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Polymers Designed to Control Nucleation and Growth of Inorganic Crystals from Aqueous Media

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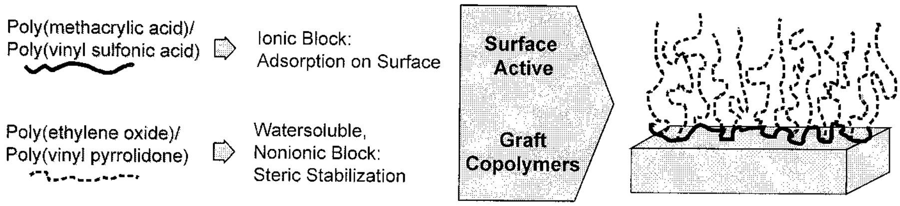
SUMMARY: Water soluble graft polymers prepared by copolymerization of either methacrylic acid (MAA) or vinylsulfonic acid (VS) with α-methoxy-ω-methacroyl-oligo(oxyethylene)s (PEO_n-MA) serve to control nucleation and crystal growth during precipitation of inorganic crystals from aqueous media. Precipitation of zinc oxide crystals ('zincite') is used as example for such mineralization processes. Homogeneous and narrow crystal size distributions are obtained in presence of ppm-amounts of graft copolymers. Copolymer is incorporated into the crystals demonstrated by using latex particles with -CO_2H-group rich surfaces as controlling additives. Incorporation of these particles leads to single crystals with pores of the size of the particles ('Swiss cheese' morphologies).

Introduction

Graft copolymers composed of a hydrophobic and ionogenic main chain and non-ionogenic but water compatible side chains act as dispersants for inorganic particles and powders in aqueous media. Their properties rest on a surface induced segregation between the segments of the main chain and those of the side chains providing an effective steric stabilization of individual particles against coaggulation or aggregation. A schematic scenario is depicted below.



Many attempts have been reported to create such graft copolymers by copolymerization of methacrylic acid or similar monomers and end-functionalized oligo(oxyethylene)s, ('macromonomers') (1-4). The latter give rise to water compatible, non-ionogenic side chains. A-B block copolymers composed of poly(methacrylic acid) and poly(oxyethylene) block have been shown to be very effective as stabilizers of aqueous suspensions of aluminum oxide

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ceramic powders (5) and in the control of nucleation and crystal growth of calcium carbonate and zinc oxide (6,7). The relevant parameters are the block length ratio and the over all molecular weight. Block copolymers were much more effective than the respective homopolymers or random copolymers. Most striking effects have been reported for the precipitation of zinc oxide ('zincite') in the presence of PMAA-PEO block copolymers (7) at a concentration of 100-300 ppm. Depending on block length ratio and overall molecular weight the habit of the crystals could be changed from long and slender hexagonal prisms to flat hexagonal platelets. Moreover, a narrow and mono disperse size distribution of the crystals was achieved in presence of the copolymers. This triggered the question whether graft copolymers exhibit similar effects and whether the polymers become incorporated into the crystals.

Synthesis of graft copolymers

A summary of the types of polymers synthesized and found to be active in control of mineralization is shown in Fig. 1.

