Polymer-Assisted Formation of Giant Polyoxomolybdate Structures

Tianbo Liu,[†] Quan Wan,[§] Yi Xie,[‡,⊥] Christian Burger,[‡] Li-Zhi Liu,[‡] and Benjamin Chu*,[§,‡]

*Contribution from the Department of Physics, Brookhaven National Laboratory,
Upton, New York 11973, Department of Chemistry, State University of New York at Stony Brook,
Stony Brook, New York 11794-3400, and Department of Materials Science & Engineering,
State University of New York at Stony Brook, Stony Brook, New York 11794-2275*

Received February 9, 2001

Abstract: A highly ordered, porous nanoscale network structure of polyoxomolybdate was prepared from the slow decomposition of an unstable precursor compound $MoO_2(OH)(OOH)$ in the presence of PEO-containing triblock copolymer gels or semidilute/concentrated poly(ethylene oxide) (PEO) homopolymer solutions. Small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) measurements of the 1-μm size crystals revealed an extremely ordered primitive cubic (pc) structure made of polyoxomolybdates. Scanning electron microscopy (SEM) measurements showed that the overall size of these single crystals was close to 1 μm, in agreement with estimates from the scattering peak widths. Evidence from both scattering measurements and transmission electron microscope (TEM) measurements suggested that the system formed a highly porous primitive cubic network similar to that of certain zeolite structures. However, the observed lattice constant of 5 nm was much larger. The function of the PEO-containing polymer network was found to be very subtle and complex. Presumably, PEO acted simultaneously as a weak reducing agent and as a viscous matrix to ensure sufficient time for the formation of long-range ordered structures, resulting in the growth of extremely uniform but probably hollow "nanospheres". We suggest that this new material may find unique applications as a high-efficiency absorbent or catalyst. Furthermore, the current synthetic method may open up new pathways to prepare similar functional nanomaterials.

Introduction

Supramolecular pre-organized microenvironments, including self-assembled surfactants or amphiphilic block copolymers, entangled polymer networks, and biological systems, have been widely employed as templates to fabricate nanostructured inorganic composites, including semiconductors, catalysts, and supermagnetic materials as well as biominerals.[1,2] The general approach is to use them as matrices to nucleate and grow nanostructures of inorganic materials with many of their physical and chemical properties showing a particle size or modified-surface dependence.[3] The materials modified on a nanometer scale are designed to achieve special structures and/or functions. Block copolymers can self-assemble into micellar structures in a selective solvent, with less soluble block(s) forming compact micellar cores and soluble block(s) forming extended micellar shells.[4] At high polymer concentrations, the entanglement of the polymer chains and the closed packing of micelles lead to the formation of gellike networks with different ordered nanostructures, such as body-centered cubic (bcc), hexagonally packed cylinders, lamellae, or bicontinuous cubic networks. These self-assembled nanostructures have already been used to synthesize inorganic compounds with nanoscale modifications.[1c] Compared to short-chain surfactants, the block copolymers provided larger and tunable domain sizes that could be used for making silica with larger cavities, an important parameter for molecular sieves.

Another approach is to grow inorganic materials or inorganic/organic composites along the polymer chains to achieve different morphologies.[2] Antonietti et al. reported the use of a triblock copolymer PEO-PMAA-C_{12} (with PEO being poly(ethylene oxide), PMAA being poly(methacrylic acid), and C_{12} being a dodecyl chain, respectively) to form inorganic nanoparticles such as $CaCO_3$. They proposed that the new materials with ordered inorganic/organic mesophase might be useful as novel ceramics precursors, reinforcing filters or biomedical implants.

Besides being synthetic matrices, some polymer chains with active functional groups were also being used to take part in the chemical reactions to form special nanomaterials. One example was given by Bronstein et al.:[5] they used amphiphilic

* To whom correspondence should be addressed.
† Brookhaven National Laboratory.
§ Department of Materials Science & Engineering, State University of New York at Stony Brook.
‡ Department of Chemistry, State University of New York at Stony Brook.
⊥ Permanent address: Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, China.
(1) (a) Mann, S. *Nature* **1993**, *365*, 499 and the references therein. (b) 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. (d) Zhao, D.; Feng, P.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. C.; Stucky, G. D. *Science* **1998**, *279*, 548. (e) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Nature* **1998**, *396*, 152. (f) Braun, P. V.; Osenar, P.; Stupp, S. I. *Nature* **1996**, *380*, 325. (g) Holland, B. T.; Isbester, P. K.; Munson, E. J.; Stein, A. *Mater. Res. Bull.* **1999**, *34*, 471.
(2) Antonietti, M.; Breulmann, M.; Göltner, C. G.; Cölfen, H.; Wong, K. K. W.; Walsh, D.; Mann, S. *Chem. Eur. J.* **1998**, *4*, 2493.
(3) Komarneni, S.; Parker, J. C.; Thomas, G. J. In *Nanophase and Nanocomposite Materials*; MRS Symp. proceeding; MRS: Pittsburgh, PA, 1993; p 286.
(4) (a) Chu, B.; Zhou, Z. In *Nonionic Surfactants: Polyoxyalkylene Block Copolymers*; Nace, V. M., Eds.; Marcel Dekker: New York, 1996, Chapter 3. (b) Tuzar, K.; Kratochvil, P. In *Surface and Colloid Science*; Matijevic, E., Ed.; Plenum Press: New York, 1993; Vol. 15.
(5) Bronstein, L. M.; Chernyshov, D. M.; Valetsky, P. M.; Wilder, E. A.; Spontak, R. J. *Langmuir* **2000**, *16*, 8221.

polymer poly(octadecylsiloxane) (PODS) to form a bilayer structure in water/ethanol solution. The silanol groups on the polymer chains were used as reducing agents to reduce $PdCl_4^{2-}$ or $PtCl_4^{2-}$ to form noble metal nanoparticles.

