studies. The functionalization and deprotection steps are quantitative irrespective of the generation (Figure 1). The quaternary carbon atom of the acetonide-protected first generation occurs at $\delta \approx 42 \text{ ppm}$, which on deprotection shifts to $\delta \approx 50.5 \text{ ppm}$. Subsequent functionalization of the first generation produces the acetonide-protected second generation ($\delta \approx 42 \text{ ppm}$) and the inner first generation ($\delta \approx 46 \text{ ppm}$); incomplete transformations are readily detected. The surface hydroxy groups of the dendrons for the fourth to sixth generations were subsequently functionalized by esterification with either protiated or deuterated heptanoic acid in CH_2Cl_2 using DCC/pyridinium 4-toluenesulfonate (DPTS)/DMAP.^[19,20] ^{13}C NMR spectroscopy of the terminal quaternary carbon atoms of bis(MPA) clearly showed quantitative conversion into the esterification product (Figure 1). Functionalization of the polymer chain with acetonide-bis(MPA) ($\delta \approx 42 \text{ ppm}$), followed by its deprotection ($\delta \approx 50.5 \text{ ppm}$), is



Scheme 1.

clearly seen for each generation (up to generation 5). The fifth generation is then deprotected and functionalized with heptanoic acid ($\delta \approx 46$ ppm). The general characteristics of the fourth–sixth generation copolymers prepared from each of the PEG oligomers, including the molecular weight and weight fraction of the dendron and the molecular weight and polydispersity of the entire copolymer, are given in Table 1. The size-exclusion chromatograms of the fourth–sixth generation copolymers **1a–c** (see Figure 1 and the Supporting Information) and (**2a–c**) clearly demonstrate monomodal, narrowly dispersed products (Figure 2). Thin films of these block copolymers show microphase-separated morphologies, as evidenced by the presence of two T_g values in the dynamic mechanical analysis (DMA) spectra for the third–sixth generation copolymers (Figure 3). Wiesner and co-workers studied the morphologies of similar macromolecular architectures in detail.^[21]

The amphiphilic polymers were dissolved in a solution containing the MSSQ prepolymer in 1-methoxy-2-propanol, and the resulting solution was spun on a silicon wafer to produce thin films that were cured to 430 °C to effect the first network formation of the MSSQ and decomposition of the sacrificial copolymer template. Representative $\tan \delta$ curves obtained from DMA for the **1a**/MSSQ hybrid (40 wt. % copolymer loading) after curing to 80 °C (minimal advancement in MSSQ molecular weight) and 150 °C (significant advancement in molecular weight of MSSQ, that is, network formation) are presented in Figure 3 (also see the Supporting Information) together with the copolymer for comparison. Irrespective of the cure temperature, a two-phase structure is clearly evident in the hybrid. The retention of the T_g value at –25 °C associated with the bis(MPA) dendron phase and the disappearance of the PEO transition (approximately –55 °C) supports the hypothesis that a two-phase structure is present

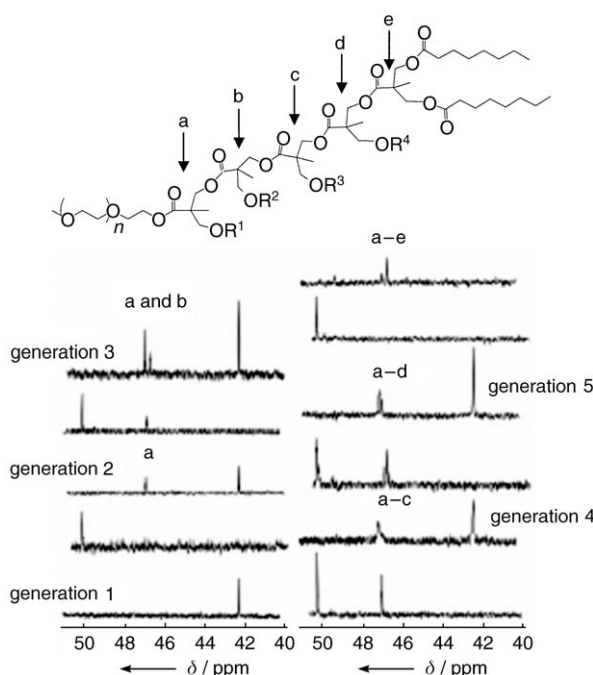


Figure 1. ^{13}C NMR spectra of copolymers **1a–c**.

