

Polymer-Controlled Crystallization of Molybdenum Oxides from Peroxomolybdates: Structural Diversity and Application to Catalytic Epoxidation

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The influence of polyoxyethylene-containing polymers on the crystal structure and habit of molybdenum-oxide-based products crystallized from peroxomolybdate solutions was investigated. Polyoxyethylene homopolymers of various molar masses were compared with a polyoxyethylene alkyl ether and a triblock copolymer of polyoxyethylene and polypropylene. Conventional hydrothermal synthesis at temperatures between 70 and 180 °C was compared with an ultrasonic pathway at 70 °C. The structure of the products was investigated by small- and wide-angle X-ray scattering. Different crystal phases were obtained depending on the polymer concentration and the preparation methods. At 70 °C, a compound with tentative formula $\text{MoO}_3-x(\text{O}_2)_x \cdot n\text{H}_2\text{O}$ ($n \approx 1$), showing X-ray diffraction patterns matching those of triclinic monohydrate molybdenum trioxide, was the product found in the absence of any polymer. However, small concentrations of any polyoxyethylene-containing polymer led to a monoclinic hemihydrate phase under the same conditions and temperature. At temperatures above 90 °C, the patterns of the resulting products could be indexed according to orthorhombic anhydrous MoO_3 , although the blue color of certain samples indicated an oxygen deficiency. At high polymer concentrations and temperatures under 90 °C, the material crystallized in an unusual primitive cubic structure, independent of the exact type of polyoxyethylene polymer used, with a very large cubic lattice constant of ~ 5 nm. However, the molar mass and the structure of the polymer do influence the lattice constants of the final crystal leading to a slight decrease with increasing molar mass. At high polymer concentrations and 180 °C, the product was identified as MoO_2 . The polymer acts not only as a structure-directing agent but also as a mild reducing agent, as judged from the nontrivial redox behavior of the molybdenum ions when the crystallization occurs in the presence of polymer. The excellent catalytic properties of representative types of the synthesized materials were demonstrated for the epoxidation of cyclohexene and cyclooctene by *tert*-butyl hydroperoxide.

Introduction

The application of polymers as additives in the crystallization of inorganic materials, known from nature and used in the industry for decades, has become a topic of increasing interest in materials research. Polymers can not only be used as surfactants or surface modifiers to facilitate the dispersion of inorganic particles in a given solvent, but they may control the nucleation and enhance or inhibit the crystal growth by adsorbing specifically on certain growing faces.^{1–3} In a different approach, polymers can also be used either as conventional templates or as structure-directing agents of growing structures in nontemplate processes.^{4–8} Metastable phases can also sometimes be stabilized by the presence of polymers. The physical properties of the resulting hybrid

materials can often be tuned by adjusting the characteristics of the polymer component. The option of completely removing the organic component from the composite by calcination or dissolution can be considered for certain applications and should be kept in mind.

Molybdenum oxides and molybdenum-oxide-based materials, such as polyoxomolybdates, are of significant importance for applications such as sensing,⁹ catalysis,^{10–12} optoelectronics and “smart windows” (photo- and electrochromism),^{13–15} and energy storage applications.^{16–18} Accordingly, considerable research effort has been made to

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- (1) Yu, S.-H.; Cölfen, H. *J. Mater. Chem.* **2004**, *14*, 2124–2147.
- (2) Wegner, G.; Demir, M. M.; Faatz, M.; Gorna, K.; Muñoz-Espí, R.; Guillemet, B.; Gröhn, F. *Macromol. Res.* **2007**, *15*, 95–99.
- (3) Gorna, K.; Muñoz-Espí, R.; Gröhn, F.; Wegner, G. *Macromol. Biosci.* **2007**, *7*, 163–173.
- (4) Liu, T. B.; Burger, C.; Chu, B. *Prog. Polym. Sci.* **2003**, *28*, 5–26.
- (5) van Bommel, K. J. C.; Arianna, F.; Shinkai, S. *Angew. Chem., Int. Ed.* **2003**, *42*, 980–998.
- (6) Li, C.; Qi, L. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 2388–2393.
- (7) del Campo, A.; Arzt, E. *Chem. Rev.* **2008**, *108*, 911–945.
- (8) Rozenberg, B. A.; Tenne, R. *Prog. Polym. Sci.* **2008**, *33*, 40–112.

- (9) Gouma, P.; Kalyanasundaram, K.; Bishop, A. *J. Mater. Res.* **2006**, *21*, 2904–2910.
- (10) Zhang, W. M.; Desikan, A.; Oyama, S. T. *J. Phys. Chem.* **1995**, *99*, 14468–14476.
- (11) Oyama, S. T.; Desikan, A. N.; Hightower, J. W. *ACS Symp. Ser.* **1993**, *523*, 1–14.
- (12) Mizuno, N.; Misono, M. *Chem. Rev.* **1998**, *98*, 199–217.
- (13) Yao, J. N.; Hashimoto, K.; Fujishima, A. *Nature* **1992**, *355*, 624–626.
- (14) He, T.; Yao, J. N. *J. Photochem. Photobiol. C* **2003**, *4*, 125–143.
- (15) Yamase, T. *Chem. Rev.* **1998**, *98*, 307–325.
- (16) Guzman, G.; Yebka, B.; Livage, J.; Julien, C. *Solid State Ionics* **1996**, *86–8*, 407–413.
- (17) Mai, L. Q.; Hu, B.; Chen, W.; Qi, Y. Y.; Lao, C. S.; Yang, R. S.; Dai, Y.; Wang, Z. L. *Adv. Mater.* **2007**, *19*, 3712–3716.
- (18) Casañ-Pastor, N.; Gómez-Romero, P. *Front. Biosci.* **2004**, *9*, 1759–1770.

synthesize nanostructures, in terms of both discrete clusters or continuous networks, of these compounds and to study their properties. The most common oxide of molybdenum is molybdenum(VI) oxide, MoO_3 , which is known to crystallize in a wide variety of polymorphic hydrates. In the anhydrous form, MoO_3 can crystallize as the orthorhombic thermodynamically stable phase ($\alpha\text{-MoO}_3$)¹⁹ or as a metastable monoclinic phase ($\beta\text{-MoO}_3$).²⁰ A high-pressure monoclinic polymorph ($\text{MoO}_3\text{-II}$)^{21,22} and a hexagonal phase ($h\text{-MoO}_3$)^{23–25} are also known. Several hydrate phases, often generically referred as “molybdic acids”, are possible: a monoclinic dihydrate, $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$;^{26,27} a yellow monoclinic monohydrate, $\text{MoO}_3 \cdot \text{H}_2\text{O}$; a white triclinic monohydrate, $\text{MoO}_3 \cdot \text{H}_2\text{O}$; a monoclinic hemihydrate, $\text{MoO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$;^{28,29} and an orthorhombic $\text{MoO}_3 \cdot \frac{1}{3}\text{H}_2\text{O}$.³⁰ Another molybdenum oxide, less common than MoO_3 , is molybdenum(IV) oxide, which crystallizes in a monoclinic cell and presents metallic conductivity. In addition, several oxides with intermediate oxidation states between Mo(IV) and Mo(VI), with defined stoichiometry and general formula $\text{Mo}_n\text{O}_{3n-1}$, are also possible.³¹

A different and structurally more complex type of molybdenum compounds are the polyoxomolybdates, constituted by a very large and diverse group of anionic clusters built from metal-oxo anions linked by shared oxide ions. Polyoxomolybdates belong to the group of compounds generically known as polyoxometalates, which have become very popular in inorganic chemistry in the last years because of their structural beauty and the wide scope of their applications.^{18,32,33} A few years ago, a polyoxomolybdate with a very unusual primitive cubic structure was synthesized in our laboratory from peroxomolybdate solutions in the presence of polyoxyethylene-containing polymers.^{34,35} Conventional molybdenum oxide hydrates and multivalent oxides

have been also prepared from similar solutions,³⁶ pointing out that there should exist a relationship between both types of products, molybdenum oxide hydrates and primitive cubic polyoxomolybdate, despite their apparently very different structures. A systematic study on the structural diversity of the products obtained from peroxomolybdate solutions has been lacking so far and the present article attempts to fill—at least partially—this gap.

