

# Nanostructured Semiconductors Templated by Cholesteryl-Oligo(Ethylene Oxide) Amphiphiles

Bryan M. Rabatic,<sup>†</sup> Martin U. Pralle,<sup>§</sup> Gregory N. Tew,<sup>||</sup> and Samuel I. Stupp<sup>\*,†,‡</sup>

Department of Chemistry, Department of Materials Science and Engineering and Feinberg School of Medicine, Northwestern University, Evanston, Illinois 60208, Ion Optics, Inc., Waltham, Massachusetts 02154, and Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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Lyotropic liquid crystals formed by cholesteryl oligo(ethylene oxide) amphiphiles were used to template the II–VI semiconductor cadmium sulfide. The amphiphiles were synthesized with average chain lengths ranging from 5 to 30 repeats of ethylene oxide and characterized by polarized optical microscopy, differential scanning calorimetry, small-angle X-ray scattering, and mass spectrometry. By varying the ratio of hydrophile coil length to hydrophobe rod length, a transition from lamellar to hexagonal mesophases occurs when the average number of ethylene oxide repeats exceeds 17 units. Inorganic semiconductor templating with these cholesterol-based amphiphiles yields CdS particles with either lamellar or hexagonal nanostructuring. The morphology of the lamellar particles is oblong with lengths of up to 400 nm and widths of 150 nm, whereas that of the hexagonal particles is typically spherical with diameters averaging 200 nm. The nanostructure of the particles consists of either periodic lamellar or hexagonal arranged pores with dimensions similar to those of the organic template.

## Introduction

The synthesis of nanostructured materials is an important goal in chemistry, as they are likely to offer novel properties. The preparation of nanoscale materials has included many methodologies including lithographic techniques, supramolecular self-assembly, colloidal crystallization, nanophase separation, and surfactant mineralization.<sup>1–8</sup> Using liquid crystals (LC) as templates has provided a means for the synthesis of a variety of mesoporous materials such as silicate/aluminosilicate molecular sieves, silica nanotubes, zirconium oxo phosphates, and ZnS nanowires.<sup>9–12</sup> Direct liquid crystalline

templating, developed in our laboratory, has advanced the techniques for the synthesis of “hard” inorganic minerals that directly reproduce dimensions and symmetry of the “soft” mesophase serving as the template. By directly copying the mesophase, structural characteristics of the inorganic material can be tailored and designed by changing the molecular structure of the liquid crystalline template.

A variety of scientifically important and technologically significant accomplishments potentially can be achieved through the use of LC-templated hybrid organic–inorganic materials. For instance, catalysts with improved photocatalytic efficiency, quantum devices such as nanoscale wires, and molecular filters are all potential applications that are possible with materials that possess nanoscale ordering. Another important direction is to template mesoscopic hybrid systems that can be interfaced with biological systems. In one strategy, the organic material could be exposed outside an inorganic substrate and provide an interface with a biological system. An example of this would be biocompatible amphiphiles that template inert inorganic phases. The inorganic phase would be chosen for its physical properties (i.e., small band-gap energy) and the organic material could be used for probing biological states. Biomineralization is another approach where the templated inorganic product could be an interface or a mimic of biological structure.<sup>13–17</sup>

\* To whom correspondence should be addressed via E-mail: s-stupp@northwestern.edu.

<sup>†</sup> Department of Chemistry, Northwestern University.

<sup>‡</sup> Department of Materials Science and Engineering and Feinberg School of Medicine, Northwestern University.

<sup>§</sup> Ion Optics, Inc.

<sup>||</sup> University of Massachusetts.

(1) Murray, C. B.; Kagan, C. R.; Bawendi, M. G. *Science* **1995**, *270*, 1335.

(2) Piner, R. D.; Zhu, J.; Xu, F.; H., H. S.; Mirkin, C. A. *Science* **1999**, *283*, 661.

(3) Park, M.; Harrison, C.; Chaikin, P.; Register, R.; Adamson, D. *Science* **1997**, *276*, 1401.

(4) Stupp, S.; Bruan, P. *Science* **1997**, *277*, 1242.

(5) Zaho, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548.

(6) Chen, W.; Wunderlich, B. *Macromol. Chem. Phys.* **1999**, *200*, 283.

(7) Lehn, J. *Supramolecular Chemistry*; VCH: New York, 1995.

(8) Stupp, S.; LeBonheur, V.; Walker, K.; Li, L.; Huggins, K.; Keser, M.; Amstutz, A. *Science* **1997**, *276*, 384.

(9) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(10) Ciesla, U.; Froba, M.; Stucky, G.; Schuth, F. *Chem. Mater.* **1999**, *11*, 227.

(11) Adachi, M.; Harada, T.; Harada, M. *Langmuir* **2000**, *16*, 2376.

