Control of ZnO Crystallization by a PEO-*b*-PMAA Diblock Copolymer

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Introduction

Some physical properties of crystalline materials such as the brilliance of color pigments or the dielectric function of electroceramics depend on crystal habit, grain size, grain size distribution, impurities, or content of polymorphous modifications. Control of nucleation, crystal growth, and organization of crystals to a superstructure ("texture") make these physical properties tuneable and are thus important for technical applications.

Biominerals such as calcite ($CaCO_3$ in shells), apatite [$Ca_5(OH,F)(PO_4)_3$ in bones] or even magnetite (Fe_3O_4 in bacteria) are crystallized by living organisms under ambient conditions. The growth of these minerals is regulated to optimally fit their functions as materials.[1] The growth control is achieved by interaction of nuclei and growing crystals with biopolymers acting as surfactants, usually peptides and glycopeptides.[2] Consequently, one major approach to influence nucleation and crystal growth is to mimic natural processes. For that purpose, the effective substances are isolated, and they or their derivatives are used as admixtures for in vitro mineralization experiments.

A second major approach is of a purely empirical nature: common surfactants are added to examine their effect on crystallization. Among the often-used reagents are polyelectrolytes.[3−7] Selected polyelectrolytes have been used to reduce the rate of crystal growth[8] or to change crystal habits.[9] A disadvantage of the trial-and-error strategy lies in the large number of hardly predictable experiments necessary to receive a polycrystalline material with desired properties. If there were admixtures with tuneable properties, experiments would become more predictable and their number could be drastically reduced. Diblock copolymers (DBCPs) are in principle substances that may serve that purpose.[10] They can be prepared reproducibly by anionic polymerization; functionality of the repeat units, overall chain length, degree of polymerization (DP) of the single blocks, and ratio of DPs are all adjustable parameters. DBCPs have already proved to be highly efficient dispersants for oxide and nitride ceramic powders.[11] There, the particles are stabilized by a mechanism specific for DBCPs: One block of a DBCP is adsorbed to the solid particle surface ("anchor block"). The other block forms a layer of a swollen polymer ("solution block" or "buoy block") bound to the same surface via the anchor blocks. The solution block thus forms a steric shield, which prevents particles from agglomeration. Reverse micelles of amphiphilic DBCPs have been used as microreactors for the preparation of nanocrystalline noble metals and oxides.[12] The study of effects that DBCPs may have on crystallization processes is thus a step to achieve tuneable admixtures to tailor polycrystalline materials.

Materials

Here, the crystallization of zinc oxide from an aqueous medium in the presence of poly(ethylene oxide)-*block*-poly(methylacrylic acid) (PEO-*b*-PMAA) is studied as a model case. Polycrystalline zinc oxide ZnO is used, e.g., as activator in the vulcanization process, as UV-absorbing and fluorescent pigment, in varistor ceramics, surface wave filters, gas sensors, or, doped with copper, as catalyst for partial oxidations.[13,14] The physical properties and therefore the applicability of functional materials based on ZnO strongly depend on grain size and dispersity as well as type of contacts among grain boundaries.[15] The wurtzite type crystal structure of zinc oxide (mineral: zincite) consists of hexagonally close-packed oxygen atoms, with zinc atoms occupying half of the tetrahedral interstitial sites.

Most of the ZnO used in technical processes is prepared by oxidation of zinc in a vapor-phase process ("French process" or "American process"[13]). Other techniques to obtain ZnO also work at elevated temperature or at high pressure.[15−17] Nanocrystalline ZnO may be prepared by hydrolysis of organometallic compounds.[18] ZnO may, however, also be prepared by precipitation from aqueous solutions of zinc salts at temperatures below 100 °C.[19,20] Spherical crystallites have already

