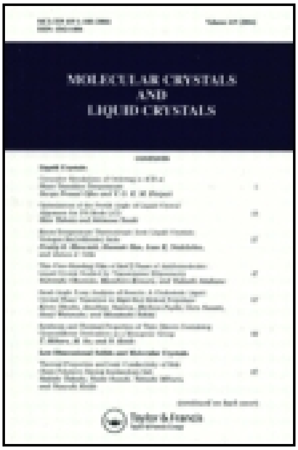

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Control of Crystal Growth Processes by Block-Copolymers

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In crystallization processes from solution, parameters like crystal habit, grain size, grain size distribution, concentration and type of impurities/dopants can be controlled by addition of admixtures.

Amphipolar diblock-copolymers (DBCP's) are shown to have unique effects on crystallization processes from solution.

With poly(ethylene oxide)-*block*-poly(methacrylic acid) (PEO-b-PMAA) as admixture in concentrations in the 100 ppm range, control of nucleation density and crystallization of calcium carbonate ($CaCO_3$) is possible. Crystal growth perpendicular to {hk0}-faces of calcite is retarded, whereas the growth perpendicular to {104}-faces remains undisturbed. In the case of growth of zincite (ZnO), the grain size distribution is narrowed and crystal growth in [001]-direction is slowed down.

To explain the special effect of the DBCP´s on crystal growth, a simple model is proposed.

Keywords: nucleation; block-copolymers; crystal growth; $CaCO_3$; ZnO; PEO-block-PMAA

INTRODUCTION

Crystallization from aqueous solutions provides a low temperature route to ceramic or preceramic materials. Thin films of ceramics for electric or optic devices can be prepared in special cases by this way at temperatures below 100°C with no need of further high-temperature annealing. Interdiffusion of dopants or related phenomena of substance transport can thus be reduced to a minimum extent. Solution growth of crystals can be controlled by addition of admixtures. In biological and technical crystallization processes, polyelectrolytes are widespread as admixtures[1-5]: Peptides and glycopeptides[6] effect the growth of $CaCO_3$ crystals or crystalline layers under ambient conditions in some biological systems, where delicate and highly functional structures are formed[7]. As a technical application, the use of polyelectrolytes, in particular polycarboxylates, to prevent $CaCO_3$ crystals to precipitate from solution needs to be mentioned. Amphipolar diblock-copolymers, where one block consists of a polyelectrolyte, are very effective to stabilize dispersions of ceramic powders like nitrides[1] and oxides[8]. Suspensions of alumina form denser sediments in the presence of PEO-b-PMAA, which is advantageous for the processing of preceramic alumina slurries. The adsorption of DBCP's to surfaces has been described by a model[9]: One block of the DBCP interacts strongly with the solid surface and becomes adsorbed as "anchor block". The other block does not bind to the surface and retains its interaction with the solvent. This "solution block" occupies a certain volume of solution near the interface of the solid. It serves as a steric shield and prevents aggregation and flocculation of the dispersed particles. In the following, the effect of PEO-b-PMAA on the crystallization of $CaCO_3$ and ZnO from aqueous media is considered as further example.

EXPERIMENTAL

The polymers synthesized at the Max-Planck-Institut für Polymerforschung (see Table 1) were prepared by "living" anionic block-copolymerization of ethylene oxide and t-butyl methacrylate. The tBMA block was then converted into a PMAA block by hydrolysis of the ester functions.

TABLE 1 Characteristics of the polymers.

Polymer	DP[b]	M_n[c] [g/mol]	Source
PMAA[a]	93	8000	MPI-P
PEO[a]	168	6800	MPI-P
PEO[a]	182	8000	MPI-P
PEO-b-PMAA[a]	23:8	1700	Th. Goldschmidt AG, Essen, Germany
PEO-b-PMAA[a]	27:27	3500	MPI-P
PEO-b-PMAA[a]	68:8	3700	Th. Goldschmidt AG, Essen, Germany
PEO-b-PMAA[a]	126:17	7000	MPI-P
PEO-b-PMAA[a]	159:8	7700	MPI-P
PEO-b-PMAA[a]	145:61	11600	MPI-P

a) PMAA: poly(methacrylic acid); PEO: poly(ethylene oxide).

b) Degrees of polymerization, in the case of DBCP, the first number refers to the PEO, the second number to the PMAA block.

c) Determined by gel permeation chromatography (GPC) (solvent = THF), calibration with PMMA as standard (Polymer Standard Service, Mainz, Germany).