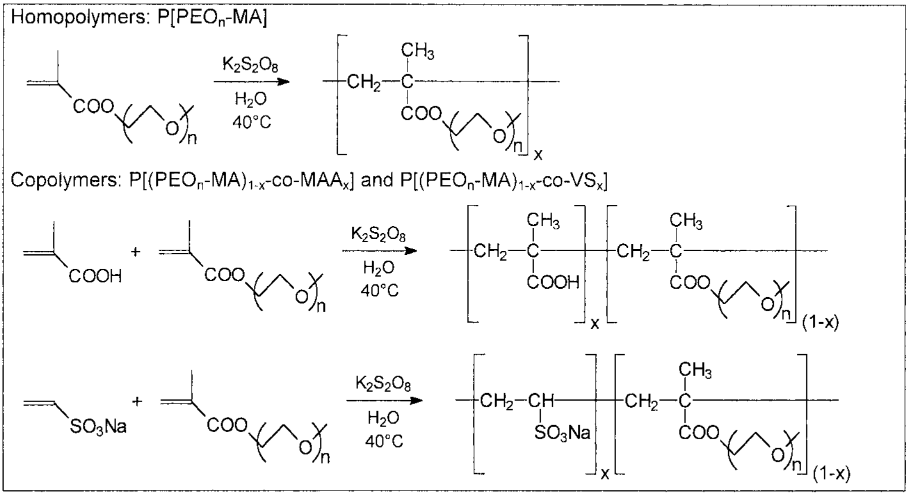

Figure 1. Overview on the synthetic procedure to obtain graft copolymers by the macromonomer route.

α-Methoxy-ω-methacroyl-oligo(oxyethylene)s (PEO$_n$-MA) were synthesized by anionic polymerization of ethylene oxide using methacroyl chloride as the end capping reagent (8). The macromonomers (PEO)$_n$ MA were homo and copolymerized by free radical initiators.

Methacrylic acid (MAA) and vinyl sulfonic acid (VS) were used as co-monomers. The co-polymerizations were carried out in water with potassium peroxodi sulfate as the initiator at 40°C. Mercapto ethanol was necessary as chain length regulator and to prevent unwanted side reactions such as gelation (1-4). Average molecular weights of the graft copolymers measured by membrane osmometry were in the range of $3–10 \cdot 10^4$ (g mol^{-1}) ($60<DP<400$) (8).

Mineralization of zinc oxide

Precipitation of crystalline zinc oxide from aqueous solution of zinc nitrate serves to demonstrate the effects when graft copolymers become involved in nucleation and growth of inorganic crystals. When an aqueous solution of zinc nitrate is heated in the presence of hexamethylene tetramine (urotropine) to a temperature between 70 and 90°C zinc oxide will be formed. Thermal decomposition of urotropine to ammonia and formaldehyde brings the solution to pH6 where zincite starts to precipitate as the only phase (7). The growth features are strongly influenced by the involvement of the graft copolymers. The consequences of a continuous change in chemical composition of copolymer vic. acidic (vinylsulfonic) groups is demonstrated by Fig. 2. The pure homopolymer formed from the macromonomer PEO_{31}-MA ($x=0$ in Fig. 2) has no effect at all. At a mole fraction of $x(VS)=0.26$ short hexagonal prisms (all of the same size) with well expressed (100) faces and central notch are formed. 'Jojo'-formed crystals are obtained in the presence of copolymers with $x(VS)=0.79$. At $x(VS) = 0.89$ the structure evolves as lamellae symmetrically organized around a central spine which entends along the c-axis of zincite. The overall shape of the crystalline particles is spherulitic. Note that the overall concentration of graft copolymer was left constant and what we observe is entirely a consequence of the change in the composition of the copolymer.

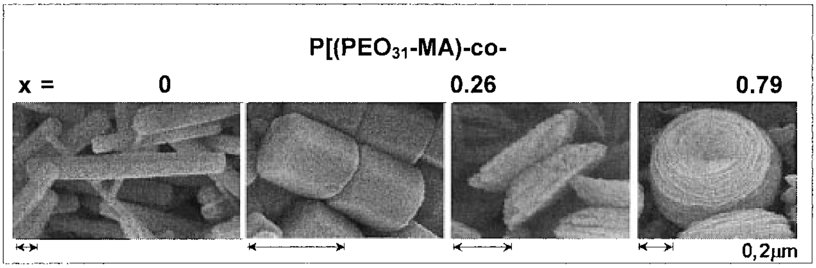

Figure 2. Change of morphology of zincite as induced by changes in the VS-content of the graft copolymers.

Copolymers containing VS-groups are much more active in growth control as their counterparts containing methacrylic acid (MA) groups at the same mole fraction. This is demonstrated by Fig. 3. Whereas 'yo-yo' crystals are seen when the VS-group containing polymer was present, the typical slender hexagonal prisms are formed in presence of the MAA-group containing polymer.