In most of the work in the area of the so-called “polymer-controlled crystallization”, the presence of polymeric additives may influence dramatically the habit and the final morphology, but typically the crystallographic phase remains invariable. However, there are cases in which the crystal phase can change in the presence of macromolecules. This is known for systems of biological importance such as calcium carbonate, in which different polymorphs are possible (vaterite, aragonite, calcite), whose occurrence can be affected by polymer additives.³⁷ A similar issue has been sporadically investigated for the case of gypsum and concrete, where polymeric additives have been reported to influence crystal hydration.^{38,39} For transition metal salts and oxides, the influence of polymers on the diversity of crystal structures remains almost unexplored. Here, we report the influence of polyethers on the hydration states and the diversity of crystalline structures of materials obtained by crystallization from peroxomolybdate solutions, comparing different synthetic pathways. The potential of such materials as catalysts for epoxidation reactions is demonstrated by taking as examples two cyclic alkenes, cyclohexene and cyclooctene.

Experimental Section

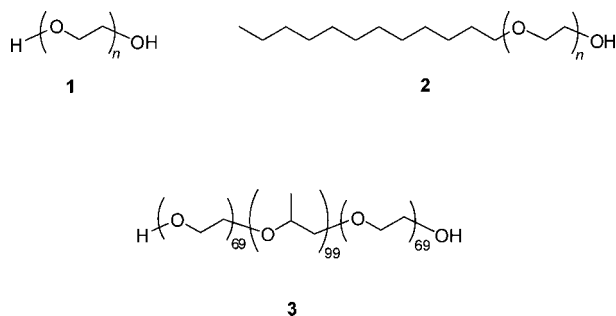
Synthesis of Molybdenum Oxide Materials. Peroxomolybdate precursor solutions were prepared by adding dropwise hydrogen peroxide (40 mL, 30 wt % aqueous solution, J. T. Baker) to molybdenum metal powder (4.78 g, 50 mmol, 99.99%, Aldrich) placed in an Erlenmeyer flask, while cooling in an ice–water bath under constant stirring (the reaction is exothermic and violent). The overall molybdenum concentration was adjusted to 0.5 mol L^{-1} by addition of deionized water. Different amounts of the following polymers, all containing polyoxyethylene (POE) chains (cf. Scheme 1), were added to aliquot parts of the peroxomolybdate precursor solution: POE homopolymers with molar masses of 600, 4600, 8000, 35 000, 100 000, and 600 000 g mol^{-1} (**1**, provided by Aldrich or Fluka); a POE alkyl ether with 23 oxyethylene units, commercially known as Brij 35 (**2**, $M_w \approx 1198 \text{ g mol}^{-1}$, Aldrich); and the triblock copolymer $\text{E}_{69}\text{P}_{99}\text{E}_{69}$ (with E and P denoting oxyethylene and oxypropylene, respectively), commercially known as Pluronic F127 (**3**, $M_w \approx 12\,600$, BASF). After adding the corresponding amounts, the mixtures were stirred under cooling until complete dissolution of the polymer. When increasing the polymer concentration, viscous solutions and gels were formed. The description of the several synthetic methods used follows.

Method 1. A volume of 10 mL of the peroxomolybdate precursor was placed in disposable 50-mL plastic centrifuge tubes (Fisher

- (19) Kihlborg, L. *Arkiv Kemi* **1963**, *21*, 357–364.
- (20) McCarron, E. M. *J. Chem. Soc., Chem. Commun.* **1986**, 336–338.
- (21) McCarron, E. M.; Calabrese, J. C. *J. Solid State Chem.* **1991**, *91*, 121–125.
- (22) Baker, B.; Feist, T. P.; McCarron, E. M. *J. Solid State Chem.* **1995**, *119*, 199–202.
- (23) Atuchin, V. V.; Gavrilo, T. A.; Kostrovsky, V. G.; Pokrovsky, L. D.; Troitskaia, I. B. *Inorg. Mater.* **2008**, *44*, 622–627.
- (24) Song, J. M.; Wang, X.; Ni, X. M.; Zheng, H. G.; Zhang, Z.; Ji, M. R.; Shen, T.; Wang, X. W. *Mater. Res. Bull.* **2005**, *40*, 1751–1756.
- (25) Song, J.; Ni, X. M.; Zhang, D.; Zheng, H. G. *Solid State Sci.* **2006**, *8*, 1164–1167.
- (26) Cruywagen, J. J.; Heyns, J. B. B. *South Afr. J. Chem.* **1981**, *34*, 118–120.
- (27) Boudjada, N.; Rodriguezcarvajal, J.; Anne, M.; Figlarz, M. *J. Solid State Chem.* **1993**, *105*, 211–222.
- (28) Fellows, R. L.; Lloyd, M. H.; Knight, J. F.; Yakel, H. L. *Inorg. Chem.* **1983**, *22*, 2468–2470.
- (29) Bénard, P.; Seguin, L.; Louer, D.; Figlarz, M. *J. Solid State Chem.* **1994**, *108*, 170–176.
- (30) Harb, F.; Gerand, B.; Nowogrocki, G.; Figlarz, M. *Solid State Ionics* **1989**, *32–3*, 84–90.
- (31) Greenwood, N. N.; Earnshaw, A., *Chemistry of the Elements*, 2nd ed.; Elsevier Butterworth-Heinemann: Oxford, U.K., 1998.
- (32) Pope, M. T.; Müller, A., *Polyoxometalate Chemistry: From Topology via Self-Assembly to Applications*; Springer, Dordrecht, The Netherlands, 2001.
- (33) Borrás-Almenar, J. J.; Coronado, E.; Müller, A.; Pope, M. T., *Polyoxometalate Molecular Science*; Springer: Dordrecht, The Netherlands, 2003.
- (34) Liu, T. B.; Wan, Q.; Xie, Y.; Burger, C.; Liu, L. Z.; Chu, B. *J. Am. Chem. Soc.* **2001**, *123*, 10966–10972.
- (35) Chen, J. L.; Burger, C.; Krishnan, C. V.; Chu, B. *J. Am. Chem. Soc.* **2005**, *127*, 14140–14141.

- (36) Krishnan, C. V.; Chen, J. L.; Burger, C.; Chu, B. *J. Phys. Chem. B* **2006**, *110*, 20182–20188.
- (37) Cölfen, H. *Curr. Opin. Colloid Interface Sci.* **2003**, *8*, 23–31.
- (38) Boisvert, J. P.; Domenech, M.; Foissy, A.; Persello, J.; Mutin, J. C. *J. Cryst. Growth* **2000**, *220*, 579–591.
- (39) Rottstegge, J.; Wilhelm, M.; Spiess, H. W. *Cem. Concr. Compos.* **2006**, *28*, 417–426.

Scheme 1



Scientific), closed, and immersed for 16 h in a conventional ultrasound water bath (35 kHz, ca. 70 °C). Yellow precipitates were obtained in the absence of polymer, whereas blue products precipitated in the presence of the indicated POE-containing polymers. The color ranged from light to deep dark blue, depending on the concentration and the molar mass of the polymers.

Method 2. To analyze the effect of the ultrasound irradiation, we carried out analogous experiments at different temperatures in a conventional water bath without stirring. At 70 °C, precipitates of similar appearance to those obtained by the sonochemical route (method 1) were formed after similar times, but no product was observed at lower temperatures. This observation could indicate that the formation of the precipitate is essentially controlled by the overall temperature and not by the ultrasound irradiation, and that the sonochemical process could take place through a pathway similar to hydrothermal one.

Method 3. A volume of the precursor (10 mL) was placed in a glass vial, closed, and kept at room temperature for several days. Although no product could be observed during the first few days, a precipitate began to form on the bottom after waiting for longer times (more than 2 weeks). The precipitates, referred to in this article as “time-aged” materials, had colors similar to those obtained by the other methods and were isolated after 40 days.

Method 4. A conventional hydrothermal route was conducted by placing 18 mL of the precursor solutions (with and without the polymers) in borosilicate-glass autoclavable 100-mL flasks (VWR) sealed with polypropylene caps and heated for 16 h at 70 or 90 °C in a laboratory oven. This method allowed the system to reach higher temperatures, not possible with the conventional plastic centrifuge tubes in a water bath. An analogous synthesis was also conducted at 180 °C but, in this case, placing the solution in a 45-mL Teflon-lined stainless steel digestion bomb (Parr Instrument Company).

In all methods, the resulting powders were separated by centrifugation, washed with water to remove the excess polymer (i.e., aggregated or nonincorporated polymer merely adsorbed on the particles), and dried under a vacuum at 45–60 °C.

Characterization Techniques. Scanning electron microscopy (SEM) images were taken using a field-emission microscope LEO EM1550 Gemini, operated at working distances of 3–8 mm and acceleration voltages in the range of 2.5–20 kV. A Robinson back-scattered detector (RBSD) and an in-lense detector were alternatively used. Thermogravimetric analysis (TGA) was conducted using a Perkin-Elmer TGA 7 thermobalance under air atmosphere and at a heating rate of 10 °C min⁻¹ from room temperature to 600 °C.