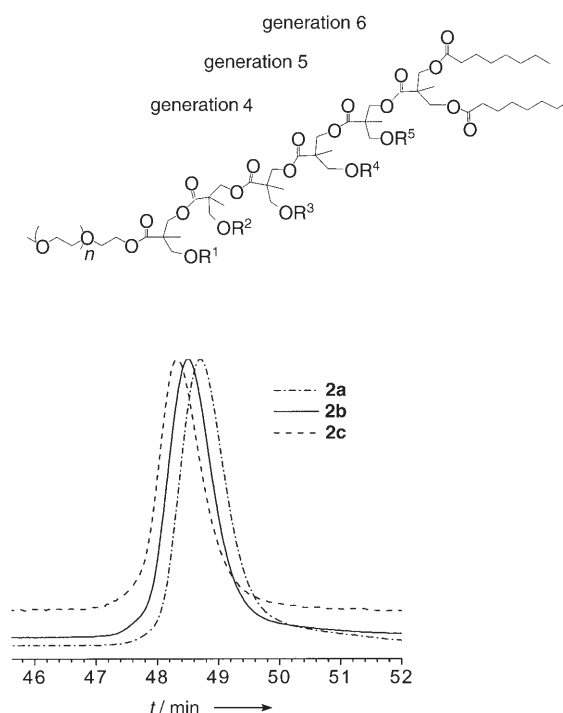


Figure 2. Size-exclusion chromatograms of copolymers **2a–c**.

Table 1: Characteristics of dendritic-linear amphiphilic copolymers.

Sample	PEO segment M_n [g mol $^{-1}$]	Dendron generation (M_n [g mol $^{-1}$])	Dendron fraction	$M_n^{[a]}$ [g mol $^{-1}$]	$M_n^{[b]}$ [g mol $^{-1}$]	PDI
1a	4800	4 (4030)	45	9000	9700	1.08
1b	4800	5 (8200)	63	13 000	11 300	1.03
1c	4800	6 (12 000)	71	16 800	14 000	1.04
2a	9800	4 (4030)	29	14 000	16 500	1.05
2b	9800	5 (8200)	45	18 000	18 200	1.05
2c	9800	6 (12 000)	55	21 500	20 000	1.04

[a] Detected by ^1H NMR spectroscopy. [b] Detected by gel-permeation chromatography.

even prior to cure. Although it is difficult to assign with certainty, we believe it is likely that the T_g value at 50°C is the mixed T_g values of the PEG and MSSQ phase as they are miscible. Small-angle neutron scattering (SANS) measurements of **1a** (in which the chain ends are selectively decorated with deuterated heptanoic acid) confirm the two-phase structure of the hybrid containing 40 wt.% copolymer (see the Supporting Information). This structure, generated upon spin coating, is thought to occur through a self-assembly process facilitated by the selective solubilization of the PEO by MSSQ and subsequent collapse of the dendron (namely, the structure-directing agent). Further heating of hybrid samples to 430°C removes the block-copolymer template to create a porous thin film. For example, a porous film derived from a hybrid containing 40 wt.% **1a** has a refractive index of 1.24 and a dielectric constant of 2.00, in comparison to the dense MSSQ matrix with values of 1.37 and 2.85, respectively. Irrespective of the PEG block length or dendron generation