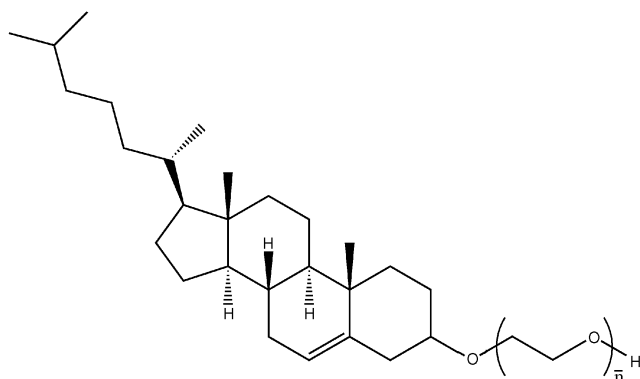
(12) Jiang, X.; Xie, Y.; Lu, J.; Zhu, L.; He, W.; Qian, Y. *Chem. Mater.* **2001**, *13*, 1213.

(13) Weiner, S.; Addadi, L. *J. Mater. Chem.* **1997**, *7*, 689.

(14) Weiner, S.; Wagner, H. D. *Annu. Rev. Mater. Sci.* **1998**, *28*, 271.

We reported earlier the synthesis of nanostructured hexagonal and lamellar group II–VI inorganic materials by direct templating.<sup>4,18–20</sup> Utilizing well-defined hexagonal or layered ordering liquid crystalline templates, cadmium sulfide and cadmium selenide with templated superlattices have been prepared. These semiconducting superlattices are considered to be directly templated from the mesophase because the morphology of the particles is commensurate with the structural characteristics and dimensions of the ordered organic gel. The typical procedure for the synthesis of these templated materials involves the formation of a self-supporting gel of the amphiphilic LC with an aqueous solution of inorganic precursors. These ionic precursors remain in the hydrophilic segments of the amphiphile. Once gelation has occurred, the mesophase is exposed to a gaseous reactive environment and mineralization occurs. The product of this precipitation is a direct mineralized copy of the ordered organic medium.

We report here on cadmium sulfide templating using an amphiphile containing a biological structural unit and biocompatible units, cholesteryl-oligo(ethylene oxide).<sup>21–23</sup> The triethoxycholesterol amphiphile was first reported by Baldeschwieler et al. and later modified to tetraethoxycholesterol semisuccinate for investigation of supramolecular structure, shape anisotropy, and mesogenic structure.<sup>24,25</sup>



In analogy to previous direct templating systems, growth of the semiconductor is expected to copy the symmetry and dimensions of the LC by occurring only in the hydrophilic regions of the hydrated amphiphile. The hydrophobic sections would act as a barrier that confines the inorganic crystallites within the hydrophilic segments of the liquid crystalline phase. The resultant product would be a superlattice structure in which the

mineralized CdS material would be a representation of the bio-organic template.

## Experimental Section

All chemicals and solvents were purchased from Aldrich. Cholesterol and naphthalene were further purified by recrystallization ( $\times 2$ ) in ethanol and ethyl acetate, respectively. Cadmium nitrate tetrahydrate [ $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ] (99.999% pure) was used as received. Gaseous ethylene oxide (EO) was condensed by cooling with liquid nitrogen in an inert environment and stored at  $-10^\circ\text{C}$ . Column chromatography was performed with 230–400 mesh size silica gel (EM Scientific).

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry was performed on a Perspectives Biosystems Voyager Pro. Thermal transitions were measured on a TA Instruments differential scanning calorimeter (DSC). Variable-temperature polarized optical microscopy was performed on a Leitz Laborlux 12 POL microscope at  $100\times$  magnification using a Linkam hot stage on glass microscope slide cover slips. Small-angle X-ray scattering (SAXS) was primarily measured on a Regaku RU-200 diffractometer with a Bruker AXS area detector. SAXS was also performed on samples at the Synchrotron Research Center located at the Argonne National Laboratory Advanced Photon Source using an X-ray energy of 9.7 keV and a Mar 135 CCD area detector. Morphologies of the inorganic particles were investigated on a Hitachi 8100 transmission electron microscope (TEM) operating at an accelerating voltage of 200 kV. Microscopy samples were observed on copper TEM grids coated with amorphous holey carbon (SPI and Quantifoil). Scanning electron microscopy was performed on a Hitachi 4500 operating at 20 kV. Elemental microanalysis was provided by Atlantic Microlab Inc. (Norcross, GA).

The synthetic procedure outlined below was adapted from Hillmyer and Bates.<sup>26</sup> Potassium naphthalide was prepared by mixing equimolar (0.4 M) quantities of potassium metal and naphthalene in anhydrous THF (186 mL, 2.06 mol) under nitrogen for 24 h. The solution was stored at  $10^\circ\text{C}$  under nitrogen when not in use.

Into a dry 250-mL Airfree sidearm round-bottom flask were added 60 mL (0.66 mol) THF and 1.2 g (3.10 mmol) cholesterol under a nitrogen environment. Via syringe, the potassium naphthalide solution was added until the reaction mixture maintained a pale green color for approximately 5 min (ca. 40 mL). Condensed ethylene oxide was cannulated into a jacketed pressure-equilibrating addition funnel cooled with a dry ice/acetone mixture. Oligomer chain length was controlled by adjusting the amount of EO (0.5–5.0 mL; 0.01–0.10 mol) that was added to the cholesterol alkoxide. By lowering the amount of ethylene oxide, shorter chain lengths resulted, whereas longer chain lengths were obtained by adding more monomer. For example, the synthesis of chol-EO<sub>5</sub> was performed by adding 0.01 mol EO to 3.1 mmol cholesterol. After addition of condensed EO, the reaction vessel was then sealed and placed in a  $40^\circ\text{C}$  bath for 24 h. Reaction termination was accomplished by adding 6 M HCl until solution pH fell below 2. The potassium chloride precipitate was vacuum filtered and the pale yellow solution was concentrated on a rotary evaporator. The product was column chromatographed with a 10% methanol/methylene chloride eluting solvent and stored under vacuum.