Transition-metal oxides such as Fe_3O_4 and TiO_2 have been studied extensively with nanoscale modifications.[1a] Yang et al. presented a general and simple procedure to synthesize ordered large-pore mesoporous bulk metal oxides (but no molybdenum oxide) by using metal chlorides as precursors and reacting with ethanol in the presence of block copolymer matrices.[1d] The final products were obtained after removing the polymer chains by calcination. The samples showed ordered packing with several scattering peaks being detected by SAXS measurements. Another typical example was the synthesis of TiO_2 hollow nanospheres[6a] or nanotubes[6b] by using supramolecular assemblies.

Among the oxides of transition metals, MoO_3 is the one with special interest because it is an electrochromic and photochromic sensitive material for optical device applications.[7] A modified MoO_3 mesophase could be a useful photocatalyst.[8] The oxides of molybdenum are known to have the tendency to form polyoxometalates, e.g., ring-shaped clusters, as reported by Müller and co-workers.[9] The diameter of different clusters ranges from 2 to 4 nm, with a unique Mo_8 fragment being the common basic unit. These clusters, with well-defined chemical composition and molecular weight, can grow into single crystals for structure determination by X-ray diffraction. The coordinative nature of Mo ions makes them suitable candidates to build up new nanostructures.

In this work, we report a novel method to synthesize inorganic materials (polyoxomolybdate as an example) with the polymer network being a simultaneous participant as a weak reagent, to affect the morphology of the final products. It should be mentioned that the final products could not be formed without the presence of PEO polymer networks. The polymer networks can be long-chain PEO homopolymers or EPE- and EBE-type triblock copolymers, with E, P, and B being blocks of poly-(oxyethylene), polyoxypropylene, and poly(oxybutylene), respectively. The phase behaviors of these triblock copolymers in aqueous solution have been widely reported before.[4] It is noted that the end −OH groups have a weak reducing effect. Here we synthesize a porous network structure of polyoxomolybdate in the presence of PEO-polymer network by using the end −OH groups to partially reduce Mo(VI). Such a synthetic pathway can without doubt be extended to processes by which new materials can be prepared. The polymer network not only provides a suitable environment for the growth of nanostructures, but also takes part in the chemical reaction.

Materials and Methods

Materials. The Pluronic triblock copolymers F127 ($E_{99}P_{69}E_{99}$), F68 ($E_{76}P_{30}E_{76}$), and P104 ($E_{27}P_{56}E_{27}$) were obtained from BASF Chemical Co., Parsippany, NJ, and B20-5000 ($E_{45}B_{14}E_{45}$) was obtained from the Dow Chemical Co., Freeport, TX, all as gifts. PEO homopolymers (MW 1M and 6M, respectively), molybdenum powder (99.99%), and 30% (wt %) H_2O_2 (analytical purity) were purchased from Aldrich Chemical Co., WI.

Sample Preparation. To synthesize the polyoxomolybdate nano-material, about 8 mL of 30 (w/w%) H_2O_2 aqueous solution was slowly added into a beaker containing 1.0 g of pure Mo powder with strong stirring and an ice−water bath. A clear, yellow solution containing the water-soluble precursor compound $MoO_2(OH)(OOH)$ would form.[10] Then, this solution was heated gently with continuous stirring to drive off excess H_2O_2, and more water was added to make the overall Mo concentration reach 10 wt %. Consequently, the solution was mixed with polymer powders by centrifuging the mixture to form a homogeneous, transparent gel or a viscous solution. The $MoO_2(OH)(OOH)$ solution and Pluronic block copolymer powders (or PEO homopolymers) were mixed in a centrifuge tube with a certain weight ratio (usually, the copolymer concentration was between 20 and 65 wt %). The mixture was centrifuged at a speed of 6000 rpm ($\approx 5.3 \times 10^3$ g) at room temperature for at least 1 day to make sure that the components were properly mixed. The presence of inorganic materials did not change the ordered structure of the gel (if any). It was kept for at least two weeks to ascertain that $MoO_2(OH)(OOH)$ had reacted into the final product with the release of O_2 gas and that the polyoxomolybdate/polymer system had reached equilibrium. The gel (or solution) was semitransparent with a dark blue color, which was the typical color for a mixture of Mo(V) and Mo(VI), suggesting that Mo(VI) in MoO_2-(OH)(OOH) had been partially reduced. After the completion of the reaction, the immobile gel structure has been destroyed and a viscous solution was formed. Then a large amount of distilled water was added to dissolve the polymer chains. Blue precipitates slowly appeared at the bottom of the container. After the water was changed several times to further remove the polymers, the blue powders were collected and then dried to remove additional water. Elemental analysis showed that in the blue-color final products, the C content was less than 1.7% and the H content was sufficiently low as to be not detectable, implying that basically the polymer network had been removed.

Calcination is a reasonable way to remove the polymer matrix and to obtain the inorganic compound. However, in the current case, we have to use a large amount of water to remove the polymer chains because the polyoxomolybdate would again be oxidized to Mo(VI) at high temperatures.