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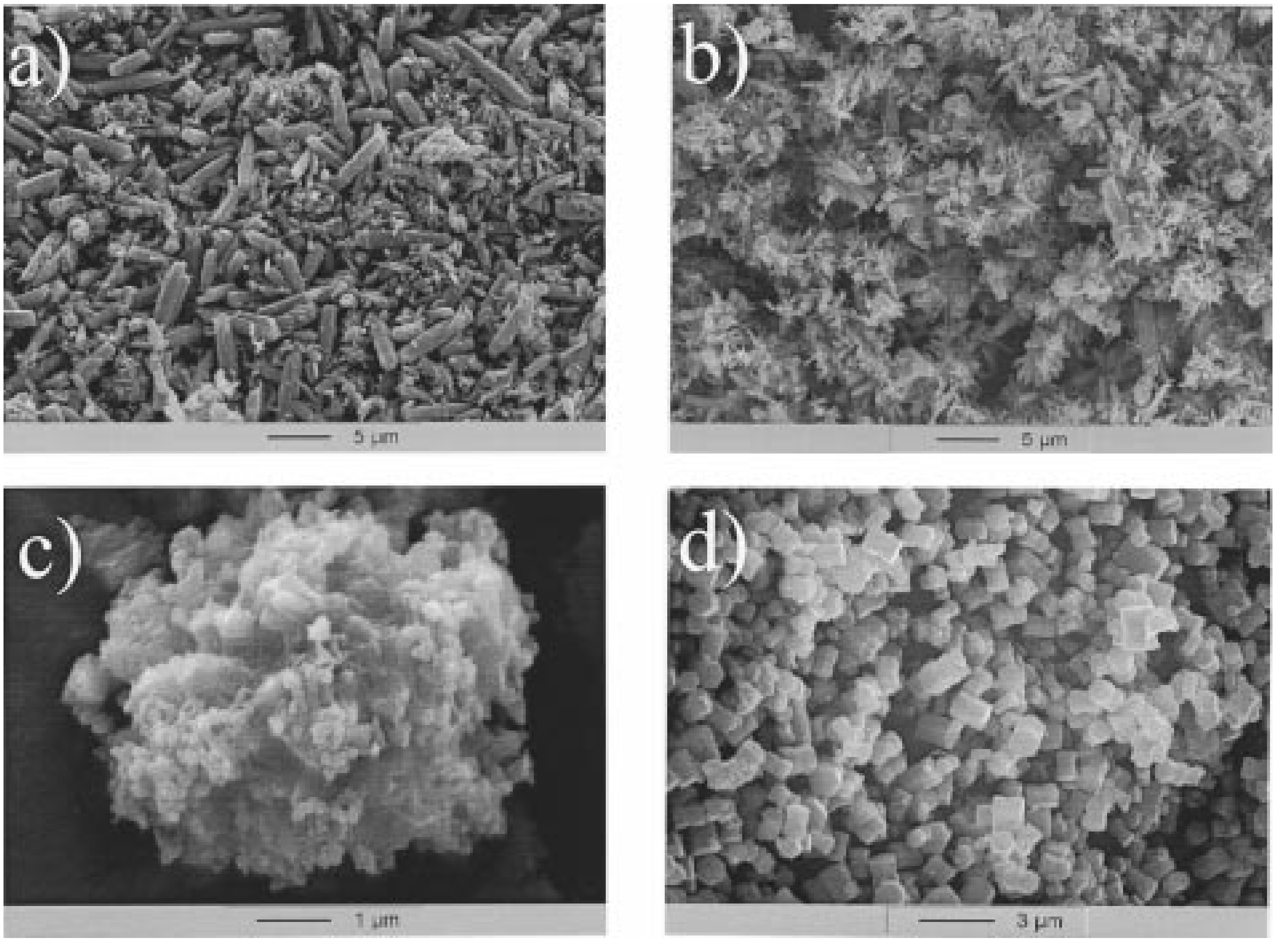

Figure 1. SEM micrographs of ZnO crystals grown from aqueous solution in the presence of (a) no admixtures, (b) 60 ppm poly(ethylene oxide) (PEO), (c) 60 ppm poly(methacrylic acid) (PMAA), (d) 60 ppm poly(ethylene oxide-*block*-methacrylic acid) (PEO-*b*-PMAA).

Table 1. Characteristics of the Polymers

polymer	DP^a	$M_n{}^c$ [g/mol]	source
PMAA^b	93	8000	MPI-P
PEO^b	182	8000	MPI-P
PEO-*b*-PMAA^b	68:8	3700	Th. Goldschmidt AG, Essen, Germany

[a] Degrees of polymerization, in the case of DBCP, the first number refers to the PEO, the second number to the PMAA block. [b] PMAA: poly(methacrylic acid); PEO: poly(ethylene oxide). [c] Determined by gel permeation chromatography (GPC), calibration with PMAA as standard (Polymer Standard Service, Mainz, Germany).

been grown with the aid of low molecular weight surfactants.[21]

In this work, crystalline ZnO was prepared by hydrolysis of zinc nitrate in the presence of polymers in aqueous solution. The pH was adjusted by in situ decomposition of hexamethylenetetramine (HMT). The solid product was analyzed by X-ray powder diffractometry. All samples consisted of zincite. The particle morphology in the absence and presence of polymers was examined by scanning electron microscopy (SEM) as shown in Figure 1. Lengths and widths of the crystallites were determined as defined in Figure 2.