**Preparation of CdS Particles.** A 0.1 M aqueous cadmium nitrate solution was prepared with deionized water. A 50 wt % gel was prepared by adding 100 mg of the 0.1 M cadmium nitrate solution to 100 mg of the viscous organic amphiphile and sealed in a 1-dram borosilicate glass vial. The mixture was shaken while heated beyond the isotropization temperature ( $T_i$ ) of the liquid crystal and then allowed to cool to room temperature. Typically, within 24 h gelation had occurred and the vial was opened and placed into a  $\text{H}_2\text{S}$  environment. Once the entire gel was yellow, the sample was removed from the

(15) Cha, J. N.; Stucky, G. D.; Morse, D. E.; Deming, T. J. *Nature* **2000**, *403*, 289.

(16) Yada, M.; Kitamura, H.; Machida, M.; Kijima, T. *Langmuir* **1997**, *13*, 5252.

(17) Hwang, J.; Jaeger, K.; Hancock, J.; Stupp, S. J. *Biomed. Mater. Res.* **1999**, *47*, 504.

(18) Braun, P.; Osenar, P.; Stupp, S. *Nature* **1996**, *380*, 325.

(19) Osenar, P.; Braun, P.; Stupp, S. *Adv. Mater.* **1996**, *8*, 1022.

(20) Tohver, V.; Braun, P. V.; Pralle, M. U.; Stupp, S. I. *Chem. Mater.* **1997**, *9*, 1495.

(21) Campbell, N. A. *Biology*, 4th ed.; Benjamin/Cummings: Menlo Park, NJ, 1996.

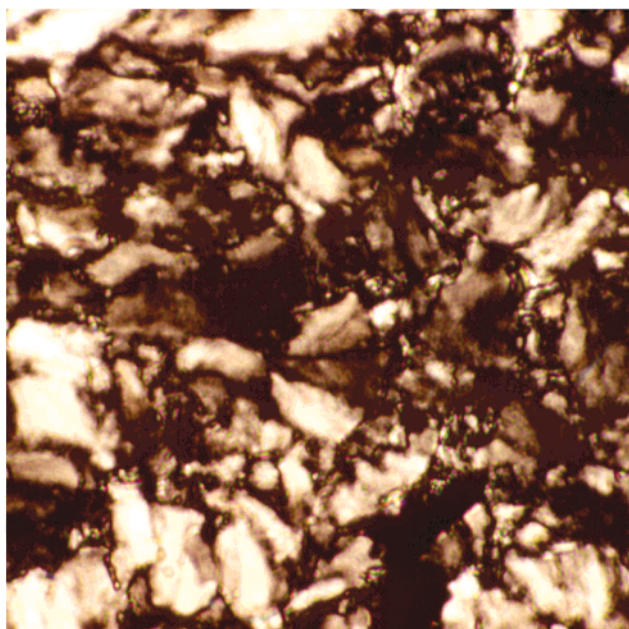
(22) Han, D. K.; Hubbell, J. A. *Macromolecules* **1997**, *30*, 6077.

(23) Thom, V. H.; Altankov, G.; Groth, T.; Jankova, K.; Jonsson, G.; Ulbricht, M. *Langmuir* **2000**, *16*, 2756.

(24) Decher, G.; Ringsdorf, H. *Liq. Cryst.* **1993**, *13*, 57.

(25) Patel, K. R.; Li, M. P.; Schuh, J. R.; Baldeschwieler, J. D. *Biochim. Biophys. Acta* **1984**, *797*, 20.

(26) Hillmyer, M. A.; Bates, F. S. *Macromolecules* **1996**, *29*, 6994.



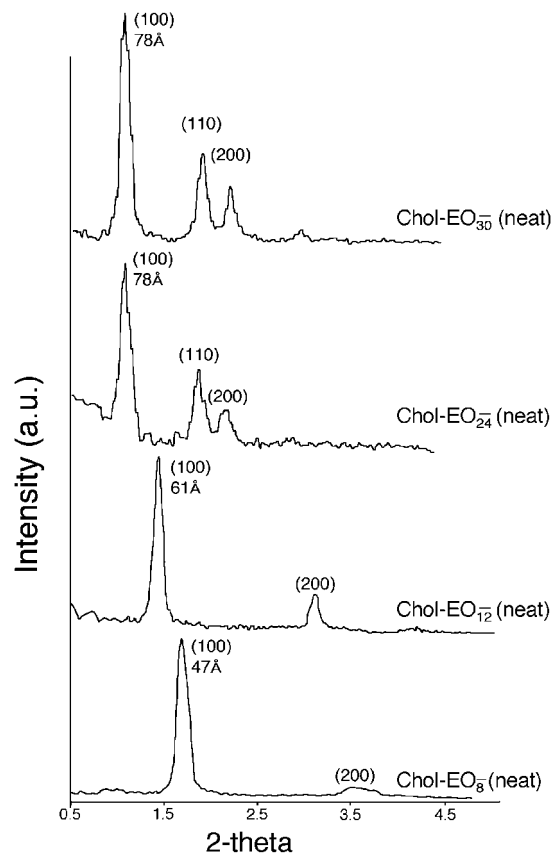
**Figure 1.** Polarized optical micrograph of the birefringent texture of cholesteryl-(ethylene oxide)<sub>12</sub>.