For comparison, MoO_3 powders were also synthesized under the same conditions, but in the absence of the polymer matrix. The MoO_2-(OH)(OOH) from the same stock solution without polymer was also washed in distilled water and dried under the same conditions.

Characterization. Small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) measurements were carried out at the SUNY X3A2 and X27C beamlines of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The X-ray wavelengths used were 1.283 (X3A2) and 1.366 Å (X27C), respectively. A pinhole collimator system was used to define the incident X-ray beam. Fuji image plates were chosen as the X-ray area detector. Scanning electron microscope (SEM) and transmission electron microscope (TEM) experiments were done at the University Microscopy Hospital Imaging Center, University Hospital and Medical Center, SUNY at Stony Brook. The voltage used for TEM was 100 000 V, and the magnification was ×500 000.

Results and Discussions

SAXS and WAXD Measurement. A typical SAXS and WAXD measurement on the final polyoxomolybdate product is shown in Figure 1 where over 100 scattering peaks can be identified. The scattering peaks extended from the SAXS regime to the WAXD regime, suggesting an extremely ordered structure. The scattering pattern in the small-angle region indicated the existence of nanoscale ordered structures in the system. For

(6) (a) Zhong, Z.; Yin, Y.; Gates, B.; Xia, Y. *Adv. Mater.* **2000**, *12*, 206. (b) Kobayashi, S.; Hanabusa, K.; Hamasaki, N.; Kimura, M.; Shirai, H. *Chem. Mater.* **2000**, *12*, 1523.

(7) (a) Svachula, J.; Tichy, J.; Machek, J. *J. Catal. Lett.* **1989**, *3*, 257. (b) King, S. T. *J. Catal.* **1991**, *131*, 215. (c) Yao, J. N.; Hashimoto, K.; Fujishima, A. *Nature* **1991**, *335*, 624.

(8) (a) Honma, I.; Zhou, H. S. *Chem. Mater.* **1998**, *10*, 103. (b) Janauer, G. G.; Dobley, A.; Guo, J.; Zavalij, P.; Whettingham, M. S. *Chem. Mater.* **1996**, *8*, 2096.

(9) (a) Müller, A.; Beugholt, C. *Nature* **1996**, *383*, 296. (b) Müller, A.; Krickemeyer, E.; Meyer, J.; Bögge, H.; Peters, F.; Plass, W.; Diemann, E.; Dillinger, S.; Nonnenbruch, F.; Randerath, M.; Menke, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2122. (c) Müller, A.; Krickemeyer, E.; Bögge, H.; Schmidtmann, M.; Beugholt, C.; Kögerler, P.; Lu, C. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1220. (d) Plenio, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 348.

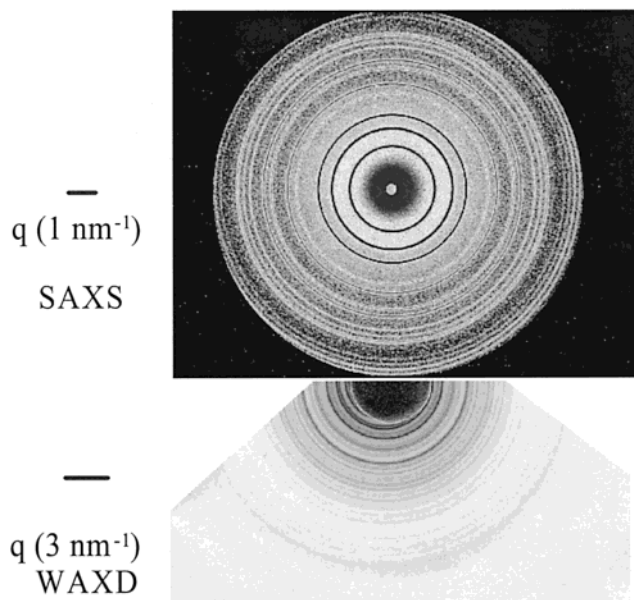(10) Kurusu, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 293.

Figure 1. SAXS and WAXD patterns of polyoxomolybdate units synthesized in the presence of a 45 wt % $E_{45}B_{14}E_{45}/H_2O$ gellike system. Over 100 scattering peaks could be identified (as labeled in the figure), which extended from the SAXS region to the WAXD region. The unit dimension was about 5.0 nm.

typical small inorganic compounds, their diffraction patterns appear at much larger angles in the WAXD regime. It becomes even more interesting when one considers that for the polymer matrix formed by the close packing of block copolymer micelles, only few scattering peaks showing bcc but not pc symmetry could be detected.[11] It is also not very clear if a very uniform size distribution of the nanospheres is sufficient to explain this extreme degree of long-range order, or if a cooperative process takes place during the formation.

Figure 2 represents the scattering intensity profile converted from Figure 1. Its *x*-axis denotes the absolute value of the scattering vector $q \equiv 4\pi/\lambda \cdot \sin(\theta/2)$, with θ being the scattering angle and λ being the wavelength of the X-ray beam, and the *y*-axis denotes the relative scattered intensity. In Figure 2, the absence of $\sqrt{7}$, $\sqrt{15}$, $\sqrt{23}$, $\sqrt{28}$, $\sqrt{31}$, $\sqrt{39}$, ... peaks relative to the first peak indicates a primitive cubic (pc) packing. The lattice constant *d* of the cubic unit cell is simply given by $d = 2\pi/q_1 = 4.98$ nm, with q_1 being the position of the primary peak.