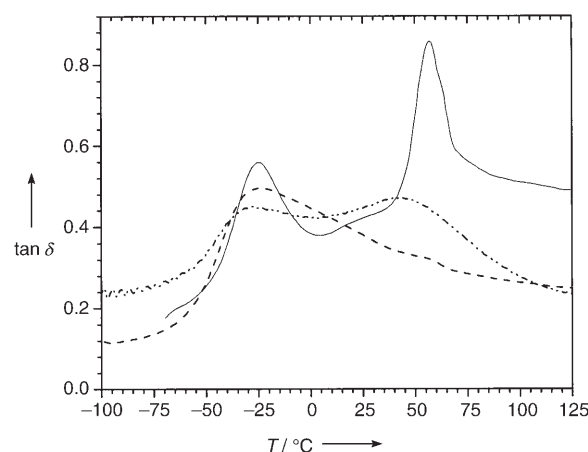


Figure 3. DMA of copolymer **1a** (—), **1a**/MSSQ mixture cured to 80°C (– · –) and 250°C (----).

surveyed, all refractive indices and dielectric constants were comparable for similar loading levels.

Cross-sectional transmission electron microscopy (TEM) images of MSSQ mixtures containing 20, 40, and 60 wt.% of **1b** are shown in Figure 4. The sample of 20 wt.% shows a porous structure (pore sizes: 4–5 nm) with a shape that resides at the interface between the spherical and cylindrical morphologies. Conversely, mixtures that contain the higher volume fractions of copolymer manifest a nanoporous lamellar structure that is oriented parallel to the surface, and this morphology is maintained over a wide compositional range (approximately 35–70%). Small-angle X-ray scattering (SAXS) measurements on the porous films show an increasing scattering intensity with porogen volume

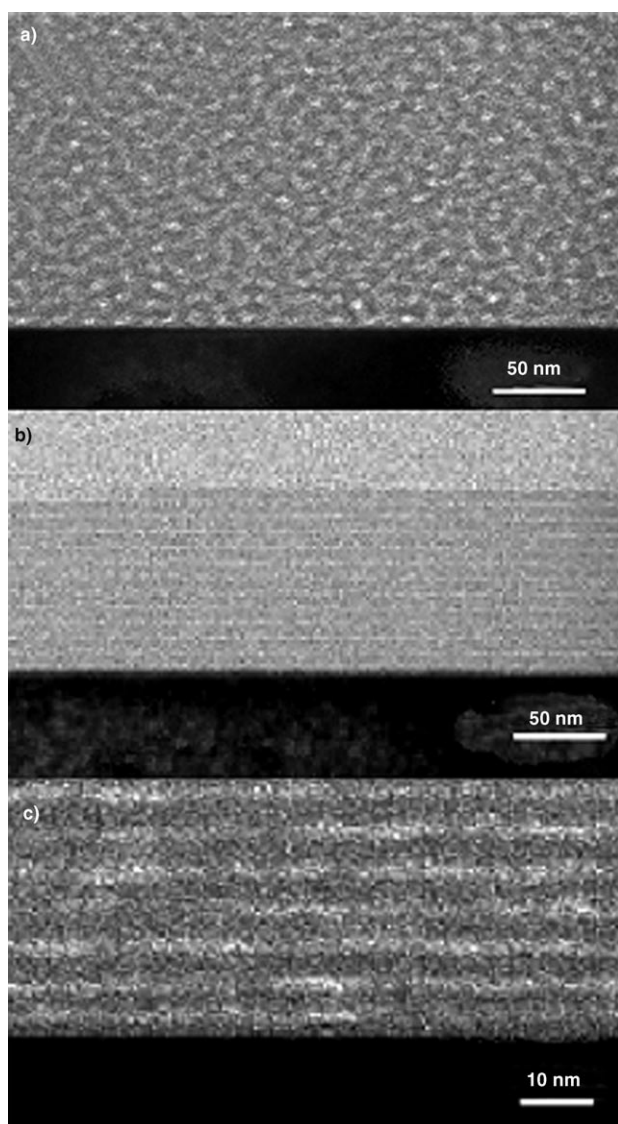


Figure 4. TEM images of copolymer **1b** with mixtures of MSSQ containing a) 20, b) 40, and c) 60 wt. % copolymer.