reaction chamber and repeatedly washed and centrifuged ( $\times 3$ ) with a 50:50 vol % solution of diethyl ether and ethanol. A dilute suspension of the sample in either absolute ethanol or the ethanol/ether solution was then dropped onto a holey carbon copper grid for observation with TEM.

## Results and Discussion

### Cholesteryl-Oligo(Ethylene Oxide) Amphiphiles.

Amphiphiles were synthesized with variable amounts of ethylene oxide to form a range of hydrophilic coil lengths. Molecules of cholesteryl-oligo(ethylene oxide) (chol-EO<sub>*n*</sub>), were synthesized with average EO lengths of 5, 8, 10, 12, 14, 15, 17, 20, 24, and 30 repeats. MALDI-TOF mass spectrometry was used to determine the degree of polymerization ( $\bar{n}$ ) for each amphiphile from the number-average molecular weight. Typical polydispersity indices of these materials ranged between 1.04 and 1.10. Attempts at controlling the lengths of the oligomers were made by varying the amount of condensed ethylene oxide as well as the time of polymerization. It was found that the most consistent results were achieved when the amount of polymerizing monomer was varied and time of polymerization was 24 h. Changing the reaction time introduced greater variability in the average length of poly(ethylene oxide) segments. In the neat state, all molecules of chol-EO<sub>*n*</sub> were found to exhibit birefringence (Figure 1). Small-angle X-ray scattering shows that chol-EO<sub>*n*</sub> packs in one of two symmetries depending on the length of the EO coil. A transition from lamellar to hexagonal ordering is observed when the average oligomer length exceeds 17 repeat units. Kunieda et al. have shown that other nonionic polyoxyethylene-type surfactants undergo a phase change from lamellar to hexagonal ordering as EO chain lengths increase.<sup>27</sup> Up to the lamellar to hexagonal transition point ( $n = 17$ ), the characteristic *d*-spacing of the amphiphiles generally



**Figure 2.** Small-angle X-ray scattering of neat cholesteryl-oligo(ethylene oxide) amphiphiles.

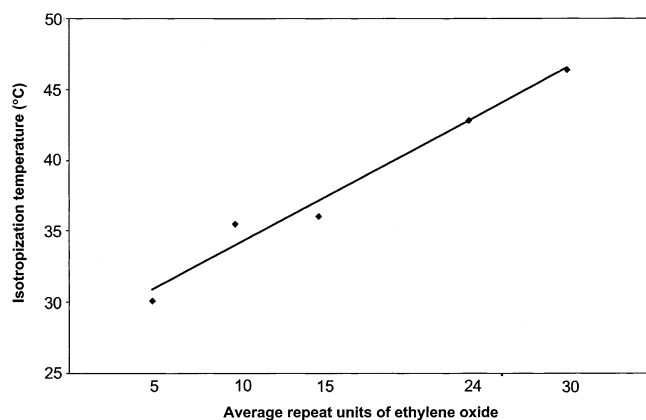
increases with length of coil. The (100) reflection of chol-EO<sub>5</sub> was found to be 47 Å whereas that of chol-EO<sub>15</sub> is 63 Å. However, at the transition length chol-EO<sub>17</sub> was repeatedly found to have a (100) *d*-spacing of 58 Å. This contraction of *d*-spacing could be attributed to the amphiphile being at the transition length of a phase change. Figure 2 shows SAXS patterns of the neat amphiphile revealing lamellar and hexagonal ordering. These neat materials possess phases similar to those of other polyalkane-poly(ethylene oxide) diblock copolymers reported by Hillmyer and Bates.<sup>28,29</sup> Tables 1 and 2 compile data obtained by SAXS for the chol-EO<sub>*n*</sub> amphiphiles discussed in this study. The temperature at which the nonhydrated material loses net anisotropy, the isotropization temperature ( $T_i$ ), was measured and found to be dependent upon the length of the hydrophilic coil. Both the lamellar and hexagonal neat state materials display increased thermal stability (i.e., increasing  $T_i$ ) as the coil becomes longer. As shown in Figure 3, differential scanning calorimetry confirms the general increase in  $T_i$  of the LC as the average length of EO coils increases. Only one thermal transition was observed in the scan range ( $-50$ – $150$  °C) of these amphiphilic materials, indicating that these materials do not have a crystallized component.

In forming a 50 wt % Cd<sup>2+</sup> gel, optical microscopy between crossed polars shows that birefringence of the LC is preserved. It was expected that the *d*-spacing of the material would increase due to water entering and

(27) Kunieda, H.; Umizu, G.; Yamaguchi, Y. *J. Colloid. Interface Sci.* **1999**, *218*, 88.