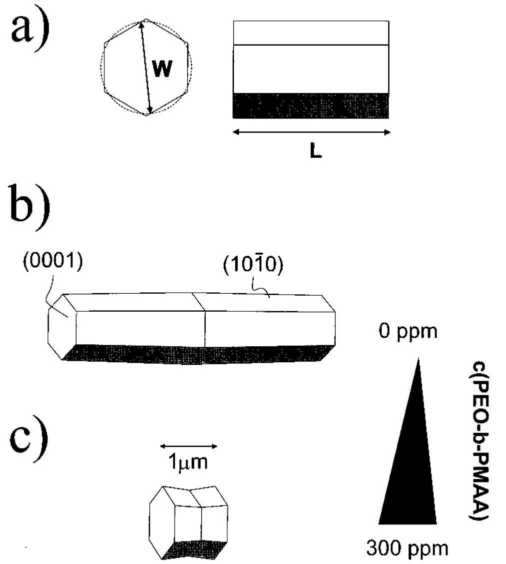

Figure 2. Schematic representation of crystal shapes. (a) Definition of length and width of hexagonal prismatic crystals used to determine crystal size distributions. (b) ZnO grown without admixtures compared to (c) ZnO grown in the presence of poly(ethylene oxide-*block*-methacrylic acid) (PEO-*b*-PMAA).

Poly(ethylene oxide) (PEO) and poly(methacrylic acid) (PMAA) were chosen as components of the DBCP. Both homopolymers are soluble in water. The DBCP can be prepared via a route involving anionic polymerization.

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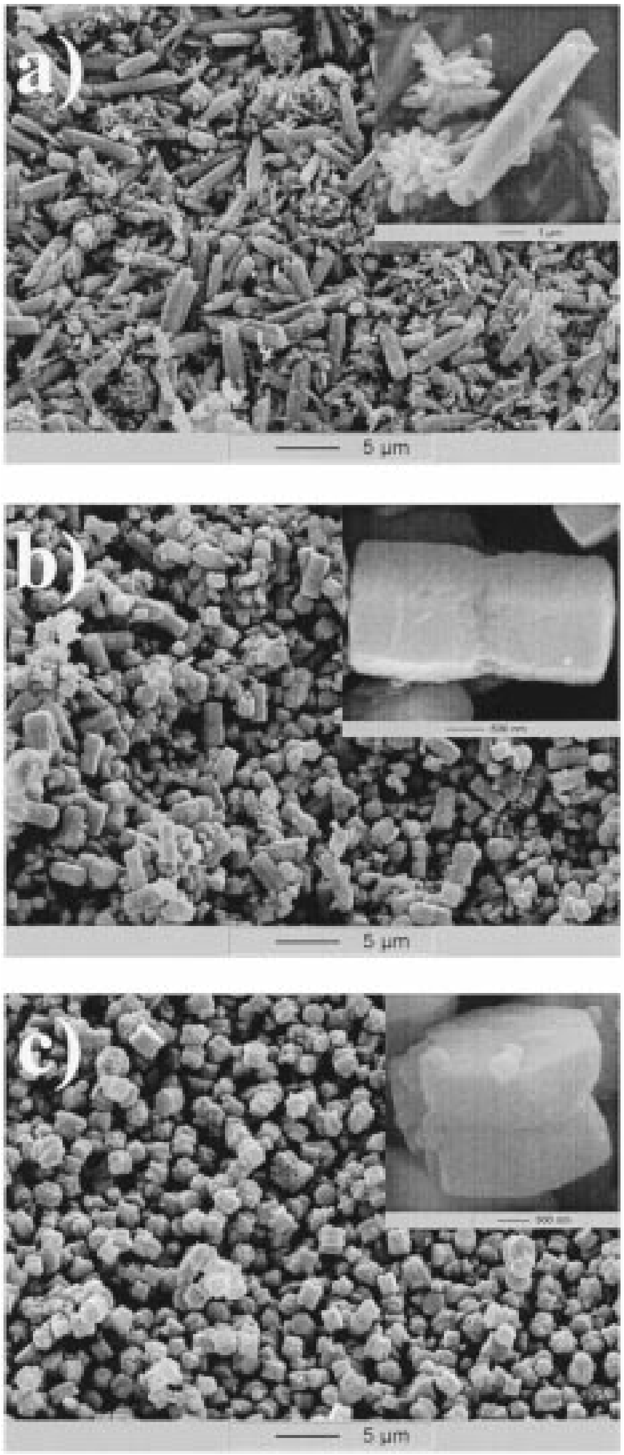

