

Nanohybrids from Liquid Crystalline Extended Amphiphilic Dendrimers

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For the past decade, nanostructured organic–inorganic hybrid materials (nanohybrids) and porous solids have been studied extensively. In particular, small-molecule surfactants¹ and linear block copolymers² have been widely used as structure-directing agents for silica-type materials. More recently, the range of organic structure-directing agents has been extended to other molecular architectures to realize advanced functionalities. For example, Aida et al. used charge-transfer complexes based on an amphiphilic triphenylene electron donor as structure-directing agents.³ They tuned the color of organic–inorganic nanohybrids depending on the electron acceptor. In another example, Kimura et al. used a disc-shaped phthalocyanine-based amphiphile.⁴ They prepared a hexagonally arrayed cylindrical nanohybrid material through sol–gel polymerization of inorganic precursors. In addition, they employed a polymeric phthalocyanine which organized into potentially conductive one-dimensional molecular cables.⁵

We have created a variety of nanoparticles and mesoporous materials ranging from spheres, cylinders, and lamellae to mesoporous hexagonal and bicontinuous cubic structures by using polyisoprene-*b*-poly(ethylene oxide) copolymers (PI-*b*-PEO) as structure-directing agents for organically modified ceramic precursors in organic solvents.⁶ We have demonstrated that a simple “one-pot” self-assembly approach allows these nanostructures to be functionalized with other transition-metal oxides such as γ -Fe₂O₃, leading to magnetic properties and potential applications in the life sciences.⁷ Besides changing the inorganic constituents, it is now interesting to explore the wide variety of polymer architectures to design novel structure-directing agents. In particular, to the best of our knowledge, dendrimer-type macromolecules have not been used to direct silica-type materials despite their fascinating structural features.⁸

Herein, we report a novel extended amphiphilic dendrimer as a structure-directing agent for silica-type materials (see Figure 1). From a structural point of view, the hydrophilic fraction consists of linear PEO attached to a PEO-like dendritic core, while the hydrophobic fraction is composed of eight docosyl branches.^{9,10} The interface of a phase-segregated bulk phase of this compound runs through the middle of the dendrimer part of the molecule and is expected to have an inherent curvature, which is unique compared to the aforementioned conventional linear amphiphiles (see below). The synthesis is accomplished through an efficient esterification reaction of carboxylic acid terminated PEO with the dendrimer hydroxyl group.¹¹ The molecular weight of the final compound as determined from mass spectrometry is 6000 g/mol, and the volume fraction of the hydrophilic block (f_{vol}) is 0.53. Polydispersities (M_w/M_n) obtained from both gel-permeation chromatography and mass spectrometry are less than 1.05 (for synthesis see also Supporting Information).

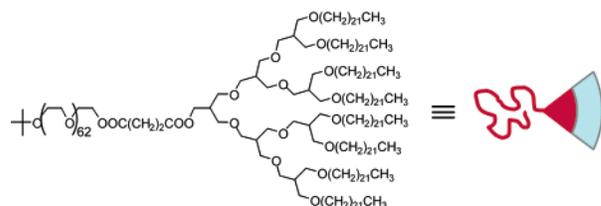


Figure 1. Molecular architecture of extended amphiphilic dendrimer.

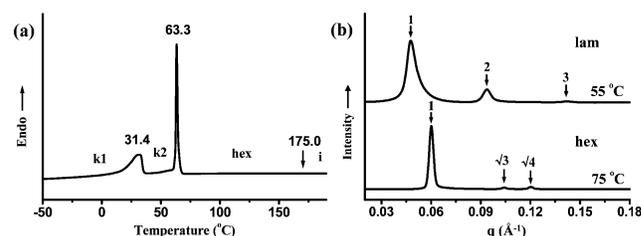


Figure 2. (a) DSC thermograph of the present extended amphiphilic dendrimer obtained upon heating. (b) SAXS patterns of extended amphiphilic dendrimer at 55 °C and 75 °C. k: crystal; hex: hexagonal columnar; i: isotropic liquid; lam: lamellae.

The extended amphiphilic dendrimer shows multiple phase transitions in the bulk. Two endothermic peaks at 31.4 and 63.3 °C in the differential scanning calorimetry (DSC) thermograph in Figure 2a correspond to the melting transitions of PEO and docosyl chains, respectively. After melting, a liquid crystalline phase (mesophase) appears, which in turn undergoes isotropization at 175.0 °C, as evidenced by temperature-dependent small-angle X-ray scattering (SAXS, data not shown). A SAXS pattern in the crystalline phase shows three reflections with q -spacing ratios of 1:2:3, consistent with a lamellar structure with a periodicity of 13.1 nm (Figure 2b, top). The SAXS pattern in the liquid crystalline phase (Figure 2b, bottom) shows three reflections with q -spacing ratios of 1: $\sqrt{3}$: $\sqrt{4}$, consistent with a hexagonal columnar structure with a lattice parameter $a = 12.1$ nm. As a result of the inherent molecular curvature, the cylinder core is expected to be occupied by the hydrophilic majority fraction, whereas the matrix should consist of the hydrophobic minority fraction; see illustration in Figure 3.