(28) Hillmyer, M. A.; Bates, F. S. *Macromol. Symp.* **1997**, *117*, 121.  
(29) Hillmyer, M. A.; Bates, F. S.; Almdal, K.; Mortensen, K.; Ryan, A.; Fairclough, P. *Science* **1996**, *271*, 976.





**Figure 3.** Differential scanning calorimetry data showing the dependence of cholesteryl-oligo(ethylene oxide) isotropization temperature on the length of ethylene oxide chain where  $R^2 = 0.9751$ .

**Table 1. Small-Angle X-ray Scattering of Neat Cholesteryl-Oligo(Ethylene Oxide) Amphiphiles**

Neat Lamellar Cholesteryl-EO $_n$			
average number of EO units	$d$ -spacings		
	(001) Å	(002) Å	
5	34		
8	47	23.6	
10	57.8	28.8	
12	61.7	28.7	
14	60	30.0	
15	63	30.9	
17	58	29.4	

Neat Hexagonal Cholesteryl-EO $_n$			
average number of EO units	$d$ -spacings		
	(001) Å	(010) Å	(002) Å
20	84.4	50.1	43.3
24	78.8	45.5	39.0
30	78.8	45.5	39.0

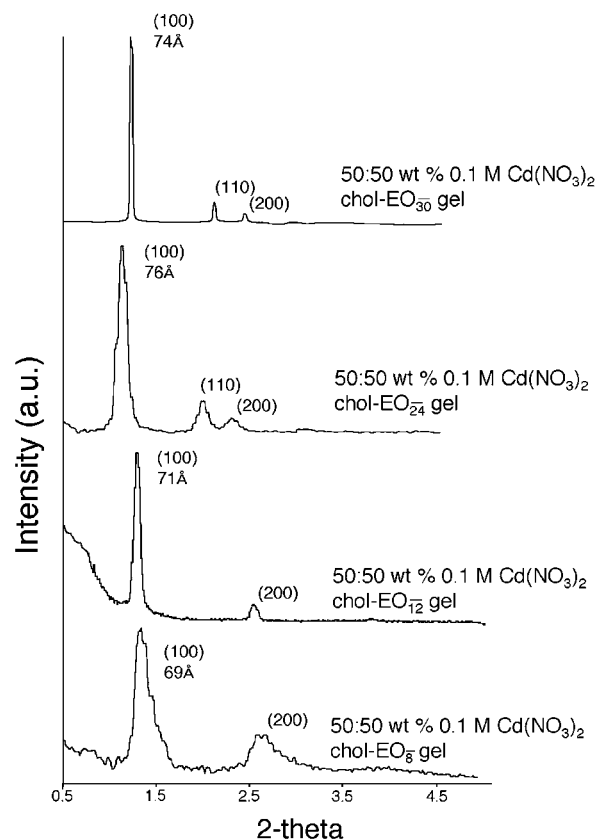
**Table 2. Small Angle X-ray Scattering of Cadmium Nitrate Gels of Cholesteryl-Oligo(Ethylene Oxide) Amphiphiles**

50:50 Wt. % 0.1 M Cd $^{2+}$ Gel of Lamellar Cholesteryl-EO $_n$			
average number of EO units	$d$ -spacings		
	(001) Å	(002) Å	
8	67.9	33.9	
10	76.4	38.8	
12	70.5	35.2	
14	82.5	41.0	
15	81.0	43.7	
17	78.0	39.4	

50:50 Wt. % 0.1 M Cd $^{2+}$ gel of Hexagonal Cholesteryl-EO $_n$			
average number of EO units	$d$ -spacings		
	(001) Å	(010) Å	(002) Å
20	78.0	45.5	39.0
24	76.0	44.0	38.3
30	73.8	42.5	36.8

swelling the hydrophilic regions. However, this trend is evident only in amphiphiles that exhibit lamellar ordering. When compared to the neat state, the lamellar chol-EO $_n$  liquid crystals swell to larger  $d$ -spacings as the aqueous cadmium solution is added. Additionally, the  $d$ -spacing of the gelled lamellar material increases with the average length of EO segments, with the exception of chol-EO $_{17}$  (discussed above). When the LC

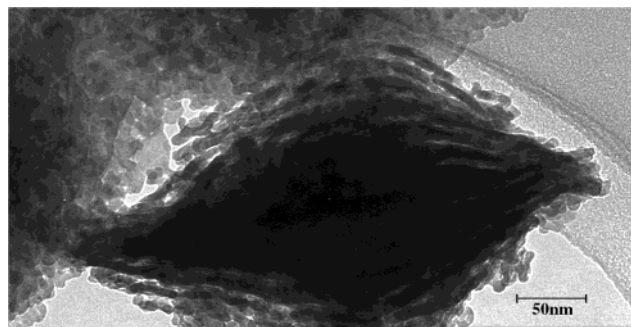


**Figure 4.** Small-angle X-ray scattering of 50 wt % cholesteryl-oligo(ethylene oxide) gels formed with a 0.1 M Cd $^{2+}$  aqueous solution.