Microscopic Measurements. A scanning electron microscopy (SEM) study was performed to determine the overall morphology of the crystals formed by the packing of polyoxomolybdate units, as shown in Figure 3. The particles were coated by a layer of gold before the experiment. It is clear that the polyoxomolybdate units form fairly uniform small cubic crystals. The average dimension of the crystals was about 0.7−0.8 μm.

It was surprising that polyoxomolybdate units could self-crystallize into a highly ordered structure. The crystallization of nanometer-scale colloidal particles has been reported before, but generally they chose closed packing structures, e.g., fcc or hexagonal closed packing (hcp), and these packings could be described well by a hard-sphere model.[12] In our case, a pc

packing is thermodynamically unstable for hard, inert spheres due to the low space occupancy when compared with close packed arrangements. The formation of pc structure requires additional forces, e.g., chemical bonds between adjacent spheres. The long-range ordered porous nanostructures should have a very large surface-to-volume ratio, resulting in the existence of a large number of surface atoms.

One explanation for the pc structure could be that polyoxomolybdate units are fitted together into a continuous porous network, as shown schematically in Figure 4a. This also ensures mechanical stability of the network. It is very interesting to note that the above model looks very similar to the Linde type-A (LTA) zeolite structure (Figure 4b). Moreover, the scattering pattern of the Linde type-A zeolite[13] (Figure 4c) is very similar to that in Figure 2, by showing an apparent pc packing with very weak (*200*) and (*310*) order scattering peaks, suggesting that these two species have similar structures. Of course, the domain size of the polyoxomolybdate network (5.0 nm) is much larger than that of the normal zeolite (~1.0 nm).

To further investigate the zeolite-like supra-nanostructures, high-resolution transmission electron microscopy (TEM) measurements were also conducted. A typical image is shown in Figure 5, where the (100) face of the sample was observed and the ordered packing of many polyoxomolybdate units into the crystal lattice could be identified. The average domain distance was about 5 nm, highly consistent with the SAXS result.

From our experimental findings, we can come up with two possibilities: (1) There is a well-defined single polyoxomolybdate cluster with a diameter of 5 nm. This cluster must be highly symmetric, because the clusters have to be packed into a cubic lattice. However, the observed primitive cubic packing suggests that the cluster is highly unlikely to have a close to perfect spherical shape. If this possibility were correct, our sample would then be the largest polyoxomolybdate cluster synthesized to-date. (2) There are no well-defined single polyoxomolybdate clusters. In this case, the crystal could consist of a zeolite-like continuous porous network that is assembled from smaller fragments in solution. If (2) were correct, then the structure is again new and different from what has been synthesized for polyoxomolybdates to-date. Single-crystal diffraction should be able to distinguish these two possibilities even though the small crystallite size has imposed some difficulties so far.

Functions of the PEO-Containing Polymers on the Formation of Polyoxomolybdate Units. The function of the polymer on the formation of polyoxomolybdate units is complex. An obvious phenomenon during the reaction was that the color of the solution changed from yellow to dark blue, which was also the color of the final product. Dark blue is the unique color for the mixture of Mo(V) and Mo(VI). Therefore, certain reducing reactions must have occurred in solution and Mo(VI) ions had been partially reduced. Considering that the −OH end groups on the block polymer chains have a weak reduction capability, and the absence of other obvious reducing agents in solution, it is reasonable to assume that the block polymer chains were involved in the reaction. This assumption can be supported from literature that polyols had certain reducing power in aqueous solution.[17] At the same time, whether the block copolymer micelles acted as synthetic templates to shape the morphology of the final products also needs to be verified.

(11) Wu, C.; Liu, T.; Chu, B.; Schneider, D. K.; Graziano, V. *Macromolecules* **1997**, *30*, 4574.

(12) (a) van Blaaderen, A.; Ruel, R.; Wiltzius, P. *Nature* **1997**, *385*, 321. (b) Míguez, H.; Meseguer, F.; López, C.; Holgado, M.; Andreasen, G.; Mifsud, A.; Fornés, V. *Langmuir* **2000**, *16*, 4405.

(13) (a) Pluth, J. J.; Smith, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 4704. (b) Gramlich, V.; Meier, W. M. Z. *Kristallogr.* **1971**, *133*, 134.
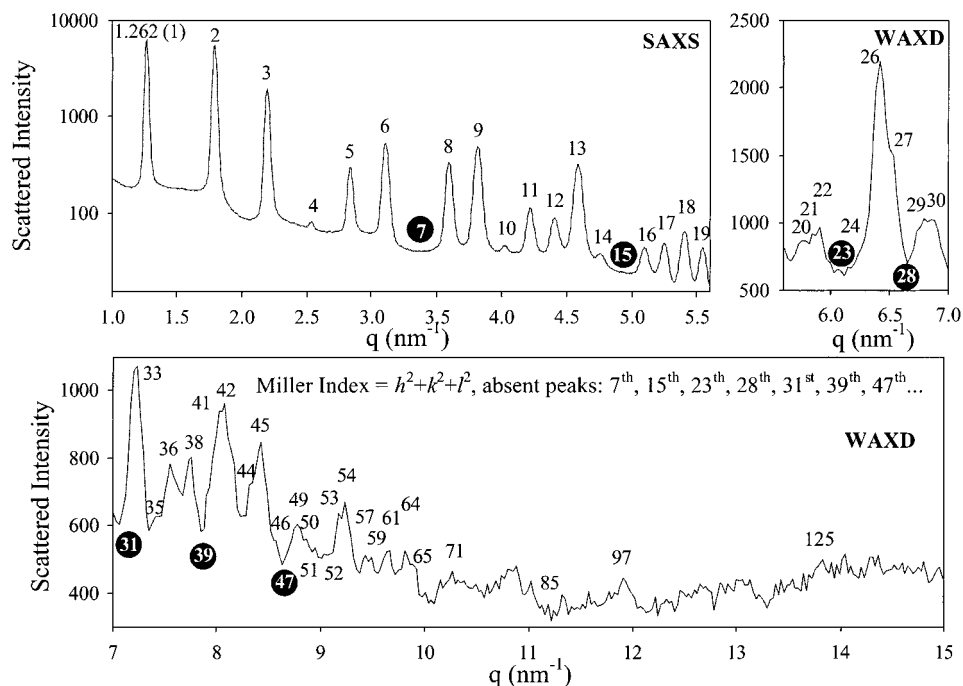
(14) JCDPS No. 5-508.