Calcium carbonate was crystallized from aqueous solutions by mixing three solutions, one of which contained 0.025 mol/l $CaCl_2$ at pH 10, the second was an aqueous solution of the polymer at concentrations typically in the range between 0 and 1,000 mg/l (pH 10), and the third solution contained 0.025 mol/l $NaHCO_3$ at pH 10. When the three solutions had been combined, the mixture was agitated briefly and then allowed to stand for 1 hour to complete crystallization. The precipitate was isolated by filtration through a membrane filter (pore size ≤ 0,22 µm) and washed with deionized water[10].

Zinc oxide (zincite) was crystallized by "homogeneous precipitation"[11,12]. 50 ml of an aqueous solution of zinc nitrate (usually 0.03 mol/l) (containing the admixture) and 50 ml of a solution of hexamethylene tetramine (HMT; usually 0.03 mol/l) were combined at room temperature (r.t.). The pH was adjusted to 3 by a few drops of nitric acid. The mixture was heated rapidly to 94°C while stirring. 90 minutes after the solution had become turbid by a precipitation of small ZnO crystals, further reaction was stopped by cooling the dispersion to r.t. The filtered or centrifuged precipitate was washed with deionized water. The solid product was dried in vacuo at $T \leq 50°C$.

The precipitates were characterized by an optical microscope (Zeiss), field emission scanning electron microscope (FESEM; JEOL, JSM 6400-F) and by X-ray powder diffraction (Philips).

RESULTS AND DISCUSSION

$CaCO_3$

Crystallization of $CaCO_3$ is influenced by PEO-b-PMAA copolymers in two ways[10]:

a) Heterogeneous nucleation at the glass surface of the vessel (scaling) is hindered, so that a smaller number of crystals grow. This effect is not observed, if only the respective homopolymers are added instead of the PEO-b-PMAA copolymer. Whereas pure PEO has no obvious effect on heterogeneous nucleation, pure PMAA tends to form irregularly shaped agglomerates in the presence of Ca^{2+}-ions.

b) Calcite crystals of control samples, which were grown without admixture, as well as calcite grown in the presence of a PEO homopolymer are rhombohedrally shaped. In the presence of PEO-b-PMAA, crystal growth perpendicular to the crystallographic c-axis of calcite (space group $R\bar{3}c$) is disturbed. The crystal habit can be described as "football-shaped" with tips consisting of well developed {104}-faces (see Figure 1). At a scale observable by scanning electron microscopy (here: > 20 nm), no other crystal faces than the {104} faces are visible. Comparing the effect of different PEO-b-PMAA block-copolymers (M_n = 3500, 7000, and 11600 g/mol, respectively; see Table 1), there is a tendency to grow more truncated rhomobohedra (leaner footballs). The lower the degree of polymerization (DP) of the PEO-block, the more intense is this effect. Comparable changes of DP of the PMAA-block, however, did not influence the crystal habit in our experiments.