has hexagonal symmetry the  $d$ -spacing decreases slightly upon gelation, as compared to that of the neat state. Furthermore, the  $d$ -spacing decreases slightly as the EO average length increases (Tables 1 and 2). As Kunieda et al. found, this could be attributed to increased attraction energy of the surfactant molecules as the curved interface of the hexagonal mesophase decreases the repulsive forces between EO chains.<sup>27</sup> Figure 4 shows typical SAXS data showing the effect of gel formation on  $d$ -spacing in lamellar and hexagonal systems.<sup>30</sup>

**Cadmium Sulfide Synthesis.** Templating was first investigated with a 50 wt % 0.1 M cadmium nitrate gel of chol-EO $_{12}$ . The gel was exposed to H $_2$ S until yellow CdS precipitate was noticed throughout the mesophase. After workup, TEM showed that the composite material was oblong in shape and possessed a layered nanostructure (Figure 5). Observation by electron microscopy elucidates distinct bands of inorganic mineral separated from each other by gaps of low-contrast material. Particles were found measuring up to 375 nm long and 175 nm wide. Elemental analysis showed that the hybrid particle contained approximately 10% organic material by weight. The layered appearance can be attributed to hydrophobic regions of organic template presumably trapped during mineralization, thus separating the layers of inorganic material from each other. The center-to-center distance between these layers is about 150 Å with the width of each inorganic layer being

(30) The exceptional signal-to-noise ratio that is shown with the chol-EO $_{30}$  gel can be attributed to the use of high-intensity X-ray source of the Advanced Photon Source at Argonne National Laboratory.

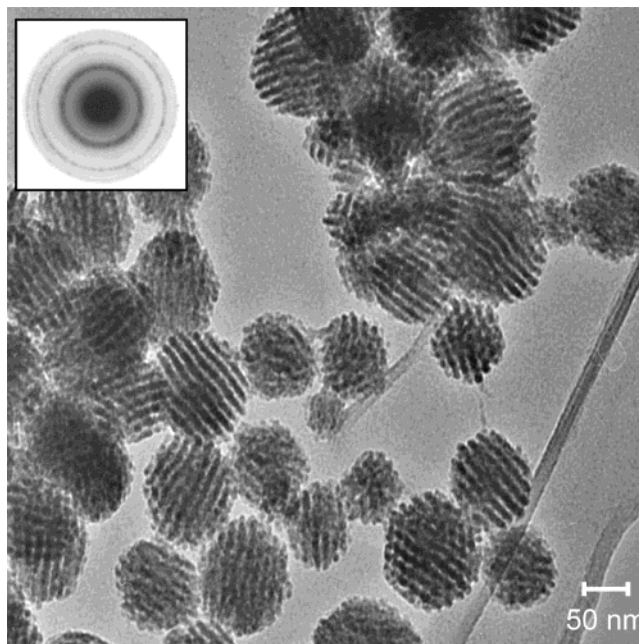


**Figure 5.** Cadmium sulfide particle templated by cholesteryl-(ethylene oxide)<sub>12</sub>.

approximately 110 Å. Tilting experiments in TEM confirm that the striations are indicative of a layered morphology similar to that of the lamellar liquid crystalline template; the layers disappear when the particle is tilted about its long axis, normal to the electron beam. Electron diffraction indicates that the CdS is in the form of a zinc blende crystal lattice structure.

As evidenced from the SAXS data (Figure 2), the *d*-spacing of neat chol-EO<sub>12</sub> is only 61 Å. Utilizing molecular modeling, the energy-minimized length of an average chol-EO<sub>12</sub> molecule is approximately 51 Å. The length of the cholesterol segment is about 15.5 Å and the length of the EO coil is about 36 Å. Packing as a noninterpenetrating layered smectic liquid crystalline material, in which hydrophobic headgroups face each other and hydrophilic coils face each other, the chol-EO<sub>12</sub> material should have a *d*-spacing of about 103 Å. The hydrophilic block would be approximately 72 Å and the hydrophobic segment would comprise about 31 Å. The discrepancy between the SAXS and molecular modeling suggests that there is interdigitation of one or both of the amphiphile blocks. This finding was also reported by Decher and Ringsdorf for a very similar compound.<sup>24</sup> Upon formation of the Cd<sup>2+</sup> gel, SAXS shows that the addition of water swells the hydrophilic segments, thus giving a wider *d*-spacing for the gelled mesophase. Data from chol-EO<sub>12</sub> Cd<sup>2+</sup> gels show (100) *d*-spacing of approximately 71 Å, indicating that interdigitation of the amphiphile blocks also occurs in the gelled state. During mineralization, it is assumed that the inorganic layer results from precipitation of CdS within the EO segments of the swollen mesophase. We have proposed that growth of the CdS layers originates at a nucleus and continues along a direction parallel to the layers of the mesophase.<sup>19</sup> Additionally, it appears as though mineralization forces the hydrophobic segments of the amphiphile out in a direction perpendicular to the CdS growth. In the case of lamellar chol-EO<sub>12</sub> particles, this expansion allows inorganic layers to be wider than predicted by SAXS data (i.e., 110 Å vs 71 Å). This deformation of LC segments during mineralization of cholesteryl-oligo(ethylene oxide) amphiphiles is different from what we previously reported from other direct LC templating systems.<sup>19,31</sup>