fraction of **1a** (Figure 5). At a loading of 40 wt. % and above, a strong intercore correlation is observed with peaks that correspond to approximately 129 Å ($2\pi/q$), and no significant change was observed by increasing the copolymer loading to 60 wt. %. Figure 5b shows the effect of PEO molecular weight and dendron generation on the pore structure. An increase in intercore distance from 129 to 137 Å was observed for a loading of 40 wt. % with increasing PEO molecular weight from 5000 to 10000. The SAXS profiles for **2a** and **2b** show the intercore distance increases from 137 to 197 Å as the dendron generation is varied from the fourth to the fifth. Although a porous morphology was observed for all calcined samples, the well-defined lamellar structure oriented parallel to the surface was observed only for the copolymer that contained the fifth generation dendron, irrespective of the PEO block length. The lamellar morphology oriented parallel to the surface was further confirmed by X-ray reflectivity (XR) by the strong scattering that satisfies the Bragg

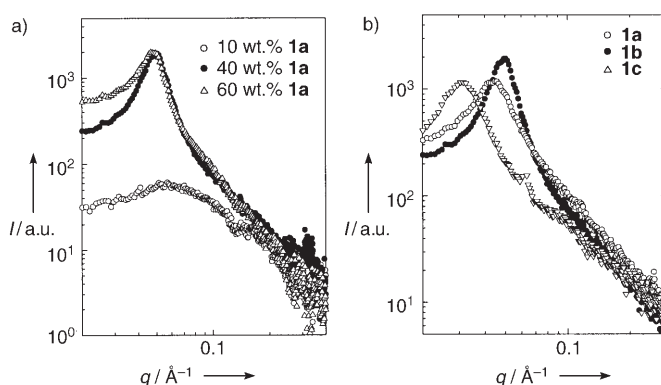


Figure 5. SAXS profiles of porous organosilicates: a) SAXS profiles as a function of weight fraction of G4-PEO5K; b) SAXS profiles of porous films generated with 40 wt. % of copolymer. The samples were prepared by thermal heating to 450 °C after spin-casting.

condition (40 wt. % loading of **1b**), thus indicating a layered structure with porosity oriented parallel to the substrate (Figure 6). The first-order Bragg peak corresponds to a period of approximately 107 Å ($2\pi/q$). The higher-order peaks correspond to periods of approximately 56 and 38 Å, respectively.

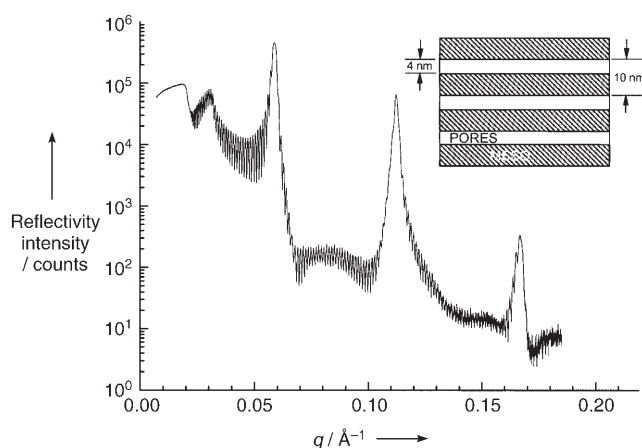


Figure 6. XR profile of porous organosilicate thin films generated with 40 wt. % **1b**. The samples were prepared by thermal heating to 450 °C after spin-casting.

In summary, environmentally responsive, topologically unsymmetrical dendritic linear diblock copolymers with a compatibilizing linear component were used to organize a MSSQ vitrificate into nanostructures through a matrix-mediated collapse of the interior core. DMA and SANS measurements strongly suggest that the dendron is phase separated in the as-cast film, and serves as the macromolecular template for a porous lamellar morphology (XR and SAXS) at copolymer compositions above 35 % volume fraction. The bulky nature of the dendron may also affect their ability to pack efficiently into the traditional spherical micelles that can form from diblock copolymers in selective solvents. The formation of elongated micellar structures, or