Conventional X-ray diffraction (XRD) patterns were registered by a Philips PW 1728 powder diffractometer with Cu K α radiation ($\lambda = 0.154184$ nm, 40 kV, 30 mA). Small-angle X-ray scattering and (SAXS) and wide-angle X-ray diffraction (WAXD) measurements were conducted at the X27C beamline of the National Synchrotron Light Source (NSLS), at Brookhaven National Labora-

tory (BNL). A pinhole collimator system was used, and the incident wavelength was 0.1371 nm. Image plates (Fujifilm) and, alternatively, a Mar-165 CCD camera were used as detection systems. The temperature-dependent measurements were carried out by using an INSTEC HSC600V temperature-controlled cell.

A qualitative identification of molybdenum(V) was carried out using the “conventional thiocyanate method”.⁴⁰ A known amount of sample was placed in a test tube containing concentrated HCl (2 mL, 10 M, EMD) and shaken. After addition of an aqueous sodium thiocyanate solution (5 mL, 10 wt %, Fisher), a very strongly colored orange-red molybdenum–thiocyanate complex was formed if Mo(V) was present. The complex was extracted by 1-methoxy-2-propyl acetate (Aldrich, 99%). Although only Mo(V) gives a colored thiocyanate complex,⁴¹ a light coloration was observed in samples containing presumably only Mo(VI). This can be explained by traces of Mo(V) present either from the beginning or formed by a partial reduction of Mo(VI) by hydrochloric acid. Nevertheless, the color was very light compared to that observed with samples containing higher concentrations of Mo(V).

The presence of peroxide in the samples could be proven by a conventional permanganate titration or by using commercial test strips for semiquantitative determination of peroxides (Quantofix P, Macherey-Nagel). In the former case, an amount of the molybdenum oxide material was suspended in a 1 M aqueous solution of H₂SO₄ and titrated with a 0.002 M potassium permanganate solution (dilution from a 0.02 M volumetric standard, Aldrich) until the pink coloration persisted.

Epoxidation Reactions of Cycloalkenes. The reagents used were cyclohexene (Fluka, $\geq 99\%$), cyclooctene (Fluka, $\sim 95\%$), and *tert*-butyl hydroperoxide (TBHP, Fluka, purum, ~ 5.5 mol L⁻¹ in nonane). Chloroform (Acros Organics, 99.8%) was used as a solvent. A triple-neck round flask containing cyclohexene (3.8 mL, 37.5 mmol) or cyclooctene (5.13 mL, 37 mmol), chloroform (6.25 mL, 77.5 mmol), TBHP (6.8 mL, 37.5 mmol), and 80 mg of the pertinent catalyst was placed in an oil bath equipped with a temperature controller and heated at 60 °C under reflux and continuous magnetic stirring (450 rpm). Sampling volumes of 250 μ L were collected at different times and kept in closed vials at ca. -20 °C until their analysis. Molybdenum(IV) oxide (99%, Aldrich), molybdenum(VI) oxide (puriss., p.a., Fluka), and molybdic acid (hydrated MoO₃, 85% min. in MoO₃, Alfa Aesar) were used as reference catalysts, to compare their efficiency with our products. ¹H NMR measurements were conducted in an AC250 Bruker spectrometer at 250 MHz by using deuterated chloroform (99.8%, Cambridge Isotope Laboratories) as a solvent. The conversion of the reactions was followed by ¹H NMR taking into account the ratio of the integrals of the peaks at ~ 5.6 (s) and ~ 3.1 (s) ppm for cyclohexene oxide, and ~ 5.6 (m) and ~ 2.9 (m) ppm for cyclooctene oxide. The first peak corresponds to the olefinic CH=CH protons of the substrate and the second to protons of the CH groups connected to the oxygen in the epoxide. It was known that the potential byproducts of the epoxidation reactions (i.e., the cycloalkene alcohols and the cycloalkene ketones) would show at least one unequivocally assignable peak without overlapping with other signals of the ¹H NMR spectrum.

Results and Discussion

The first observation when comparing the solid products obtained by crystallization from an aqueous solution of

(40) Das, A. K.; Chakraborty, R.; Cervera, M. L.; de la Guardia, M. *Talanta* **2007**, *71*, 987–1000.

(41) Sandell, E. B., *Colorimetric Determination of Traces of Metals*, 3rd ed.; Interscience Publishers: New York, 1959; p 644, et seq.

peroxomolybdates, in the absence or presence of different polyethers, and independently of the synthetic pathway, is the change of color in the precipitated powders. In the absence of any polymer, the powders obtained were yellow or white-yellowish, while in the presence of polyoxyethylene (POE) homopolymers or POE-containing polymers, the coloration ranged from light to very dark blue, depending on the concentration of polymer and its molar mass (i.e., the number of oxyethylene units in the chains). Molybdenum trioxide or its hydrates are typically white or yellow, but blue compounds from molybdenum have been known for decades and are imprecisely referred to as “molybdenum blues”. The label “molybdenum blues” comprises a wide range of compounds including oxide/hydroxide species of mixed valence that form a series between the extremes of $\text{Mo}^{\text{VI}}\text{O}_3$ and $\text{Mo}^{\text{V}}\text{O}(\text{OH})_3$,³¹ but it can also refer to more complex polyoxomolybdates, typically soluble in water. In general, the blue color is characteristic for the presence of subvalent Mo(V) and/or Mo(IV) species, which may coexist with Mo(VI), whereas white and yellow colors indicate pure Mo(VI). In our experiments, it has been clearly found that an increase in the polymer concentration during the precipitation results in a darker blue color. Accordingly, it was already suggested in previous works that the polyether chains act as a mild reducing agent of Mo(VI) to Mo(V) [or Mo(IV)].³⁶ Here, we have compared POE homopolymers of different molar masses (structure **1** in Scheme 1, labeled as PEG or PEO depending on the molar mass), the POE alkyl ether Brij 35 (**2**), and the triblock copolymer Pluronic F127 (**3**), but it is worth mentioning that we have also observed blue coloration when using other polymers without ethylene oxide groups (not reported here), such as poly(vinyl alcohol), which indicates that the reducing effect is not unique for polyoxyethylene.

The chain length of the polymer also appeared to influence the color of the samples: the addition of homopolymers with very large molar masses was observed to lead to a lighter blue color than the addition of the same mass concentrations (in g L^{-1}) of polymers with low molar mass. This proves that the terminal $-\text{OH}$ end groups in the chains must have played an important role in the reduction process, because at the same mass concentration the number of end groups will be larger for lower molar mass polymers.

The higher concentration of Mo(V) with an increasing blue color of the samples was qualitatively demonstrated by complexation of the Mo(V) with thiocyanate (see Experimental Section for details). The red coloration of the solutions containing the extracted molybdenum(V)–thiocyanate complex was typically stronger for samples with a darker blue color.

Influence of Concentration and Polymer Structure on Crystal Morphology. In a first part of the work, we have focused on the systematic study of the materials obtained by a sonochemical process previously reported^{35,36} in the presence of different polymer concentrations. As a representative example, Figure 1 compares the SEM micrographs of the products crystallized at different concentrations of the poly(ethylene oxide) homopolymer with $M_w = 35\,000$ g mol^{-1} (PEO-35k). The product precipitated without polymer

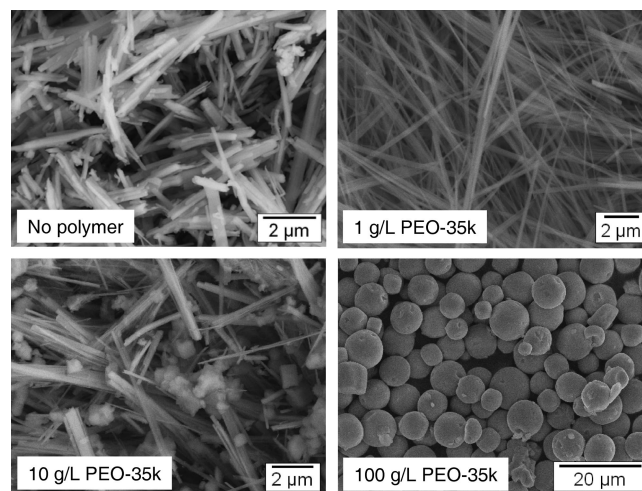


Figure 1. SEM micrographs of the molybdenum oxide products obtained from a 0.5 M peroxomolybdate precursor solution after sonication at 70 °C, in the absence and in the presence of different concentrations of PEO homopolymer ($M_w = 35\,000$).

contained prismatic rods of different sizes. The polydispersity of the particle size distribution was reduced (i.e., the shape homogeneity in the sample was improved) by the presence of small quantities of the polymer, and very thin nanowires of micrometric length were obtained at polymer concentrations of 1 g L^{-1} . The polymer concentration dramatically affected the crystal morphology, and spheres several micrometers in diameter were formed at high concentrations ($>100\text{ g L}^{-1}$) of PEO-35k. In some cases, at intermediate concentrations, morphological mixtures of rods and spheres (or polyhedra) were observed (see third micrograph of Figure 1). Transmission electron microscopy (TEM) investigations showed that these products were not only a mixture of different morphologies but also of different crystal phases, that is, the different morphologies can also correspond to different crystal structures.