Figure 3. SEM micrographs of ZnO crystallites grown with admixtures of poly(ethylene oxide-*block*-methacrylic acid) (PEO-*b*-PMAA): (a) 0, (b) 60, and (c) 300 ppm.

The carboxylic groups of the PMAA block should interact more strongly with cations and oxidic surfaces than the ether groups of the PEO block. The characteristics of the polymers used in this study are listed in Table 1.

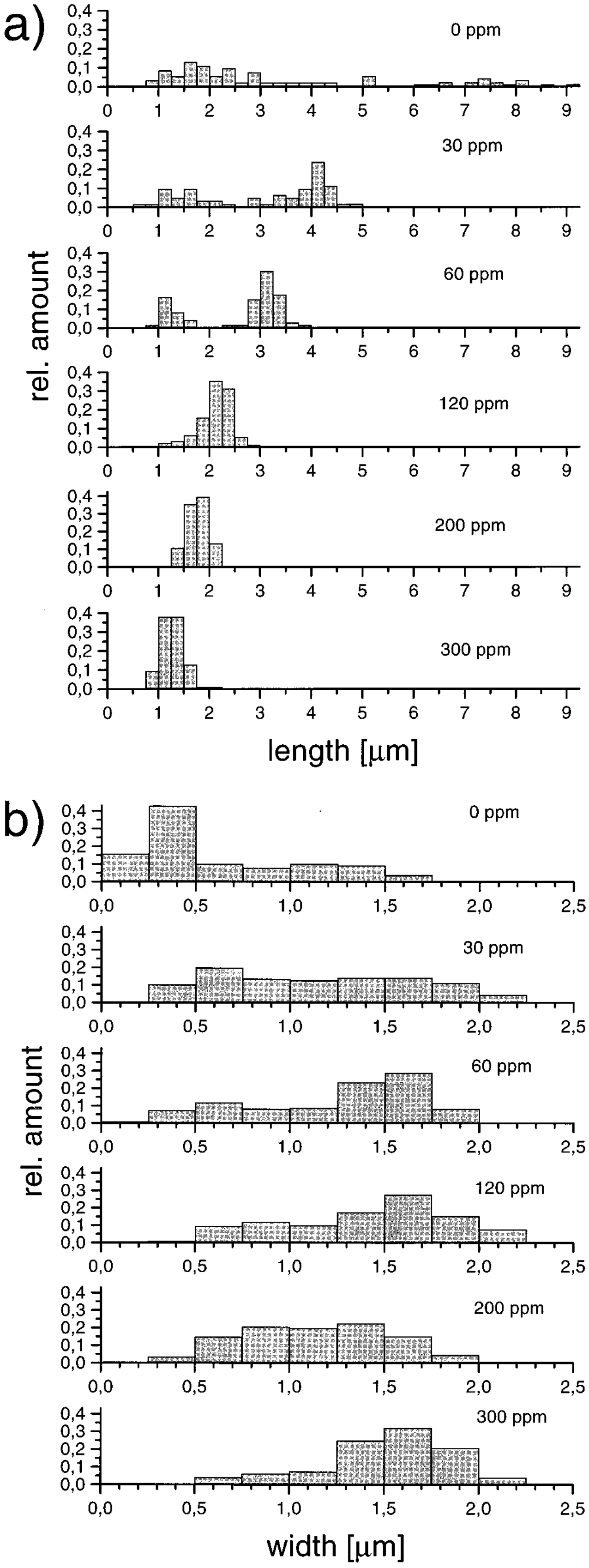

Figure 4. Distribution of crystal lengths (a) and widths (b) of hexagonal prismatic ZnO crystals related to the concentration of the admixture (PEO-*b*-PMAA).