“worm-like micelles”, would help relieve some of the packing constraints of the dendrons and may require less distortion of the molecules from their single-molecule conformation.^[11b,12c] This outcome, in turn, may explain the porous lamellar structure (4 nm) obtained between organosilicate sheets (6–9 nm) that persist over a wide temperature range. Moreover, the substrate surface SiO₂ causes the lamellar structure to orient in a parallel fashion over the entire substrate. Although inorganic hybrids with well-defined lamellar morphologies have been reported and are well characterized, this structure, although observed before,^[22] is largely unstable at calcination temperatures.^[8h,j,22,23]

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- [1] For example: a) R. H. Baney, M. Itoh, A. Sakakibara, T. Suzuki, *Chem. Rev.* **1995**, 95, 1409; b) D. Loy, K. J. Shea, *Chem. Rev.* **1995**, 95, 1431; c) D. Radu, C. Lai, J. Wiench, M. Pruski, V. S.-Y. Lin, *J. Am. Chem. Soc.* **2004**, 126, 1640; d) J. L. Hedrick, T. Magbitang, E. F. Connor, T. Glauser, W. Volksen, C. J. Hawker, V. Y. Lee, R. D. Miller, *Chem. Eur. J.* **2002**, 8, 3308; e) R. Hernandez, A. Tranvill, P. Minoofar, B. Dunn, J. I. Zink, *J. Am. Chem. Soc.* **2001**, 123, 1248; f) R. Hernandez, H. Tseng, J. W. Wong, J. F. Stoddart, J. I. Zink, *J. Am. Chem. Soc.* **2004**, 126, 3370; g) V. S.-Y. Lin, D. R. Radu, M.-K. Han, W. Deng, S. Kuroki, B. H. Shanks, M. Pruski, *J. Am. Chem. Soc.* **2002**, 124, 9040; h) V. S.-Y. Lin, C.-Y. Lai, J. Huang, S.-A. Song, S. Xu, *J. Am. Chem. Soc.* **2001**, 123, 11510; i) D. R. Radu, C.-Y. Lai, J. W. Wiench, M. Pruski, V. S.-Y. Lin, *J. Am. Chem. Soc.* **2004**, 126, 1640; j) S. H. Tolbert, A. Firouzi, G. D. Stucky, B. F. Chmelka, *Science* **1997**, 278, 264; k) M. Antonietti, B. Berton, C. Göltner, H.-P. Hentze, *Adv. Mater.* **1998**, 10, 154; l) E. Krämer, S. C. Förster, Göltner, M. Antonietti, *Langmuir* **1998**, 14, 2027; m) Q. R. Huang, H.-C. Kim, E. Huang, D. Mecerreyes, J. L. Hedrick, W. Volksen, C. W. Frank, R. D. Miller, *Macromolecules* **2003**, 36, 7661.
- [2] For example: a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, 359, 710; b) J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, et al., *J. Am. Chem. Soc.* **1992**, 114, 10834; c) Q. Huo, D. I. Margolese, P. Feng, T. E. Gier, G. D. Stucky, R. Leon, P. M. Petroff, U. Ciesla, F. Schüth, *Nature* **1994**, 368, 317; d) M. E. Davies, C. Saldarriaga, C. Montes, J. Garces, C. Crowder, *Nature* **1988**, 331, 698; e) Q. Huo, D. I. Margolese, U. Ciesla, D. P. Feng, T. E. Gier, P. Sieger, A. Firouzi, B. F. Chmelka, F. Schüth, G. D. Stucky, *Chem. Mater.* **1994**, 6, 1176; f) P. Yang, T. Deng, D. Zhao, P. Feng, D. Pine, B. F. Chmelka, G. M. Whitesides, G. D. Stucky, *Science* **1998**, 282, 2244–2246; g) Y. Chujo, H. Matsuk, S. Kure, T. Saegusa, T. Yazawa, *J. Chem. Soc. Chem. Commun.* **1994**, 635.