CdS mineralization within chol-EO<sub>15</sub> gels also results in very well defined templated nanostructures. These particles are of smaller size than those of lamellar chol-EO<sub>12</sub> and they are typically more spherical rather



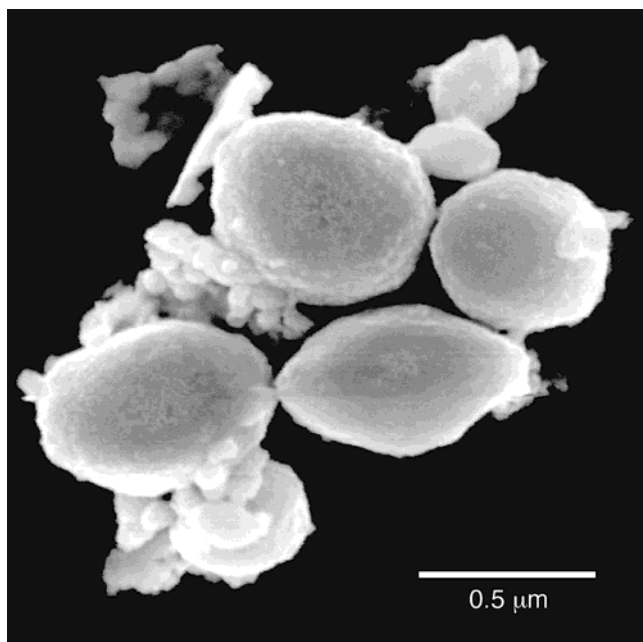
**Figure 6.** Cadmium sulfide particles templated by cholesteryl-(ethylene oxide)<sub>15</sub>.

than oblong with average diameters of 100 nm. The center-to-center distance of the layers is approximately 135 Å and the layers are approximately 100 Å wide with about a 35 Å separation between layers. These numbers are slightly longer than the findings from SAXS on the gels and molecular lengths determined by molecular modeling. According to SAXS of the chol-EO<sub>15</sub> gel, the expected length of EO segments is approximately 80 Å. Again, the thicker width of the CdS layers can be attributed to pushing away of the hydrophobic segments during the precipitation. As shown in Figure 6 most particles appear to be lamellar, however some have hexagonal-like symmetry. Tilting experiments have proven that these particles are in fact hexagonal in morphology. This is in contrast to that expected from SAXS experiments. According to X-ray analysis, the template is lamellar with a *d*-spacing of 81 Å in the gelled state. The resultant templated particles have a hexagonal array of pores within the bulk structure. These pores are areas in which CdS mineral is excluded, and they have a diameter of about 6 Å and an interpore spacing of 90–100 Å. During mineralization, there appears to be a phase transition toward the higher-symmetry hexagonal structure. The mineralization of hexagonal structures from lamellar templates was also observed with chol-EO<sub>14</sub>. Other investigators have also observed similar transitions with mesophase mineralizations.<sup>32,33</sup> With the chol-EO<sub>14</sub> template, particles that possessed hexagonal ordering were the primary morphology observed; however, lamellar, oblong-shaped particles were also found (Figure 7). There also appear to be particles that are a hybrid of lamellar and hexagonal particles, suggesting that for some EO chain lengths the lamellar morphology is an intermediate step in particle formation (Figure 8). Tilting of the biphasic

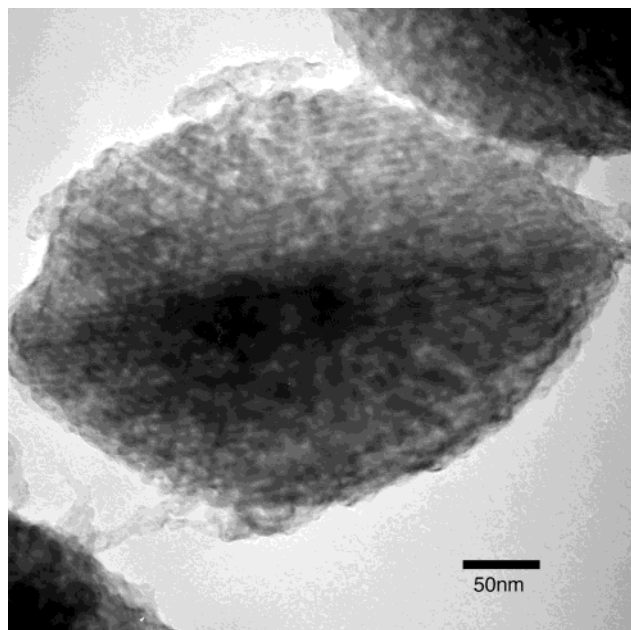
(31) Braun, P. V.; Osenar, P.; Tohver, V.; Kennedy, S. B.; Stupp, S. I. *J. Am. Chem. Soc.* **1999**, *121*, 7302.

(32) Tolbert, S.; Landry, C.; Stucky, G.; Chemelka, B.; Norby, P.; Hanson, J.; Monnier, A. *Chem. Mater.* **2001**, *13*, 2247.

(33) Templin, M.; Frack, A.; Du Chesne, A.; Leist, H.; Zhang, Y.; Ulrich, R.; Schädler, V.; Wieser, U. *Science* **1997**, *278*, 1795.