The morphologies obtained at the highest concentration depend, as shown in Figure 2, on the polymer structure and the degree of polymerization (number of oxyethylene units in the chain). The crystal shape ranges from cubic to spherical, going through various polyhedral morphologies with the rhombic dodecahedron and the truncated cube being among the unambiguously identifiable ones. The effect of the polymer chain length not only on the morphology but also on the external appearance of the samples appears to be nontrivial. Although the blue color of the powder is, in general, darker at larger molar mass, for very long chain polymers, such as PEO with $M_w = 600\,000\text{ g mol}^{-1}$, the color begins to become lighter and the morphology returns to spherical again. At this point, it is difficult to draw a clear conclusion on the mechanism. The presence of groups of different polarity, as is the case for polyoxyethylene alkyl ether and the $\text{E}_{69}\text{P}_{99}\text{E}_{69}$ copolymer, also seems to have an influence on the resulting morphology. To explain these changes, we suggest a possible coordination of the pseudocrown ether from the ethylene oxide groups and the molybdenum atoms. The crystal growth proceeds by incorporating building units at steps on the crystal faces. The polymer may reversibly adsorb onto these steps, blocking and freeing them,

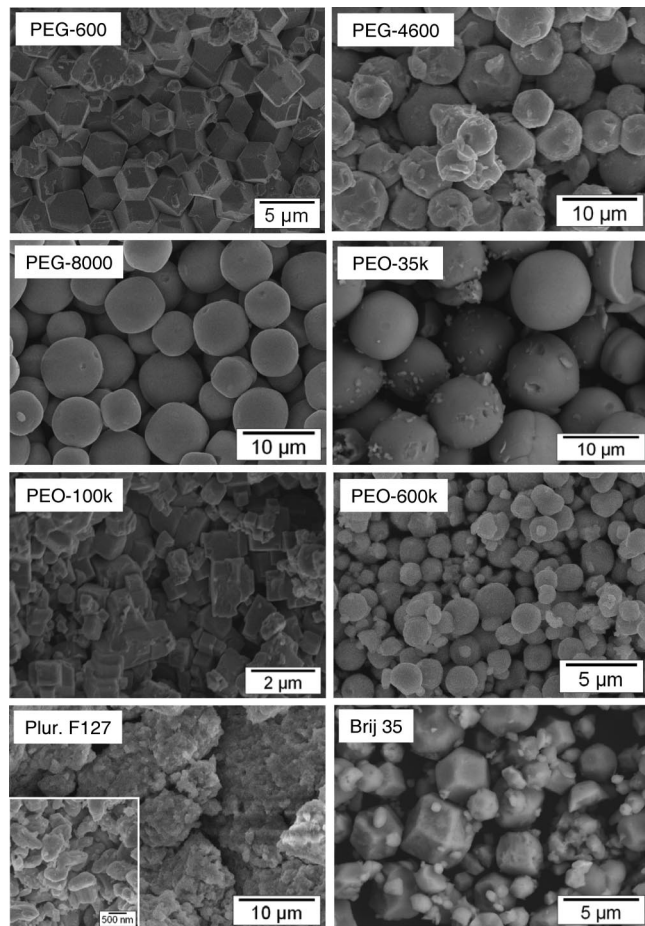


Figure 2. SEM micrographs of the products obtained from a 0.5 M peroxomolybdate solution after sonication at 70 °C in the presence of 200 g L⁻¹ of the indicated polyoxyethylene-containing polymers.

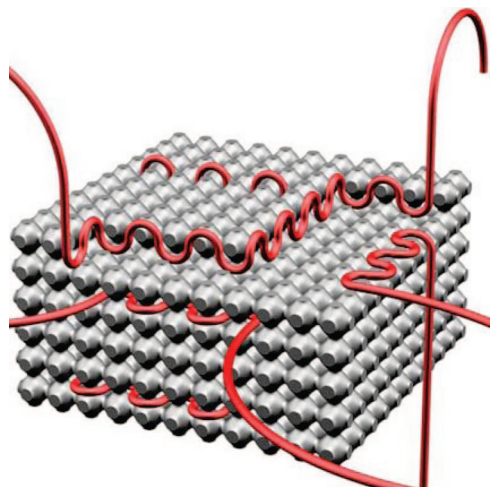


Figure 3. Schematic representation of the interaction of the polyether chains with the growing molybdenum oxide crystals.

and thereby controlling the growth of the crystal. A schematic representation of the proposed mechanism is depicted in Figure 3. The poisoning of the growth of inorganic crystals in certain directions by the presence of organic impurities is a known phenomenon,⁴² and similar mechanisms have been described for hydrophilic polymers in other transition metal

(42) Mullin, J. W., *Crystallization*, 4th ed.; Butterworth-Heinemann: Oxford, U.K., 2001.

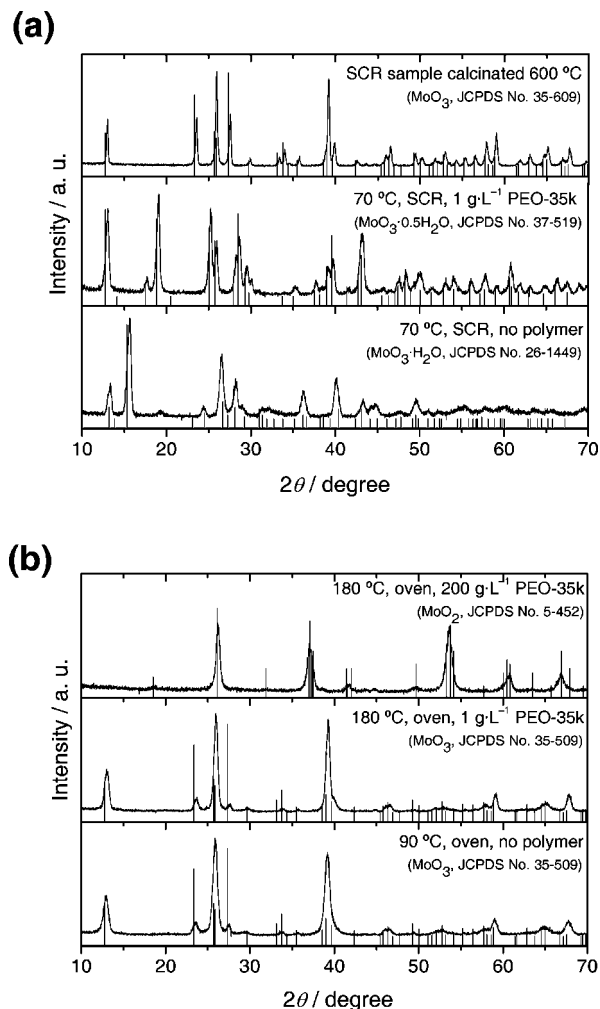


Figure 4. XRD patterns of representative molybdenum oxide samples synthesized (a) by the sonochemical route (SCR) at 70 °C and (b) by conventional autoclave hydrothermal synthesis (90 and 180 °C). Vertical lines show the position and relative intensity of the known crystal phases that match best the experimental patterns. [Cu K α radiation, $\lambda = 0.154184$ nm].

oxides, such as ZnO.⁴³ However, we are aware that this is not the only factor to take into account when considering the effect of the polyethers, because in addition to the morphological evolution, there are also crystal phase changes, as will be discussed below.

Effect of Ultrasound Irradiation, Temperature, and Synthesis Method. The ultrasonication causes an increase in the temperature of the bath from room temperature to ca. 70 °C. Therefore, and taking into account that the recipients containing the solution are closed, it can be considered that the sonochemical pathway is actually a sort of hydrothermal process. To analyze the effect of the ultrasound and the temperature, we carried out similar experiments by placing sealed containers of the peroxomolybdate solution in a water bath, at different temperatures and in the absence of ultrasound. At low temperatures (30 and 40 °C), no precipitate was obtained after keeping the solutions in the water baths for 2–3 days. The solutions must be aged for several weeks until the molybdenum oxide products are

(43) Muñoz-Espí, R.; Qi, Y.; Lieberwirth, I.; Gómez, C. M.; Wegner, G. *Chem.—Eur. J.* **2006**, *12*, 118–129.