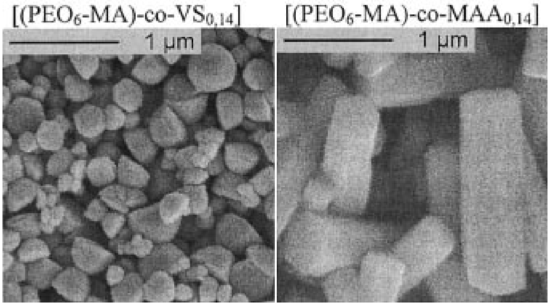
[(PEO$_6$-MA)-co-VS$_{0.14}$] [(PEO$_6$-MA)-co-MAA$_{0.14}$]

Figure 3. Zincite obtained at the same overall concentration of copolymer (120 ppm) but differing in chemical composition.

The effect of the different copolymers on the size and shape of the crystals is also seen from Fig. 4. Here, histograms of the length and width distribution of the crystals obtained in presence of a) a typical MAA-group containing and b) a VS-group containing copolymer are compared with a reference (no polymer). The striking effect of a narrow length and width distribution achieved by the polymer additive is obvious.

Origins of the activity of the polymers

Graft copolymers of the structure described here have similar effects as already known of simple diblock copolymers. Chemical analysis suggests that the polymers become incorporated into the crystals. Experiences and observations made in the study of biomineralization (9,10) are relevant. Combining all available evidence the hypothesis is put forward that the polymers interact reversibly or irreversibly with the growth steps at the surface of the crystals. Adsorption to the steps of growth spirals will poison these sites and thereby retard the crystal growth. This will a) change the shape of the resulting crystal and b) give the less favorable surfaces a chance to grow. The size of the polymer gives rise to a large defect which must be overcome to complete the growth of the plane in which the spirals are active. Eventually polymers may be overgrown which in consequence must give rise to a multiplication of dislocations as new centers of the growth spirals. The process is schematically depicted in Fig. 5a where evidence for the presence of the spirals is seen in Fig. 5b.

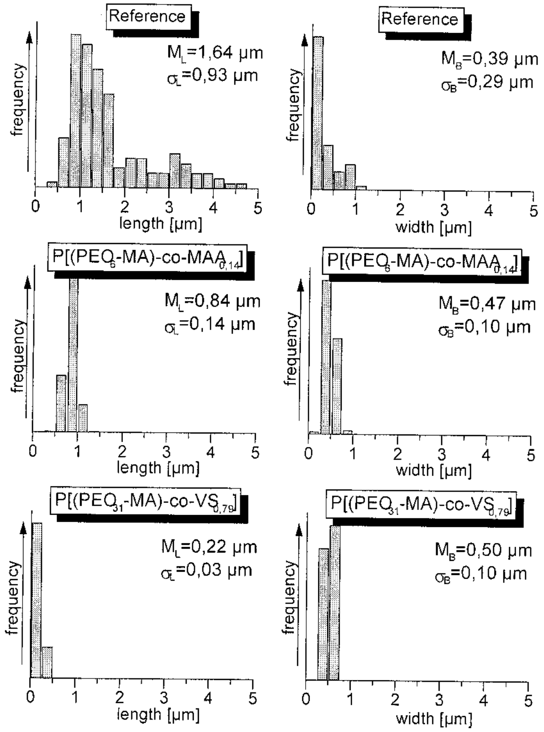

Figure 4. Histograms of length (left) and width (right) distributions of the zincite crystals obtained from a reference (no polymer added) and when two different graft copolymers of the composition indicated in the graph were present at the same concentration (300 ppm) and the same conditions of precipitation.