Figure 2. SAXS and WAXD profiles obtained from the patterns in Figure 1. The large number of high-order scattering peaks indicated a very ordered structure on a comparatively large scale. The scattering peaks showed a relative position of 1: $\sqrt{2}:\sqrt{3}:\sqrt{4}:\sqrt{5}:\sqrt{6}$..., indicating a cubic packing. The missing of certain scattering peaks (7th, 15th, 23rd, 28th, 31st, 39th, 47th, ...) suggests a rare primitive-cubic (pc) structure.

6.23 μm
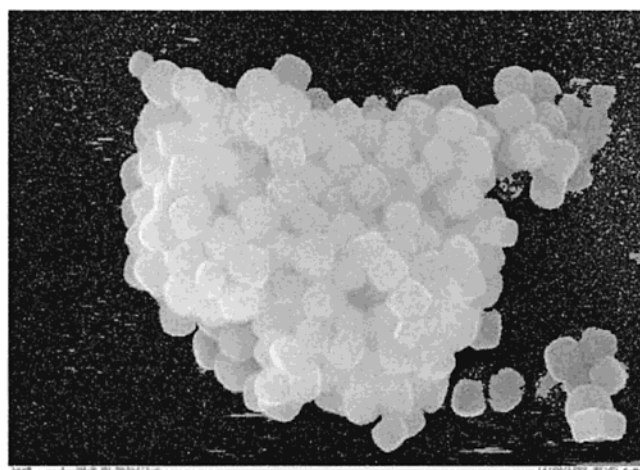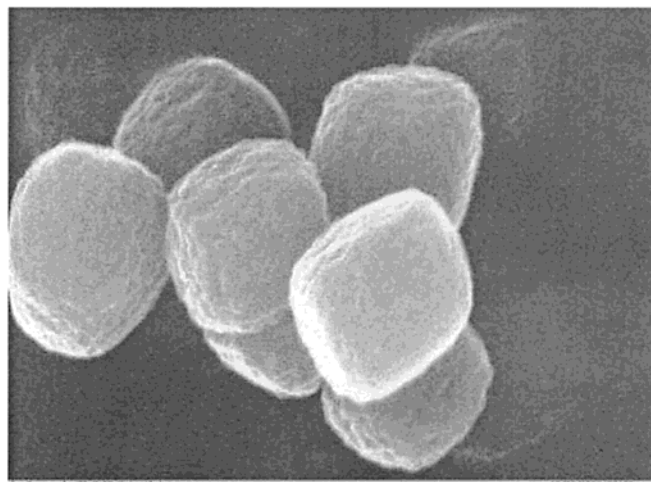
1.45 μm

Figure 3. Scanning electron microscopy (SEM) study of the crystallized polyoxomolybdate nanomaterial. The basic units of these crystals are not traditional atoms or molecules, but polyoxomolybdate units, as shown by scattering and other techniques.

To prove these points, several experiments were carried out. In the first experiment, long-chain PEO homopolymers (molecular weight 100K and 600K, respectively), instead of short-chain block copolymers, were used to prepare the $MoO_2(OH)$-(OOH) solutions. The same polyoxomolybdate units could also be obtained. This result ruled out the possibility that copolymer micelles acted as templates during the reaction, as widely

(15) (a) *Gmelin Handbook of Inorganic Chemistry Mo Supplement*; Vol. B1, Compounds with H, O, Anhydrates, Sb, Bi, Alkali Molybdates; Springer-Verlag: Berlin, Germany 1975; p 88. (b) Kerbs, H.; Walter, P. H. L. *Fundamental of Inorganic Crystal Chemistry*; McGraw-Hill: London, 1968, Chapter 26.
(16) *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C, p 141.
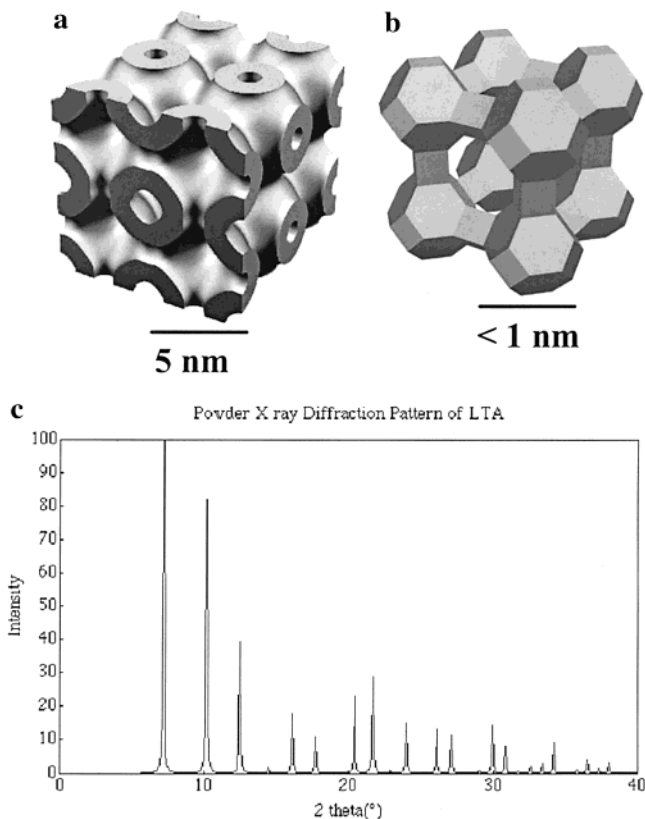(17) Fievet, F.; Lagier, J. P.; Figlarz, M. *MRS Bull.* **1989**, *14* (12), 29.