Table 1. Crystal Structures and Colors of the Products Obtained by the Different Synthetic Pathways in the Absence and Presence of POE-Containing Polymers, Comparing Low and High Concentrations (abbreviations: t, triclinic; m, monoclinic; o, orthorhombic; MB, molybdenum blue; pc, primitive cubic)

Synthesis method	T (°C)	no polymer	POE polymer 1 g L ⁻¹	POE polymer > 100 g L ⁻¹
ultrasound	70	MoO _{3-x} (O ₂) _x ·H ₂ O (t) [yellow]	MoO _{3-x} (O ₂) _x ·0.5H ₂ O (m) [light blue]	“MB” (pc) [dark blue]
water bath	70	MoO _{3-x} (O ₂) _x ·H ₂ O (t) [yellow]	MoO _{3-x} (O ₂) _x ·0.5H ₂ O (m) [light blue]	“MB” (pc) [dark blue]
autoclave (oven)	70	MoO _{3-x} (O ₂) _x ·H ₂ O (t) + α-MoO _{3-x} (o) [brownish]	MoO _{3-x} (O ₂) _x ·0.5H ₂ O (m) + α-MoO _{3-x} (o) [blue]	“MB” (pc) [dark blue]
	90	α-MoO _{3-x} (o) [white-gray]	α-MoO _{3-x} (o) [blue]	“MB” (pc) [dark blue]
	180	α-MoO _{3-x} (o) [gray-bluish]	α-MoO _{3-x} (o) [blue]	MoO ₂ (m) [dark blue]
time aging	25	MoO _{3-x} (O ₂) _x ·H ₂ O (t) [yellow]	MoO _{3-x} (O ₂) _x ·H ₂ O (t) [light blue]	“MB” (pc) [dark blue]

formed. At 70 °C (i.e., the same temperature as in the described sonochemical route), the precipitates begin to form at approximately the same time as in the presence of ultrasound. This indicates that the temperature and not the ultrasonication is the crucial aspect to speed up the precipitation of the materials; the ultrasound irradiation interacts, though, with the growing crystals, homogenizing the resulting shapes. Conventional hydrothermal synthesis, autoclaving the precursor solutions at 70, 90, and 180 °C, was also considered. When comparing the different materials by electron microscopy, the materials prepared by ultrasonication had smaller particle sizes and were morphologically more homogeneous, and the aggregation was less significant than in those prepared by the hydrothermal route.

Influence of Polymer on Crystal Structure. The X-ray analysis of the materials demonstrated that the morphological differences and the different appearance of the powders were in some cases related to changes in the crystal phase. XRD

patterns of representatives samples prepared by the sonochemical route and by conventional hydrothermal synthesis at temperatures from 70 to 180 °C are compared in Figure 4. Figure 4a contains the data of samples prepared via the sonochemical route (SCR) at 70 °C: a reference no-polymer sample, a sample prepared in the presence of 1 g L⁻¹ of PEO-35k, and the same sample after oxidative calcination at 600 °C. XRD patterns of hydrothermally synthesized samples at 90 and 180 °C in the absence and presence of PEO-35k (1 and 200 g L⁻¹) are shown in Figure 4b. The patterns were compared and identified with known crystal phases. As an overview, Table 1 summarizes the different phases obtained from the peroxomolybdate solutions under

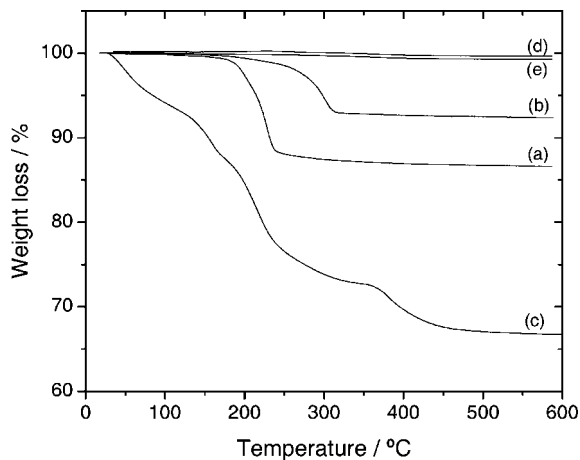


Figure 5. Thermogravimetric analysis (TGA) curves registered under air for samples prepared by the sonochemical route at 70 °C (a) without polymer, (b) in the presence of 1 g L⁻¹ of PEO-35k, and (c) in the presence of 200 g L⁻¹ of PEO-35k; and for samples prepared by the hydrothermal route at 180 °C (d) without polymer and (e) in the presence of 1 g L⁻¹ of PEO-35k.

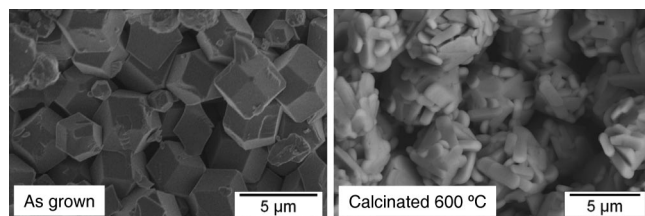


Figure 6. Comparison of the SEM micrographs before and after calcination at 600 °C for a molybdenum blue sample prepared by the sonochemical route at 70 °C in the presence of 200 g L⁻¹ of PEG-600.

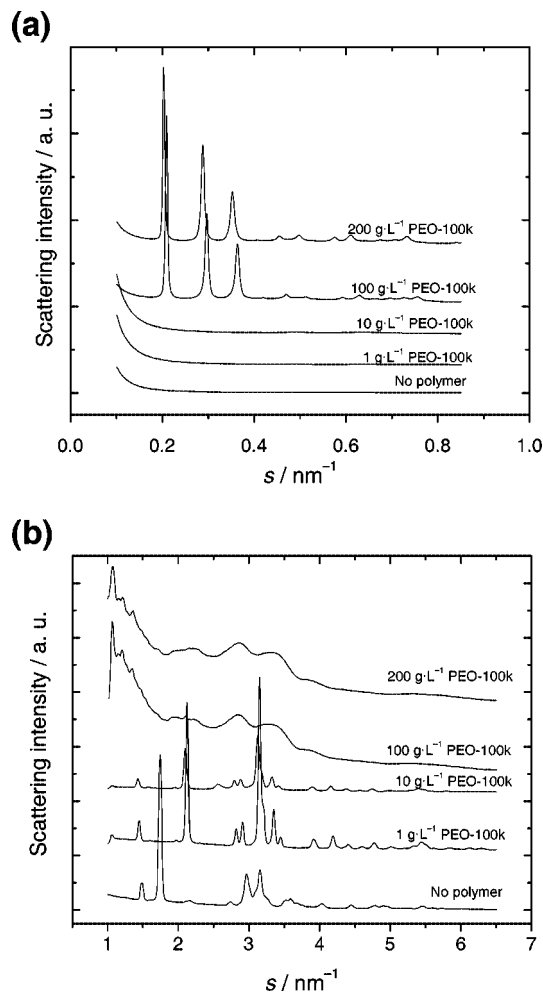


Figure 7. (a) Small- and (b) wide-angle X-ray scattering patterns of the products obtained from a 0.5 M peroxomolybdate solution in the absence and in the presence of different concentrations of PEO homopolymer (*M_w* = 100 000).

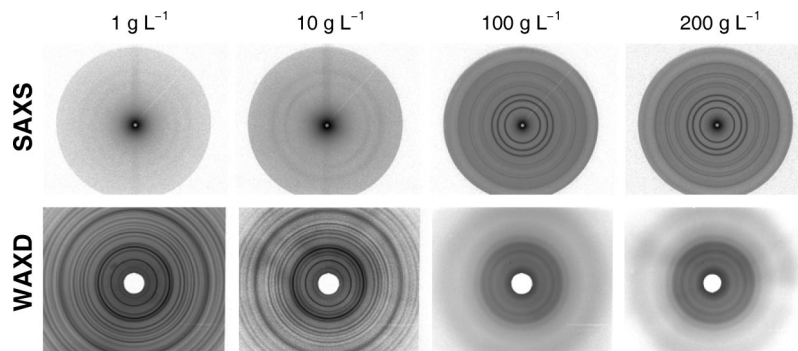


Figure 8. SAXS and WAXD patterns of the products obtained in the presence of different concentrations of PEO-100k (cf. Figure 5).