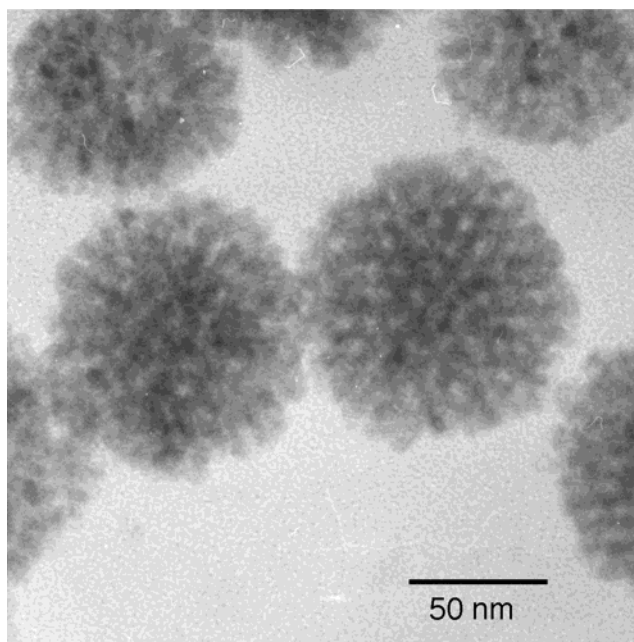
**Figure 7.** SEM image of cadmium sulfide particles templated by cholesteryl-(ethylene oxide)<sub>14</sub>.



**Figure 8.** TEM image of biphasic CdS particle templated by cholesteryl-(ethylene oxide)<sub>14</sub>.

particle confirms that there is lamellar and hexagonal structuring with the same particle. Additional mineralizations with chol-EO<sub>14</sub> gels of varying cadmium nitrate concentrations (i.e., 0.001, 0.01, and 1.0 M) have been performed, however, these have resulted in only hexagonal morphology particles.

Further experiments were performed to investigate the templating effect of cholesteryl-oligo(ethylene oxide) amphiphiles with other coil lengths. Specifically, average chain lengths of 8, 10, 17, 20, 24, and 30 EO repeats were prepared and mineralized. Particles that resulted from chol-EO<sub>*n*</sub> with  $n \leq 17$  all exhibit the lamellar or hexagonal morphology as observed from the chol-EO<sub>*n*</sub> ( $n = 12, 14, 15$ ) amphiphiles. The longer chain length



**Figure 9.** CdS templated from cholesteryl-(ethylene oxide)<sub>24</sub> exposed to H<sub>2</sub>S gas for 10 minutes.

amphiphiles ( $n > 17$ ) resulted in particles that were spherical and displayed hexagonal symmetry.

To compare mineralization of lamellar and hexagonal templates, separate gels of 50 wt % chol-EO<sub>14</sub> and chol-EO<sub>24</sub> were prepared and exposed in parallel to an H<sub>2</sub>S environment for varying lengths of time. Specifically, gels of each material were exposed for 1, 5, 10, 30, and 60 min, and particles were harvested and observed by TEM. It was found that after as little as one minute both samples contained particles that were nanostructured. From the one-minute exposure, templated particles from each amphiphile were of smaller size (50–100 nm) and possessed initial characteristics of a mature particle. The growth of these particles seems to be restricted by the limited exposure to H<sub>2</sub>S gas. Observation of longer H<sub>2</sub>S exposure times shows that there is an ideal exposure time for hexagonal templates, after which a templated particle is not observed. The optimal time for exposure for these long EO<sub>*n*</sub> ( $n \geq 20$ ) cholesterol amphiphiles was found to be 10 min. The samples of chol-EO<sub>24</sub> that were exposed for 60 min display few, if any, templated particles. At exceedingly longer exposures (2–3 h) the nontemplated particles were found to be spherical and large, approximately 1 μm. In contrast, lamellar chol-EO<sub>*n*</sub> ( $n \leq 17$ ) molecules template CdS over a wide range of H<sub>2</sub>S exposure times, including and beyond 60 min. For templating of longer oligomer length chol-EO<sub>*n*</sub> ( $n \geq 20$ ), gel H<sub>2</sub>S exposure time was reduced to the optimal time of 10 minutes. As shown in Figure 9, CdS from hexagonal templates are spherical in overall appearance. The particle dimensions measure up to 100 nm in diameter with pore diameters of 60 Å and interpore spacing of approximately 110 Å. From SAXS experiments, shown in Figure 4, the expected center-to-center pore distance is 76 Å, which indicates that the hydrophobic sections of a hexagonal template are also subject to mechanical displacement as mineralization occurs.



### Conclusions

Cholesterol-based lyotropic liquid crystalline materials can function as three-dimensional templates to synthesize nanostructured organic–inorganic particles. The synthesis of cadmium sulfide–organic hybrid materials takes place at ambient temperature and pressure and results in a nanostructured particle. The nanoscale features of the templated material are commensurate with the length of the hydrophilic segment of the cholesteryl-oligo(ethylene oxide) amphiphile. Short ethylene oxide segments ( $n \leq 17$ ) order as lamellar mesophases and template both lamellar and hexagonal hybrid particles, whereas longer ethylene oxide coils ( $n > 17$ ) order and mineralize into materials with only hexagonal symmetry.

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