- [3] D. L. Gin, W. Gu, B. A. Pindzola, W.-W. Zhou, *Acc. Chem. Res.* **2001**, 34, 973.
- [4] Y. Zhou, J. H. Schattka, M. Antonietti, *Nano Lett.* **2004**, 4, 477.
- [5] B.-H. Han, S. Poarz, M. Antonietti, *Chem. Mater.* **2001**, 13, 3915.
- [6] A. Okabe, T. Fukushima, K. Ariga, T. Aida, *Angew. Chem.* **2002**, 114, 3564; *Angew. Chem. Int. Ed.* **2002**, 41, 3414.
- [7] M. Kimura, K. Wada, K. Ohta, K. Hanabusa, H. Shirai, N. Kobayashi, *J. Am. Chem. Soc.* **2001**, 123, 2438.
- [8] For example: a) M. Templin, A. Franck, A. Du Chesne, H. Leist, T. Ahang, R. Ulrich, V. Schädler, U. Wiesner, *Science* **1997**, 278, 1795; b) D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, 279, 548; c) E. F. Connor, L. K. Sundberg, H.-C. Kim, J. J. Cornelissen, T. Magbitang, P. M. Rice, V. Y. Lee, C. J. Hawker, W. Volksen, J. L. Hedrick, R. D. Miller, *Angew. Chem.* **2003**, 115, 3915; *Angew. Chem. Int. Ed.* **2003**, 42, 3785; d) Y. Y. Yuan, P. Hentze, W. M. Arnold, B. K. Marlow, M. Antonietti, *Nano Lett.* **2002**, 2, 1359; e) A. Jain, U. Wiesner, *Macromolecules* **2004**, 37, 5665; f) P. Simon, R. Ulrich, H. W. Spiess, U. Wiesner, *Chem. Mater.* **2001**, 13, 3464; g) T. Magbitang, V. Y. Lee, R. D. Miller, M. F. Toney, Z. Lin, R. M. Briber, H.-C. Kim, J. L. Hedrick, *Adv. Mater.* **2005**, 17, 1031; h) B. Smarsly, G. Komeritakis, K. Yu, N. Liu, H. Fan, R. A. Assink, C. A. Drewien, W. Ruland, C. J. Brinker, *Langmuir* **2003**, 19, 7295; i) K. Yu, A. Hurd, A. Eisenburg, C. J. Brinker, *Langmuir* **2001**, 17, 796; j) J. M. Kim, Y. Sakamoto, Y. K. Hwang, Y. U. Kwon, O. Terasaki, S. E. Park, G. D. Stucky, *J. Phys. Chem. B* **2002**, 106, 2552; k) J. N. Cha, G. D. Stucky, D. E. Morse, T. J. Deming, *Nature* **2000**, 403, 289; l) P. Yang, T. Deng, D. Zhao, P. Feng, D. Pine, B. F. Chmelka, G. M. Whitesides, G. D. Stucky, *Science* **1998**, 282, 2244; m) A. Sellinger, P. M. Weiss, A. Nguyen, Y. Lu, R. A. Assink, C. J. Brinker, *Nature* **1998**, 394, 256; n) Y. Lu, H. Fan, T. Ward, T. Reiker, C. J. Brinker, *Nature* **1999**, 398, 223.
- [9] For example: a) E. L. Thomas, *Polymer* **2003**, 44, 6725; b) E. W. Cochran, D. C. Morse, F. S. Bates, *Macromolecules* **2003**, 36, 782; c) Z. Q. Lin, D. H. Kim, X. D. Wu, L. Boosahda, D. Stone, L. LaRose, T. P. Russell, *Adv. Mater.* **2002**, 14, 1373.