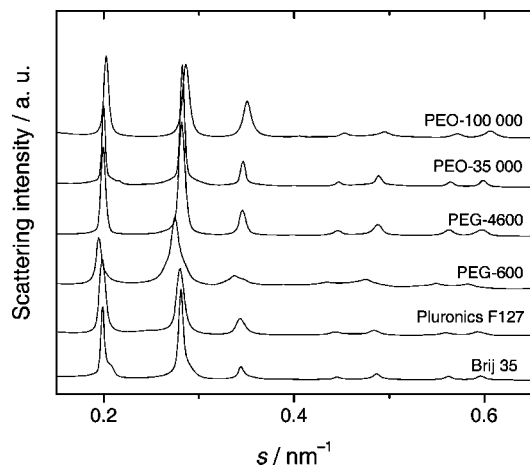


Figure 9. SAXS curves of the materials obtained by the sonochemical route in the presence of a high concentration (200 g L^{-1}) of different polyethers.

the different conditions. The results contained in this table can be generalized for the various polymers used.

In the absence of any polymer, the triclinic monohydrate $\text{MoO}_3 \cdot \text{H}_2\text{O}$ (JCPDS card No. 26–1449) is the phase identified by XRD in the products prepared in the water bath at 70°C (with and without ultrasound) and in the precipitates resulting after time aging of the peroxomolybdate solution at room temperature. Considering the possible remaining peroxy groups in the final materials, a formula $\text{MoO}_{3-x}(\text{O}_2)_x \cdot n\text{H}_2\text{O}$ has been suggested for products synthesized in a similar way to that reported here.⁴⁴ We could identify the presence of peroxide in our samples by conventional titration with permanganate and with commercial test strips specific for peroxide (see Experimental Section). Therefore, this tentative formula seems reasonable for the obtained compounds. In samples crystallized in the presence of the polymers, the peroxide concentration ranged from very low (light blue powders) to undetectable (dark blue powders), as judged from these identification methods. The presence of Mo(V) and Mo(IV) was observed to interfere, though, during the permanganate titration method, especially in the darker samples. Apparently, the presence of the peroxide was not noticeable on the XRD patterns, but a detailed and accurate refinement of the patterns, beyond the scope of this study, would be necessary to confirm the minor lattice distortions introduced by peroxides and oxygen defects.

(44) Fang, L.; Shu, Y. Y.; Wang, A. Q.; Zhang, T. *J. Phys. Chem. C* **2007**, *111*, 2401–2408.

At low concentrations of POE-containing polymers (cf. fibrous morphologies shown in Figure 1), the XRD peaks could be unequivocally assigned to the hemihydrate $\text{MoO}_3 \cdot 0.5 \text{H}_2\text{O}$ (JCPDS card no. 37–519), which crystallizes in the monoclinic system. The calcination in air of the samples, both monohydrates and hemihydrates, resulted in orthorhombic $\alpha\text{-MoO}_3$ (anhydrous, JCPDS no. 35–509). The effect of additives (including macromolecules) on the hydration state is indeed not unusual and is known for other common systems of everyday life, such as gypsum (calcium sulfate) or cement (mixtures containing calcium silicates, aluminum oxide and gypsum). The hemihydrate $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ can be hydrated to gypsum (dihydrate form), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The presence of organic and polymer additives have been reported to retard the hydration of the hemihydrate.^{38,45} Similar effects have also been found when adding polymers to commercial cement.³⁹

In general, the autoclaved samples prepared at temperatures higher than 90°C without polymer and with low polymer concentration ($1\text{--}6 \text{ g L}^{-1}$) were identified as $\alpha\text{-MoO}_3$ (molybdate). However, the relative intensity of the peaks was different from that of the mineral molybdate, with the (040) reflection being the one with the highest intensity in our case. Similar relative intensities to those presented here have often been reported for hydrothermally prepared samples, with prominence of the (0k0) reflections.^{44,46–49} This finding has typically been explained in terms of preferred orientation effects or an anisotropic crystal growth.

The blue color of some of the powders, uncharacteristic for $\alpha\text{-MoO}_3$, indicated a partial reduction of molybdenum(VI) to lower oxidation states. The XRD peaks for these samples are also relatively broad, which may suggest the presence of oxygen defects in the structure. In a recent paper, Hu et al.⁵⁰ reported the synthesis of blue samples, which they identified as hydrogen molybdenum bronzes with the formula H_xMoO_3 , having diffraction patterns very close to orthorhombic $\alpha\text{-MoO}_3$. The authors had first synthesized the

(45) Ersen, A.; Smith, A.; Chotard, T. *J. Mater. Sci.* **2006**, *41*, 7210–7217.

(46) Li, X. L.; Liu, J. F.; Li, Y. D. *Appl. Phys. Lett.* **2002**, *81*, 4832–4834.

(47) Li, G. C.; Jiang, L.; Pang, S. P.; Peng, H. R.; Zhang, Z. K. *J. Phys. Chem. B* **2006**, *110*, 24472–24475.

(48) Xia, T. A.; Li, Q.; Liu, X. D.; Meng, J. A.; Cao, X. Q. *J. Phys. Chem. B* **2006**, *110*, 2006–2012.

(49) Zakharova, G. S.; Taeschner, C.; Volkov, V. L.; Hellmann, I.; Klingeler, R.; Leonhardt, A.; Buechner, B. *Solid State Sci.* **2007**, *9*, 1028–1032.

(50) Hu, X. K.; Qian, Y. T.; Song, Z. T.; Huang, J. R.; Rao, R.; Xiao, J. Q. *Chem. Mater.* **2008**, *20*, 1527–1533.

(51) Wang, G.; Ji, Y.; Zhang, L. H.; Zhu, Y. M.; Gouma, P. I.; Dudley, M. *Chem. Mater.* **2007**, *19*, 979–981.

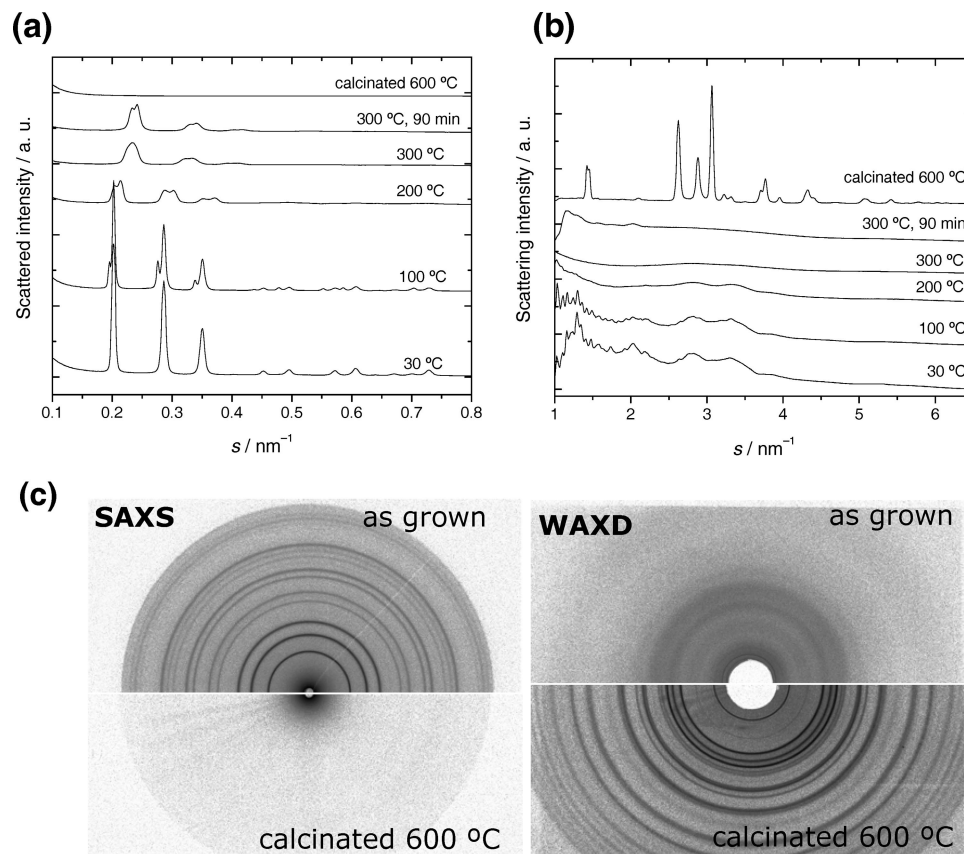
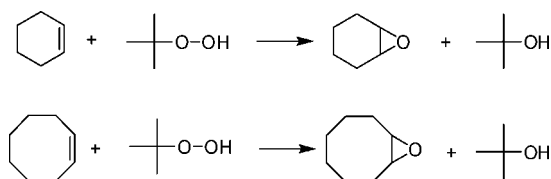


Figure 10. Temperature dependence of the (a) SAXS and (b) WAXD scattering curves of a sample prepared by the sonochemical route in the presence of 200 g L^{-1} of PEO-100k. (c) Experimental SAXS and WAXD patterns on image plates for the sample as grown and after calcination at $600 \text{ }^\circ\text{C}$.