Sol–gel polymerizations of (3-glycidyoxypropyl) trimethoxy silane and aluminum *sec*-butoxide in the presence of the extended amphiphilic dendrimer were carried out using a procedure described previously.⁶ Volatiles were evaporated at 63 °C for the sol–gel condensation to take place in the liquid crystalline phase and to suppress the docosyl chain crystallization. We first discuss a nanohybrid **1** with 0.44 aluminosilicate weight fraction (f_w). Its microstructure was identified by employing a combination of SAXS, transmission electron microscopy (TEM), and atomic force microscopy (AFM). The SAXS pattern of bulk hybrid **1** shows two reflections with q -spacing ratios of 1:2 (Figure 3a, $d_{(100)} = 11.3$

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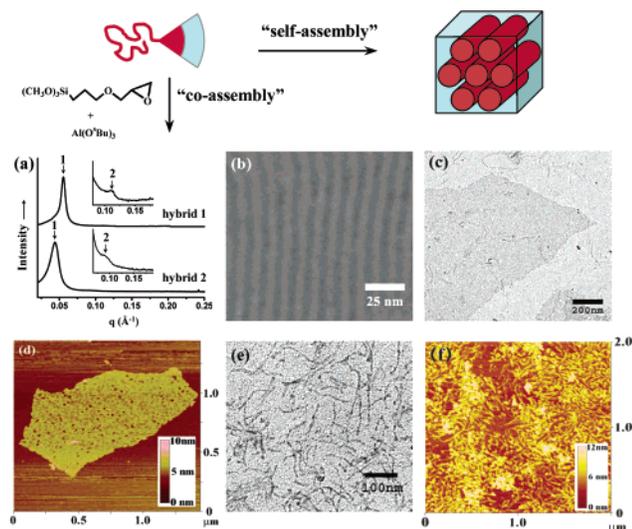


Figure 3. Top: schematic illustration of hybrid synthesis. Bottom: analysis of hybrids **1** (a–d) and **2** (a,e,f). (a) Bulk SAXS patterns at 25 °C. (b) TEM image of bulk sample. (c,e) TEM images of solution cast nanoparticles. (d,f) AFM images of calcined nanoparticles (lamellar thickness $d \approx 4$ nm).

nm). For further analysis, the bulk hybrid was microtomed in 50-nm thin sections and examined using TEM. Figure 3b shows a bright field image revealing periodic organic (bright regions) and inorganic (dark regions) layers. With about 10 nm, the lamellar spacing from TEM is smaller than predicted from SAXS, which can be attributed to convex bending of liquidlike lamellar surface as described in ref 2b. The lamellar structure was corroborated by studies of the morphology of individual nanoparticles obtained from dissolution of the bulk material. For imaging individually dispersed nanoparticles, a solution of hybrid **1** (5 mg of hybrid in 10 g of toluene) was ultrasonicated and cast (i) on a carbon-coated copper grid for TEM and (ii) on a mica sheet and calcined at 400 °C for AFM. TEM and AFM images are shown in Figure 3c,d, respectively, clearly exhibiting platelike nanosheets. These results suggest that nanohybrids with various architectures may be induced by simply adding different amounts of inorganic precursors to the same extended dendrimer amphiphile. It should be emphasized that the reduction in lamellar spacing upon addition of inorganic (compare Figures 2b and 3a) can only be explained by a fundamental change in the molecular packing. Studies to elucidate these effects in detail are currently under way.

By loading a smaller amount of the ceramic precursors, a second hybrid **2** with $f_w = 0.21$ was prepared. The SAXS pattern of bulk hybrid **2** shows two reflections consistent with q -spacing ratios of 1:2 (Figure 3a, $d_{(100)} = 14.3$ nm).¹² To elucidate the hybrid morphology, Figure 3e shows a TEM image of isolated nanoparticles obtained through dissolution of bulk hybrid material **2**. The nanoparticles exhibit cylinder morphology corroborated through AFM studies (Figure 3f). This suggests that in contrast to hybrid **1**, the lower amount of inorganic does not suffice to induce a morphological transition away from the cylindrical structure of the parent amphiphile. It also corroborates the earlier assignment that although majority fraction ($f_{vol} = 0.53$), the hydrophilic block of the extended amphiphilic dendrimer occupies the core cylinder domain of the hexagonal structure. From all these results, the self- and co-assembly phase behavior of the present extended dendrimer is quite different from that of conventional block copolymers with linear architecture, consistent with recent theoretical predictions.¹³

In conclusion, we have prepared a liquid crystalline extended amphiphilic dendrimer and aluminosilicate-based nanostructured hybrids with lamellar and cylindrical morphologies from it. To the best of our knowledge, our results are the first successful examples of the use of dendrimer-based amphiphiles as structure-directing agents for silica-type nanostructures. The versatility of the dendrimer architecture now allows various functionalities to be introduced in the nanohybrids. Thus, the present extended amphiphilic dendrimer architecture may provide an exciting novel materials platform for formation of multifunctional nanostructured hybrid materials.

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Supporting Information Available: Experimental details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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