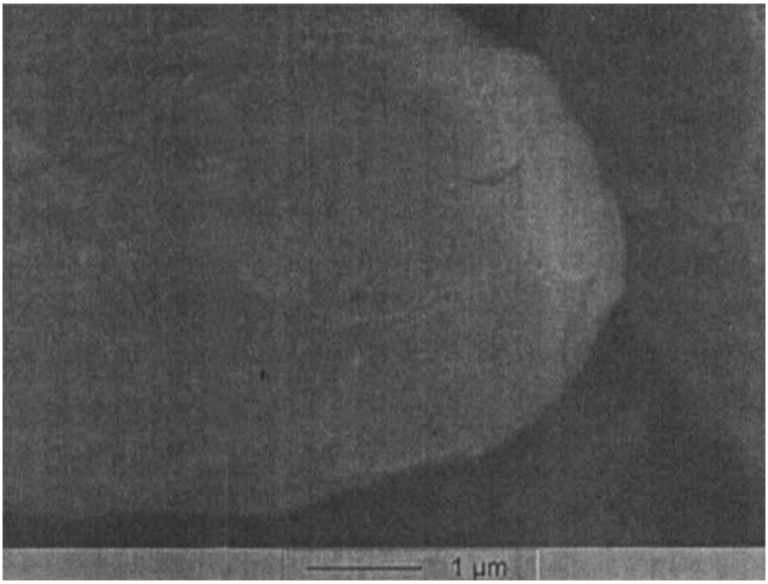

FIGURE 1 Scanning electron micrograph of a tip of a calcite-crystal grown in the presence of PEO-b-PMAA. In contrast to the rhombohedral habit of crystals observed in control samples, here the {104}-faces of regular rhombohedra are truncated to form football shaped species.

ZnO

Powders of ZnO grown without admixtures under the conditions described above consist of hexagonal prismatic crystals with a broad size distribution (0.6 - 9.3 μm)[13]. Similar to the crystallization of $CaCO_3$, crystal growth of ZnO is not influenced by the addition of PEO. With PMAA as admixture, small (< 0.5 μm) globular crystals are observed, the habit of which cannot be described in terms of simple polyhedra. By addition of PEO-b-PMAA, the grain size distribution is narrowed and the crystal lengths (parallel to [001]) become restricted[13]. The widths of the basal pinacoids ($\{0001\}$- or $\{000\bar{1}\}$-faces) are not changed as drastically as the lengths of the crystals, but the size distribution is narrowed, too. The average of the widths is slightly increased. All these effects depend on polymer concentration in such a way that the size distribution grows narrower and the aspect ratio (length/width) of the crystals becomes smaller at increasing polymer concentration[13].

If the DP of the PEO-block is increased maintaining the DP of the PMAA-block, the effect of PEO-b-PMAA on crystallization of ZnO is weakened (see Figure 2). As the total molecular weight of PEO-b-PMAA copolymers is increased from $M_n = 1700$ to 3700 and eventually 7700 g/mol (see Table 1), the average crystal lengths and the widths of the size distribution tend to adopt the values observed in the control samples (ZnO grown without admixtures). It is interesting to note that the absolute concentration of carboxylic groups increases from 0.282 mmol/l in the first to 0.811 mmol/l in the second and to 0.519 mmol/l in the last case. Recent experiments with the latter polymer at higher concentrations of carboxylic groups (1.0 mmol/l) reveal that the aspect ratio of the ZnO crystals is still not as low as in the case of the second polymer shown in Figure 2. Thus , the