Scheme 2



samples hydrothermally from peroxomolybdate solutions and then treated them with hydrated hydrazine. Hydrazine is a strong reductant, whereas polyoxyethylene should be, if at all, a mild reducing agent. However, the similarity of those results with the ones reported here is remarkable.

The limit for the reduction of the molybdenum was found for samples synthesized at $180 \text{ }^\circ\text{C}$ at very high concentrations of PEO-35k (200 g L^{-1}). XRD patterns of these samples [see Figure 4b] perfectly matched with MoO_2 (monoclinic system, JCPDS card No. 5–452). MoO_2 has been reported to be occasionally found as a byproduct in mixed phases during the synthesis of MoO_3 ,^{47,51} but in this case, MoO_2 was the only phase present. The “thiocyanate test” (formation and extraction of a molybdenum(V)–thiocyanate complex) previously described was negative for these samples, that is, the characteristic deep red-orange coloration was not observed. This observation confirms that most of the molybdenum has indeed been reduced to Mo(IV), which does not form any colored complex with thiocyanate.

Thermogravimetric analysis (TGA) confirmed the contents of water expected from XRD data. From the weight loss, the products corresponding to the triclinic monohydrate could

be assigned a tentative formula “ $\text{MoO}_3 \cdot x\text{H}_2\text{O}$ ” with $x = 0.90\text{--}1.05$. The experimental values of x for the products with XRD peaks coinciding with the hemihydrate ranged from 0.35 to 0.65. The presence of peroxide and possible oxygen deficiencies (MoO_{3-x}) were neglected in these estimations. The thermal decomposition showed essentially a single step for both types of products, being in the range $285\text{--}300 \text{ }^\circ\text{C}$ for the hemihydrate and in the range $225\text{--}240 \text{ }^\circ\text{C}$ for the monohydrate, indicating that the hemihydrate is thermally more stable than the monohydrate polymorph. To illustrate this, we present in Figure 5 the weight loss with temperature for samples prepared in the absence and presence of PEO-35k by using the sonochemical route at $70 \text{ }^\circ\text{C}$ and the hydrothermal route at $180 \text{ }^\circ\text{C}$. It can be observed that samples identified as anhydrous $\alpha\text{-MoO}_3$ by XRD showed a practically negligible weight loss. It is especially noticeable that samples prepared at very high polymer concentrations (200 g L^{-1}) suffer a weight loss of up to 40%, which can only indicate that the polymer is still present in the sample. The washing process with water (or other solvents as ethanol) of these type of samples showed a partial redissolution of the material, and SEM images of powders repeatedly washed clearly indicated a deterioration of the spherical or polyhedral morphology. On the one hand, big aggregates of polymer could not be observed by electron microscopy. On the other hand, the brightness of the particles during analysis by scanning electron microscopy using a back-scattered electron detector showed that their main component could not be simply polymer, because, in this case, darkness and not

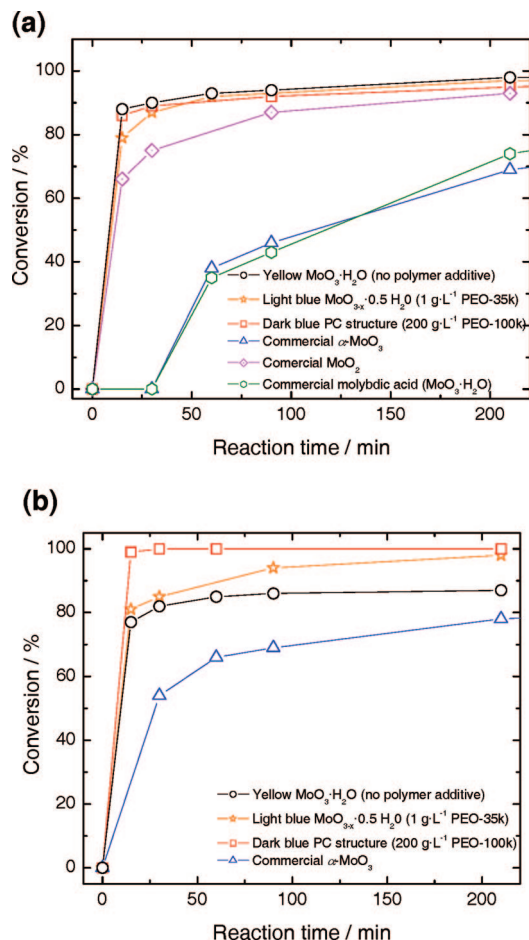


Figure 11. Catalytic conversion of (a) cyclohexene and (b) cyclooctene in the respective epoxide products in the presence of representative synthesized catalysts, compared to commercially purchased molybdenum oxides.

brightness should be observed. In addition, energy dispersive X-ray analysis (EDX) indicated that molybdenum is homogeneously distributed in the spheres (or polyhedra or cubes). The data seem to indicate that some polymer becomes incorporated into the structure, creating hybrid materials with features that are very different from the polymer itself and from conventional molybdenum oxides. The calcination of the samples allow to remove completely the polymer, but it also changes the morphology and structure, as it can be observed in Figure 6. The polyhedra and spheres recrystallize to prismatic, rodlike shapes, which correspond to a crystallographic change to the anhydrous MoO_3 , as described below.

The effect of the polymer concentration on the crystal structure is presented in Figures 7 and 8, considering the case of a batch of samples prepared by the sonochemical route in the presence of PEO-100k. Figure 7 shows the small- and wide-angle X-ray scattering curves, whereas Figure 8 shows the corresponding evolution of the experimental patterns in the image plates used for detection. In the absence and at low concentrations of polymer, no peaks are found at low scattering angles, as expected for a conventional inorganic oxide; at wide angles, the peaks showed the transition from the triclinic monohydrate (in the absence of polymer) to the monoclinic hemihydrate (at low polymer concentrations). SAXS patterns for samples prepared at high

concentrations of polymer ($> 100 \text{ g} \cdot \text{L}^{-1}$) indicate that these products have an unusual primitive cubic (PC) structure with a very large unit cell as reported in a previous work of our laboratory.³⁵ The present experiments confirmed that this uncommon PC structure can be formed in the presence of different POE-containing polymers, as illustrated by Figure 9. To the best of our knowledge, this is the only case of a PC structure known so far for a compound of molybdenum and we have not been able to obtain an analogous cluster with any other polymer not containing ethylene oxide groups. Note the slight but distinct shift toward smaller lattice constants from the sample at $100 \text{ g} \cdot \text{L}^{-1}$ to the one at $200 \text{ g} \cdot \text{L}^{-1}$.

The lattice dimension, d , can be calculated from the position of the reflections ($d = 1/s$), and small differences were observed for different polymers, ranging from $\sim 5.2 \text{ nm}$ for PEG-600 to $\sim 4.8 \text{ nm}$ for PEO-100k, with an intermediate value of $\sim 5.0 \text{ nm}$ for PEO-35k. Although the differences are slight, the tendency observed for the polyoxyethylene homopolymers seems to suggest that the unit cell is compressed when the crystallization occurs in the presence of polymers with higher molar mass. As mentioned above, it exist a limit in the effect of the chain length and the lattice is again slightly larger ($\sim 5.0 \text{ nm}$, data not shown in Figure 9) for the sample prepared in the presence of PEO-600k. This observation is consistent with the apparently unsystematic change in the morphology for larger molar masses shown in the micrographs of Figure 2.

A compression of the lattice constants during polymer-controlled crystallization of inorganic materials has been reported for other systems, such as zinc oxide or calcium carbonate, although one has to be cautious with direct comparisons with this systems, as the variations in the lattice constants are in a different scale (tiny fractions of an ångström in zinc oxide and calcium carbonate and more than a full ångström difference in our case). In the case of zinc oxide precipitated in the presence of latex additives, the compression has been assigned to the strain exerted by crystalline defects, which is considered to be an indirect effect induced by the polymer.⁵² Similarly, Pokroy et al.⁵³ found a compression of the lattice parameters of biological calcite (grown in nature in the presence of biomacromolecules), when compared to geological calcite. The authors justified this fact by the effect of magnesium impurities in the calcite lattice, pointing out that magnesium incorporation led to a compression of the lattice. Accordingly, they applied a “correction” and suggested calibration curves relating a and c with the Mg content. These explanations coincide with the suggestions for zinc oxide that point defects can exert a lattice compression. Similarly, in the present case, we can tentatively attribute the compression of the primitive cubic cell of the polyoxomolybdate to the point defects due to low-valence Mo(V) species originated by the polymer-induced reduction of Mo(VI). When the polymer chains are longer, the ratio between ethylene oxide groups (acting as mild

(52) Muñoz-Espí, R.; Chandra, A.; Wegner, G. *Cryst. Growth Des.* **2007**, *7*, 1584–1589.