reported in the literature for other inorganic materials, because the PEO chains do not form any ordered nanostructure in an aqueous solution.

In the second experiment, $MoO_2(OH)(OOH)$ was decomposed in water without adding any polymer. The final products were normal MoO_3 crystals, with sharp, characteristic diffraction peaks that could be observed in the WAXD region. These peaks could be identified with the normal MoO_3 crystalline structure (Figure 6a). All peaks can be indexed on the basis of an orthorhombic structure with $a = 3.962$ Å, $b = 13.858$ Å, and $c = 3.697$ Å, as shown schematically in Figure 6 (cartoon a).[14] The strong and sharp peaks show the presence of a well-defined crystalline structure. The family of MoO_3 has a complicated structure made up of MoO_6 octahedrons, which is an isostructure

Figure 4. (a) A cartoon of molybdenum oxide zeolite-like network; (b) a cartoon of Linde type-A zeolite; (c) powder diffraction curve of Linde type-A zeolite, cited for comparison with that of the polyoxomolybdate units, as shown in Figure 2.
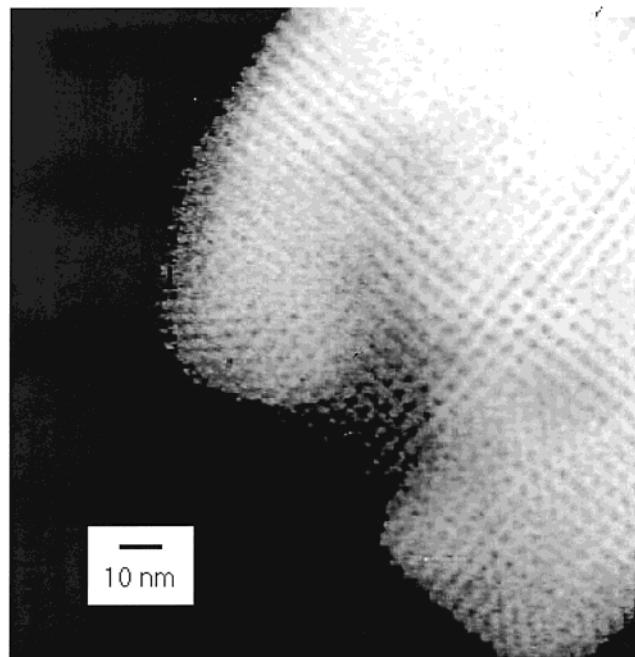

Figure 5. High-resolution transmission electron microscope (TEM) measurement on the network formed by polyoxomolybdate units.

of the basic unit of the perovskite structure. A possible sheer structure appears when the compound is nonstoichiometric.[15] No scattering peak was detected in the low q range (below 6.0 nm^{-1}) for MoO$_3$, indicating that there was no ordered nanoscaled structure. For polyoxomolybdate synthesized in the presence of a polymer network, the sharp scattering peaks in the WAXD region disappeared, as shown in Figure 6b. However, the shape

of the scattering curve was quite similar to that of Figure 6a, suggesting that polyoxomolybdate still chose the octahedral structure similar to that of MoO$_3$, but the crystalline lattice had been seriously distorted due to the different reaction environment, more specifically, due to the formation of polyoxomolybdate units, as shown schematically in Figure 6 (cartoon b).

In the third experiment, several small-molecule reducing agents, e.g., oxalic acid, SnCl$_2$, and glycerol, were separately added into different MoO$_2$(OH)(OOH) aqueous solutions. The color of all the solutions changed into dark blue, indicating the occurrence of the reducing reaction. The speed of color change showed a certain dependence on the reducing strength and concentration of the reagents. Finally, dark blue powders could be collected at the bottoms of all the solutions with a faster precipitation speed. However, SAXS and WAXD measurements showed that all these final products were different from the product obtained in the presence of the polymer network, by showing different scattering patterns and smaller domain sizes. Therefore, the polymer solution should have a special function on the formation of the unique polyoxomolybdate units by providing a network to slow the precipitation of the insoluble final product and to provide enough time for the growth of polyoxomolybdate units into unique crystals.