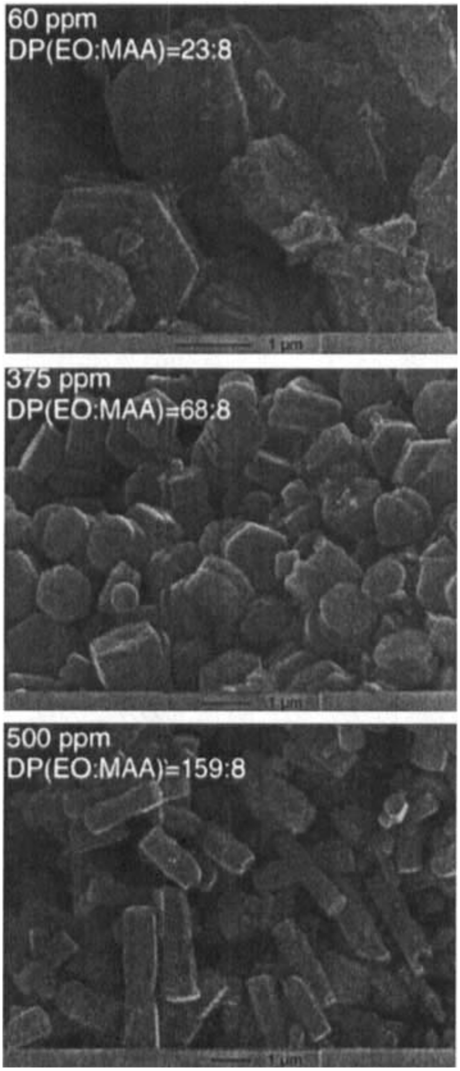

FIGURE 2 Scanning electron micrographs of ZnO powders grown from aqueous solutions in the presence of PEO-b-PMAA copolymers. The higher the degree of polymerization (DP) of its PEO-block, the less intense is the effect of a PEO-b-PMAA copolymer on the growth of ZnO.

observed effects are strongly correlated to both the ratio of the block lengths and the absolute length of the PEO block.

Model

Nucleation and crystal growth of calcite as well as zincite are influenced by adding small amounts of a diblock-copolymer. The effect of these admixtures on crystal growth can be described by a simple model:

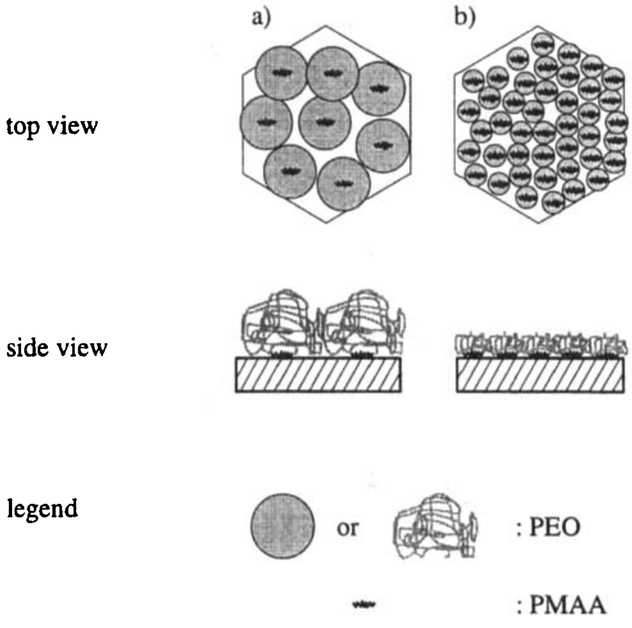

FIGURE 3 Proposed effect of PEO-b-PMAA diblock-copolymers used as admixture on crystal growth of calcite and zincite: The number density of adsorbed anchor blocks (here: PMAA) on a crystal surface is limited by a steric screening by solution blocks (here: PEO): The bigger the solution block [a)>b)], the less block-copolymer molecules can be adsorbed, the less crystal growth is hindered by adsorbed admixture.

Amphipolar diblock-copolymers adsorb to surfaces of solids in a specific manner[8,9]: One block interacts strongly with the surface ("anchor block"), the other block is not adsorbed at all and behaves like a solvent swollen polymer localized near the surface ("solution block"). Extending this theory, one may assume specific interactions of the anchor block with different (growing) crystal faces. The development of $\{10\bar{1}0\}$-faces of zincite and $\{104\}$-faces of calcite are hardly disturbed, the interaction of the anchor block should therefore be less strong as with $\{10\bar{1}0\}$-faces (ZnO) or $\{001\}$-faces ($CaCO_3$). With the experiments with the homopolymers in mind, the anchor block must consist of PMAA in both crystallization processes. Molecular dynamics modelling of the adsorption energies of polymethacrylate ions to the respective crystal faces support this model[10].

The degree of polymerization of the solution block, PEO, plays another important role. The solution block (PEO) occupies a certain space in solution near the surface where the anchor block is adsorbed. The solution block may thus act as a barrier preventing further polymer molecules from adsorbing to the surface. The higher the degree of polymerization of the solution block, the bigger is the area at the surface it is shielding. With bigger solution blocks therefore less anchor blocks can be adsorbed per unit surface area. So crystal growth perpendicular to this surface is less affected by tightly adsorbed anchor blocks (Figure 3).

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