- [10] For example: a) V. Percec, C. Ahn, G. Ungar, D. Yeardley, M. Moller, S. Sheiko, *Nature* **1998**, 391, 161; b) S. A. Prokhorova, S. S. Sheiko, C. A. Ahn, V. Percec, V. Moller, *Macromolecules* **1999**, 32, 2653; c) Z. Liu, W. S. Zhou, S. Z. D. Cheng, V. Percec, G. Ungar, *Chem. Mater.* **2002**, 14, 2384.
- [11] For example: a) I. Gitsov, J. M. J. Frechet, *J. Am. Chem. Soc.* **1996**, 118, 3785; b) J. C. M. Van Hest, W. M. P. L. Bars, M. H. P. van Genderen, W. W. Meijer, *Science* **1995**, 268, 1592; c) A. Heise, J. L. Hedrick, C. W. Frank, R. D. Miller, *J. Am. Chem. Soc.* **1999**, 121, 8647; d) Q. Ma, E. E. Remsen, T. Kowalewski, K. L. Wooley, *J. Am. Chem. Soc.* **2001**, 123, 4627; e) Q. Zhang, E. E. Remsen, K. L. Wooley, *J. Am. Chem. Soc.* **2000**, 122, 3642; f) J. Pyun, X. Zhou, E. Drockenmuller, C. J. Hawker, *J. Mater. Chem.* **2003**, 13, 2653; g) L.-S. Li, S. I. Stupp, *Angew. Chem.* **2005**, 117, 1867; *Angew. Chem. Int. Ed.* **2005**, 44, 1833; h) F. J. Solis, S. I. Stupp, M. O. de la Cruz, *J. Chem. Phys.* **2005**, 122, 054905; i) H. T. Jung, S. O. Kim, S. D. Hudson, V. Percec, *Appl. Phys. Lett.* **2002**, 80, 395; j) V. Percec, A. E. Dulcey, V. S. K. Balagurusamy, Y. Miura, J. Smidrkal, M. Peterca, S. Nummelin, U. Edlund, S. D. Hudson, P. A. Heiney, H. Duan, S. N. Magonov, S. A. Vinogradov, *Nature* **2004**, 430, 764; k) S. Liu, S. P. Armes, *J. Am. Chem. Soc.* **2001**, 123, 9910; l) I. Gitsov, J. M. J. Frechet, *J. Am. Chem. Soc.* **1996**, 118, 3785; m) M. A. Johnson, C. M. B. Santini, J. Iyer, S. Satija, R. Ivkov, P. T. Hammond, *Macromolecules* **2002**, 35, 231; n) M. E. Mackay, Y. Hong, M. Jeong, B. M. Tande, N. J. Wagner, S. Hong, S. P. Gido, R. Vestberg, C. J. Hawker, *Macromolecules* **2002**, 35, 8391.
- [12] a) J. P. Kampf, C. W. Frank, E. E. Malmstrom, C. J. Hawker, *Science* **1999**, 283, 1730; b) J. P. Kampf, C. W. Frank, E. E. Malmstrom, C. J. Hawke, *Langmuir* **1999**, 15, 227; c) A. Wursch, M. Moller, T. Gluser, L. S. Lim, S. B. Voytek, J. L. Hedrick, C. Frank, J. G. Hilborn, *Macromolecules* **2001**, 34, 6601; d) V. Percec, B. Barboiu, C. Grigoras, T. K. Bera, *J. Am. Chem. Soc.* **2003**, 125, 6503; e) T. Glauser, C. M. Stancik, M. Moller, S. Voytek, A. P. Gast, J. L. Hedrick, *Macromolecules* **2002**, 35, 5774.
- [13] B. K. Cho, A. Jain, S. M. Mahajan, H. Ow, S. M. Gruner, U. Wiesner, *J. Am. Chem. Soc.* **2004**, 126, 4070.
- [14] For example: a) A. W. Bosman, H. M. Jansen, E. W. Meijer, *Chem. Rev.* **1999**, 99, 1665; b) S. Hecht, J. M. J. Fréchet, *Angew.*