Density Measurement. It is important to determine the nature of the pores. It was found that most of the Mo polyoxometalate nanoclusters were hollow, due to the special structure of the Mo$_8$ building unit, as reported by Müller et al.[9] It is not unreasonable to assume that the present clusters or network could also be hollow nanospheres. As we could not determine the molecular structure of the current species by single-crystal X-ray diffraction, we had to try to find some other indirect evidence. One way was to measure the density of the final product. A standard way was to use a mother liquor, the saturated aqueous solution.[16] At the same time, small-molecule organic nonsolvents (e.g., xylene or CCl$_4$) for the nanomaterial were also used for the density measurement. All the measurements gave the density of the new nanomaterial as 2.1−2.2 g/mL, much lower than that of the MoO$_3$ crystal (4.7 g/mL). It should be reasonable to assume that the small solvent molecules could enter the empty space among the "nanospheres", but not the interior in each nanosphere. Although the new sample should not have the exact identical molecular structure as that of MoO$_3$, their local densities should be reasonably similar. Therefore, the huge difference in density has provided indirect evidence for the highly porous nature of our sample.

Our new products show some similarities to those Mo−O clusters reported by Müller et al.,[8] e.g., both kinds of materials are blue-black [Mo(V) and Mo(VI) mixture] crystals, with nanoscale dimensions and large cavities. However, the packing of polyoxomolybdate units into the pc structure has never been reported before, and the unit size of the new material is much larger than the former reported ones. From IR measurements, characteristic absorbance peaks of the OH-group deformation at 3400(w) and 1620(w) cm^{-1} could be clearly detected. The symmetrical and antisymmetrical terminal Mo−O stretch were found at 980(m) and 910(w) cm^{-1}, respectively, in good agreement with previous reports on similar compounds.[9,10]

For the density measurements, we also need to show that the small solvent molecules can enter the empty space among the polyoxomolybdate units freely. Therefore, we designed another set of experiments. First, we grew the polyoxomolybdate porous material in aqueous solution. The polyoxomolybdate material was paste-like. The empty space among the polyoxomolybdate units was assumed to be filled with solvent molecules (sample
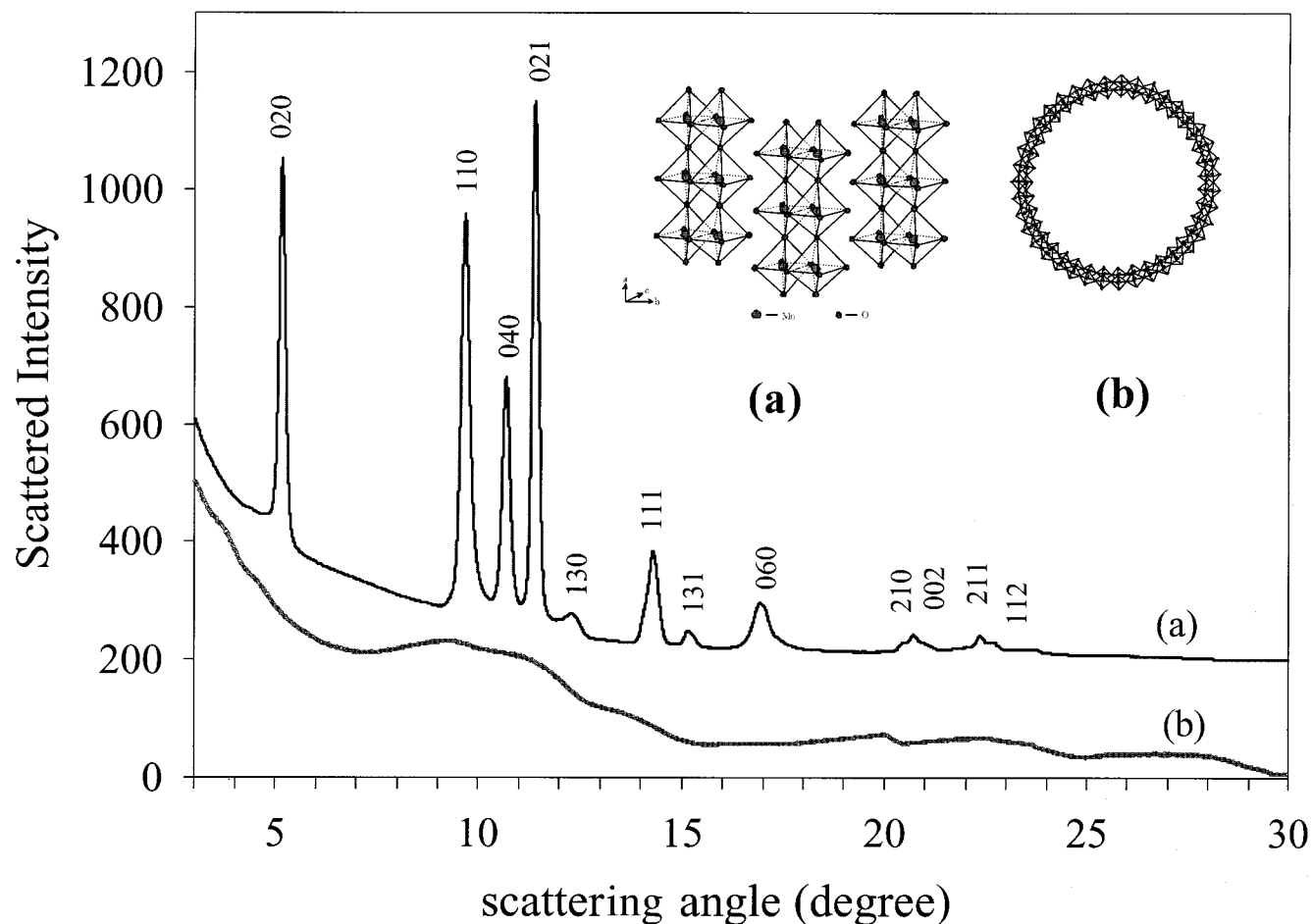
Figure 6. Wide-angle X-ray diffraction (WAXD) profiles of the polyoxomolybdate powders synthesized (b) without the $E_{45}B_{14}E_{45}$ matrix and (a) with the $E_{45}B_{14}E_{45}$ matrix, and after removing all the block copolymers. The corresponding cartoons are also shown in the figure. The relevant cartoons are shown in insets a and b, respectively.