(53) Pokroy, B.; Fitch, A. N.; Marin, F.; Kapon, M.; Adir, N.; Zolotoyabko, E. *J. Struct. Biol.* **2006**, *155*, 96–103.

reducing agents) and the molybdenum ions is higher and, therefore, the final concentration of low-valent species will be higher, explaining thereby the apparent dependence between the molar mass of the polymer and the lattice compression. This would be an important observation and, to the best of our knowledge, no systematic study has been done correlating the molar mass of polymer additives and the compression of lattice constant of inorganic materials obtained in polymer-controlled crystallization. Therefore, further work will be conducted to demonstrate our suggestion.

The similarity of this structure to that of certain zeolites, albeit in a much larger length scale, seems to be a promising analogy for catalytic applications. However, our experiments have demonstrated that the structure begins to degrade irreversibly at temperatures above 100 °C. Figure 10 shows the evolution of the SAXS and WAXS patterns measured in situ during heating from 30 to 300 °C, and the scattering curves for the same product after calcination at 600 °C. While heating, the product was converted to the most stable form of MoO₃, the anhydrous orthorhombic phase, and the PC structure was completely destroyed.

Catalytic Potential of the Materials. Molybdenum catalysts obtained from the dissolution of molybdenum metal by hydrogen peroxide have been successfully applied as catalyst of different alkenes.^{54,55} To study the potential application of the materials in catalysis, we used the as-grown products for the catalytic epoxidation of two cyclic olefins, cyclohexene and cyclooctene, with *t*-butyl hydroperoxide (Scheme 2).

As representative catalysts, we applied two materials prepared by the sonochemical route: a light blue powder with fibrous morphology prepared in the presence of 1 g L⁻¹ of PEO-35k (labeled further on as CAT-1) and a dark blue primitive cubic material obtained at a concentration of PEO-100k of 200 g L⁻¹ (CAT-200). We have compared the results with those of the yellow powders analogously obtained in the absence of any additive (CAT-0). As reference catalysts, we have also used commercially purchased molybdenum oxides: MoO₂, MoO₃, and molybdic acid (MoO₃·*x*H₂O). Under the reaction conditions (70 °C and chloroform as a solvent), the epoxides were formed without any byproducts (i.e., ≥99% selectivity), as judged by ¹H NMR. Figure 11 presents the conversion of the two olefins in the presence of the selected catalysts. The reaction runs faster and with a significant higher yield in the presence of the materials obtained from the peroxomolybdate precursors, when compared with the commercial molybdenum oxides. In the cyclohexene epoxidation, an induction time is required for the commercial MoO₃, but not for our products. The efficiency of MoO₂ is shown to be higher than that of MoO₃. Therefore, and taking into account the reducing effect of polyoxyethylene, the comparison between the efficiency of crystals obtained in the absence of any polymer (the yellow catalyst, CAT-0) and in the presence of the polymers (the blue catalysts, CAT-1 and CAT-200) is of special importance. In the epoxidation of cyclohexene, the conversions

are, within the limits of error, very similar for both yellow and blue powders. This result may suggest that the remaining peroxy groups present in our catalysts (blue and yellow powders) positively influence the development of the reaction and may be more important than the presence of reduced molybdenum species. However, the differences are significantly more pronounced for the cyclooctene. In this case, the blue powders precipitated in the presence of polymer are more efficient than those precipitated without additive. When the primitive cubic catalyst (CAT-200) is used, the reaction is almost fully completed after a few minutes, which proves the great catalytic potentiality of the materials. The large surface and porosity of these type of products, reported in previous work,³⁵ can explain the high efficiency.

A decolorization of the reaction medium was observed for the blue catalysts, CAT-1 and CAT-200, being especially noticeable for the latter, which indicates an oxidation of the subvalent molybdenum to Mo(VI). In addition, CAT-200 seems to partially dissolve or degrade during the reaction. The change of color and the apparent degradation could suggest that the material is not a true catalyst, but rather a reagent, which would imply that they are not reusable. It could be argued that the as-grown products are not “true” catalysts, but rather a precursor of another species that acts as the actual catalyst. However, this does not change in any way the usefulness or high efficiency of these materials. The exact mechanism of the olefin epoxidation in the presence of molybdenum and molybdenum peroxide complexes is a controversial matter and has been largely debated,⁵⁶ but it is of secondary importance in the context of the present paper. To prove the turnover of the catalyst, the powders were separated after the reaction and successfully reused for several times. After four reaction cycles of 3.5 h, the catalytic conversion of cyclohexene in the corresponding epoxides was more than 90% for CAT-1 and more than 80% for CAT-200, which demonstrates the reusability of the catalysts.

Conclusions

Polyoxyethylene-containing polymers are shown to play a double role in the crystallization of molybdenum oxides from peroxomolybdate aqueous solutions: they act both as reducing agents of the molybdenum metal ions, leading to mixed-valence oxides characterized by a blue color, and as structure-directing agents, changing not only the morphology of the resulting crystals, but also the structure of the crystal lattice, as judged from the different crystal phases found. The polymer appears to influence the arrangement of the water molecules and, therefore, the hydration state of the products. Thus, under similar conditions (typically at 70 °C), a fibrous monohydrate triclinic trioxide with remaining peroxy groups (tentative formula: MoO_{3-x}(O₂)_x·H₂O) is obtained in the absence of any additive, whereas in the presence of the polymers, the products crystallize in a hemihydrate monoclinic phase (MoO_{3-x}(O₂)_x·¹/₂H₂O) with rodlike morphology. Crystallization at higher temperatures and pressures (precursor solutions autoclaved at temperatures higher than 90 °C) resulted in materials whose X-ray

(54) Goto, M.; Goto, S. *J. Mol. Catal.* **1990**, *57*, 361–366.

(55) Kurusu, Y.; Masuyama, Y.; Saito, M.; Sakuyuki, S. *J. Mol. Catal.* **1986**, *37*, 235–241.

(56) Thiel, W. R.; Priemeier, T. *Angew. Chem.* **1995**, *107*, 1870–1871.

diffraction patterns could usually be matched with those of the thermodynamically stable form of molybdenum trioxide, the anhydrous orthorhombic $\alpha\text{-MoO}_3$. However, the blue coloration of some of the powders clearly indicates an oxygen deficiency and the presence of Mo(V) and/or Mo(IV).

Very high concentrations of polymer at $T < 90$ °C lead to a very unusual primitive cubic structure with a large lattice constant (ca. 5 nm, the exact value varies slightly with concentration and molar mass of the polymer). From its structure, dark blue color, and solubility in water, this primitive cubic phase can most likely be considered to be a polyoxomolybdate. It was demonstrated that the primitive cubic structure degrades irreversibly after calcination to anhydrous $\alpha\text{-MoO}_3$. At 180 °C (hydrothermally in an autoclave) and high concentrations of polymer, the resulting product was identified as MoO_2 and the primitive cubic phase was not observed.

The structural diversity described has been shown to occur in a very similar way for different polymers containing polyoxyethylene groups, including homopolymers of different molar mass, a polyoxyethylene alkyl ether, and a more complex triblock copolymer. This seems to indicate that the reducing effect of the polymer, rather than its chain length and structure, is the most crucial factor in the formation of the crystal structures. However, the chain length appears to influence the lattice constants of the materials, which is attributed to the compression exerted by the point defects introduced by the presence of the polymer.

The application of representative samples as catalysts for the epoxidation of cyclic olefins (cyclohexene and cyclooctene) by *tert*-butyl hydroperoxide, taken as an example reaction, was successful, demonstrating the potential application of such materials in catalysis. In all cases, the materials showed conversions higher than 95% after 210 min, clearly superior to conventional commercial molybdenum oxides, and with an absence of any detectable byproduct. The epoxidation of cyclooctene showed a very clear difference in the efficiency of the catalysts crystallized in the absence and in the presence of polymer. When the dark blue materials (primitive cubic structure) obtained at high polymer concentrations were applied, the reaction was practically completed after few minutes, which can be explained by the porosity of these zeolite-like materials, in addition to the mixed-valence nature of the molybdenum ions. On the other hand, catalysts synthesized without polymer required longer times and yielded a lower cyclooctene conversion.

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