- Chem.* **2001**, *113*, 76; *Angew. Chem. Int. Ed.* **2001**, *40*, 74; c) D. A. Tomalia, D. H. Dupont, *Top. Curr. Chem.* **1993**, *165*, 193; d) C. Gorman, *Adv. Mater.* **1998**, *10*, 295; e) M. Fischer, F. Vögtle, *Angew. Chem.* **1999**, *111*, 934; *Angew. Chem. Int. Ed.* **1999**, *38*, 885; f) H. Frey, *Angew. Chem.* **1998**, *110*, 2313; *Angew. Chem. Int. Ed.* **1998**, *37*, 2193; g) S. G. Grayson, J. M. J. Fréchet, *Chem. Rev.* **2001**, *101*, 3819; h) C. J. Hawker, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1990**, *112*, 7368; i) E. M. Meijer, E. M. M. de Brabender-van den Berg, *Angew. Chem.* **1993**, *105*, 1370; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1308; j) S. Vetter, S. Koch, A. D. Schluter, *J. Polym. Sci. Part A* **2001**, *39*, 1940; k) R. Gronheid, J. Hofkens, F. Köhn, T. Weil, E. Reuther, K. Müllen, F. C. De Schryver, *J. Am. Chem. Soc.* **2002**, *124*, 2418.
- [15] a) H. Ihre, O. L. Padilla De Jesu, J. M. J. Frechet, *J. Am. Chem. Soc.* **2001**, *123*, 5908; b) H. Ihre, A. Hult, E. Soderlind, *J. Am. Chem. Soc.* **1996**, *118*, 6388; c) E. Malmstrom, M. Johansson, A. Hult, *Macromolecules* **1995**, *28*, 1698; d) M. Malkoch, E. Malmstrom, A. Hult, *Macromolecules* **2002**, *35*, 8307.
- [16] a) J. L. Hedrick, R. D. Miller, C. J. Hawker, K. R. Carter, W. Volksen, D. Yoon, M. Trollsås, *Adv. Mater.* **1998**, *10*, 1049; b) C. Nguyen, K. R. Carter, C. J. Hawker, J. L. Hedrick, R. Jaffy, R. D. Miller, J. Remenar, H. Rhee, P. Rice, M. Toney, D. Yoon, *Chem. Mater.* **1999**, *11*, 3080; c) C. Nguyen, C. J. Hawker, R. Miller, J. L. Hedrick, J. G. Hilborn, *Macromolecules* **2000**, *33*, 4281.
- [17] a) E. Malmstrom, M. Johansson, A. Hult, *Macromolecules* **1995**, *28*, 137; b) E. Malmstrom, M. Johansson, A. Hult, *Macromol. Chem. Phys.* **1996**, *197*, 3199; c) M. Trollsås, J. L. Hedrick, *J. Am. Chem. Soc.* **1998**, *120*, 4644; d) M. Trollsås, B. Atthoff, H. Claesson, J. L. Hedrick, *Macromolecules* **1998**, *31*, 3439.
- [18] H. Ihre, O. L. Padilla De Jesus, J. M. J. Frechet, *J. Am. Chem. Soc.* **2001**, *123*, 5908.
- [19] a) J. S. Moore, S. I. Stupp, *Macromolecules* **1990**, *23*, 65; b) H. Ihre, A. Hult, E. Soderlind, *J. Am. Chem. Soc.* **1996**, *118*, 6388; c) E. Malmstrom, M. Johansson, A. Hult, *Macromolecules* **1995**, *28*, 1698.
- [20] H. R. Ihre, O. L. P. De Jesus, F. C. Szoka, J. M. J. Frechet, *Bioconjugate Chem.* **2002**, *13*, 443.
- [21] B.-K. Cho, A. Jain, S. M. Gruner, U. Wiesner, *Science* **2004**, *305*, 1598.
- [22] For example: a) J. M. Kim, Y. Sakamoto, Y. K. Hwang, Y. Kwon, O. Terasaki, S.-E. Park, G. D. Stucky, *J. Phys. Chem. B* **2002**, *106*, 2552; b) S. H. Tolbert, C. C. Landry, G. D. Stucky, B. F. Chemlka, P. Norby, J. Hanson, A. Monnier, *Chem. Mater.* **2001**, *13*, 2247; c) K. Yu, A. J. Hurd, A. Eisenberg, C. J. Brinker, *Langmuir* **2001**, *17*, 7961.
- [23] The experimental procedures used and the SEC, DMA, and SANS characterization of the copolymers are given in the Supporting Information.