A). Then, the paste-like material was collected without further drying at high temperatures. This wet material was spread on a clean surface for about 1 h to evaporate the water molecules surrounding the material to get sample B. Sample B was already fairly dry from visual observation. The density of Sample B was again 2.1 g/mL, the same as the dried samples. Therefore, we can conclude that the mother liquor solvent molecules cannot be held effectively in the empty space among the polyoxomolybdate units. This observation suggests that the size of the empty region is substantially larger than that of zeolites used as molecular sieves. Consequently, small solvent molecules can move in and out freely in the empty region.

To further prove this supposition, we collected a small amount of sample B and heated it to over 120 °C for 6 h to drive out all the water molecules that were not chemically bound to the material. The weight of the material (we called it sample C) decreased by only ∼5 wt % of its original mass, indicating that sample B could store at most a small amount of nonchemically bound water. Furthermore, by leaving sample C in air for about 15 h, its weight slowly increased again to close to the original value of sample B. This experiment showed that the small amount of nonchemically bound water in sample B should be the water molecules physically adsorbed on the surface of the porous material.

Effect of Polymer Concentration. The polymer concentration has a certain effect on the size of the final product. We found that at lower polymer concentrations, the inter-unit distance in the polyoxometalate increased with increasing polymer concentration. Figure 7 showed that by using the same
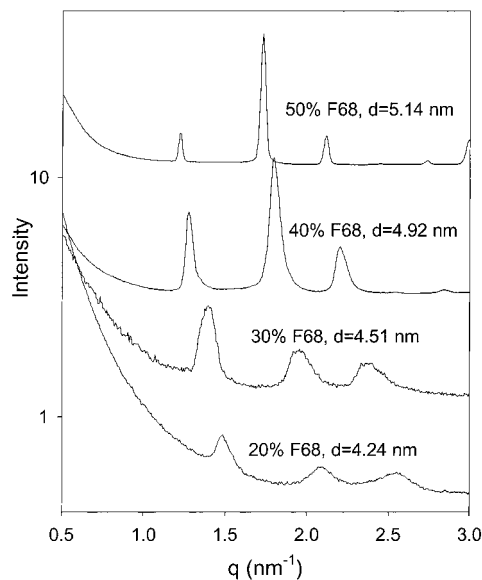

Figure 7. SAXS profiles of polyoxomolybdate nanostructures prepared in the presence of different F68 block copolymer concentrations. The difference in the primary scattering position indicates the difference in the size of the polyoxomolybdate units.

block copolymer (F68, or $E_{76}P_{30}E_{76}$) at different polymer concentrations, the final products had very similar zeolite-like structures, but their primary peak position (q_1) showed quite obvious polymer concentration dependence. The q_1 value

decreased with increasing polymer concentration, indicating an increase in the domain distance from 4.2 nm (20 wt % F68) to 5.1 nm (50 wt % F68). However, further increasing the polymer concentration could not further increase the size of the polyoxomolybdate units, i.e., the size of the "spheres" had an upper limit of 5.1−5.2 nm at sufficiently high polymer concentrations. Also, the packing of the polyoxomolybdate units became much less ordered when the size of the polyoxomolybdate units was smaller than 5.0 nm, which could be proven by the fact that their scattering peaks became broader and less scattering peaks could be identified. It suggests that, at lower polymer concentrations, the network was too loose to hold the polyoxomolybdate units for a long enough time to grow better crystals, i.e., the polyoxomolybdate units precipitated too fast so that they could not be packed into a very ordered structure. Therefore, we can conclude that a critical polymer concentration exists above which the polyoxomolybdate units can grow into very nice structures. For the F68/water gellike system, it is around 50 wt %. A similar phenomenon was also observed when other block copolymers and homopolymers were used. The critical concentrations for long-chain PEO polymers were lower than that of small amphiphilic block copolymers.

Conclusions

PEO-containing block copolymers or homopolymers were used for the nanofabrication of possibly hollow polyoxomolybdate units, which were extremely homogeneous in size and could crystallize into crystals (about 0.8 μm in size) with a primitive-cubic packing. The polymer in aqueous solution functioned both as a weak reducing agent to reduce Mo(VI) to a mixture of Mo(V) and Mo(VI) and also as a support material to ensure enough reaction time for the final products to grow into perfect polyoxomolybdate units. A certain polymer concentration was necessary for growing highly regular nanostructures. For the final nanomaterials, over 100 orders of scattering peaks could be detected from SAXS and WAXD measurements, which suggested a highly ordered Linde type-A zeolite-like structure formed by chemically connected polyoxomolybdate units. High-resolution TEM measurement also confirmed this result by observing a lattice formed by inter-connected 5-nm cells. The density measurement suggested that the polyoxomolybdate units were possibly hollow inside, which was reasonable when compared with other similar Mo−O clusters. We believe that the new material could find applications as a high-efficiency catalyst or absorbent, and possibly a new electronic material. Also, we present a new approach of using a polymer network as both a reagent to be involved in the reaction and a supporting matrix to hold the final products long enough to grow into ordered structures, which can be applied in synthesizing other functional nanomaterials.