Experimental Section

Zinc nitrate solutions ($Zn(NO_3)_2 \cdot 6H_2O$, Aldrich) were mixed with HMT and polymer solutions at room temperature. Under these conditions, no ZnO is formed. The final concentrations of zinc and HMT were 0.03 mol/L, the polymer concentration in solution was kept at 60 ppm, and for the study of possible effects of polymer concentration on crystallization it was varied from 30 to 300 ppm. Before annealing, the pH of the mixtures was adjusted to 3 by the addition of nitric acid. Crystal growth experiments were made in water-jacketed cells of 100 mL capacity at a temperature of 94 ± 0.5 °C. A magnetic stirrer was used to gently agitate the solution. The experiments were conducted for 45 min. At the end of the reaction time the suspensions of zincoxide were rapidly cooled to room temperature and filtered through a membrane of cellulose acetate/cellulose nitrate with a pore size of 0.22 μm. The residue was washed with deionized water and dried in vacuo at 50 °C. The precipitates were characterized with an optical microscope (Zeiss), SEM (JEOL, JSM-6400 F), and by X-ray powder diffraction (Philips).

Results and Discussion

Crystallization of ZnO without any admixtures results in elongated hexagonal prismatic crystals (Figure 1a). Their equators are wider than the basal hexagonal pinacoids ({0001} faces, see Figure 2).

Addition of PEO influences neither morphology nor dispersity of the growing crystallites (Figure 1b). In the presence of PMAA, crystallites without a uniform habit form agglomerates apparently interconnected by polymer (Figure 1c).

If, however, the block PEO-*b*-PMAA is added, several effects become evident:

(a) The crystals grow shorter along their 6-fold screw axis with increasing polymer concentration, the prismatic $\{10\bar{1}0\}$ faces are truncated perpendicular to [001] (Figures 1d and 2).

(b) The width of the crystals as defined in Figure 3 is less affected by the polymer admixture but grows somewhat larger with increasing concentration of the additive.

(c) The aspect ratio (L/W) is thus strongly dependent on the concentration of the block copolymer and becomes smaller as the polymer concentration increases. Whereas elongated prisms are obtained at the lowest polymer concentration of 30 ppm, almost flat hexagonal prismatic platelets are formed, if 300 ppm of the polymer is added.

(d) The most dramatic effect is seen when the histograms displayed in Figure 4 are considered. Figure 4a shows the length distribution as affected by the polymer concentration, Figure 4b the distribution of widths. The strong decrease of the width of the distribution in the lengths of the crystals as the polymer is added hints for a retardation of crystal growth perpendicular to {0001} faces (the basal hexagonal pinacoids). For the distribution of crystal widths narrowed, too, we also assume a change in the mechanism of nucleation from thermal (no polymer present) to athermal nucleation (polymer added at concentrations above 100 ppm). Here we follow the nomenclature suggested by ref 22. The presence of the polymer thus leads to rather narrow and homogeneous particle size distributions. This is immediately evident to the eye when comparing Figure 1d with Figure 1a−c.

From the observations given above, we deduce a first simple model of the interaction of PEO-*b*-PMAA with growing ZnO crystals: PEO does not influence the crystallization of ZnO, whereas PMAA interacts strongly with growing crystals of ZnO. Therefore, regarding PEO-*b*-PMAA, we propose a mechanism of adsorption being involved in crystal growth of ZnO which is similar to that leading to the stabilization of ceramic particles (see above). Here, the strongly interacting PMAA serves as anchor block and PEO as solution block. If PMAA is preferentially adsorbed to {0001} faces of ZnO, it will retard crystal growth perpendicular to this face. The steric shielding of the solution block (PEO) prevents crystals from agglomeration, which is observed if a PMAA homopolymer is added instead.

At present it remains unclear where the block copolymer ends up in the course of the crystal growth process.

Preliminary information obtained from thermogravimetrical analysis of the zincite crystals grown in the presence of the DBCP indicate that the polymer is either adsorbed at the crystals or incorporated. The former is to be expected since block copolymers of the type used here are excellent dispersants for metal oxide powders.

In summary, we have demonstrated two very important effects occurring when a PEO-*block*-PMAA copolymer is used as an admixture in the crystallization of zinc oxide from an aqueous solution of a zinc salt, namely (a) control of the habit and (b) control of particle size distribution. We believe therefore that the system investigated and discussed here constitutes a very helpful model system to study effects of polymer admixtures to crystallizing solutions in aqueous media.

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