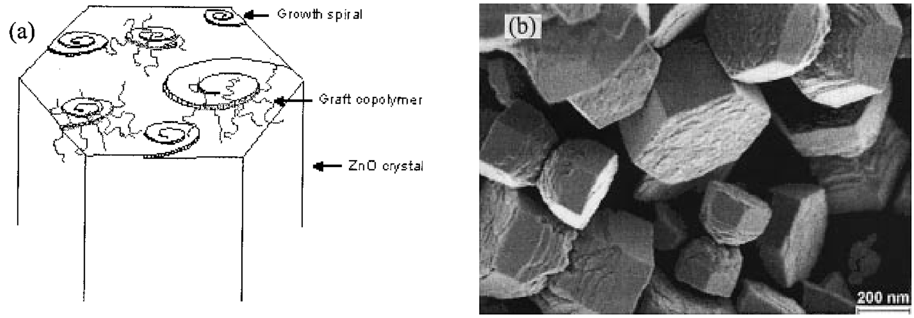

Figure 5. a) Schematic depiction of the poisoning of growth spirals by adsorption of polymer; b) evidence for the presence and multiplication of growth spirals on the basal plane of zincite crystals grown in presence of 300 ppm P(PEO$_{31}$-MA)-CO-VS$_{0.3}$

Incorporation and location of the polymer inside the crystal could be demonstrated when latex particles of 80-160 nm diameter obtained by polymerization of a mini-emulsion (11,12) of styrene and acrylic acid were used as additive. These latex particles have a dense population of carboxyl groups at their surface and interact with the growing crystal species in very much the same way as block or graft copolymers. Homogeneous crystal size distributions are obtained as is visually obvious form Fig. 6. The important fact, however, is that the latex particles can be identified by scanning electron microscopy. If the crystals are washed by a solvent for the latex or heat treated in oxygen to 'burnout' the polymer, holes of exactly the size of the original latex particles remain. Crystals of well-defined 'Swiss cheese' morphology are thus obtained. Depending on the concentration of the latex particles even crystals with a percolating structure of the holes can be prepared.

These results shed a surprising light on effects seen typically in biomineralized materials such as bone and offer much potential for the creation of new materials. They also corroborate the hypothesis put forward in Fig. 5a.

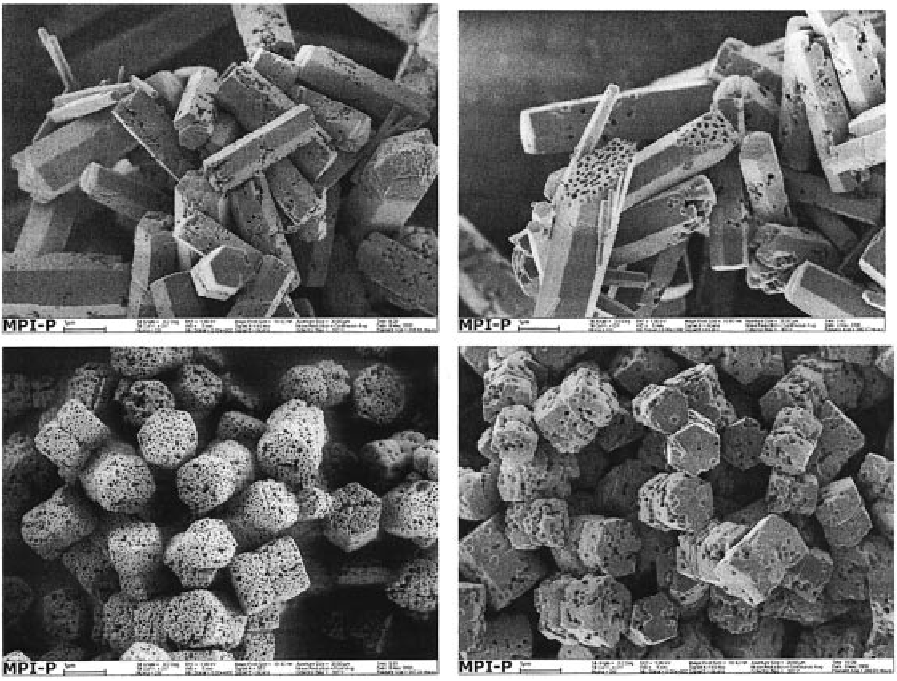

Figure 6. Zincite crystals obtained in the presence of latex particles from polymerization of styrene and acrylic acid in a miniemulsion (11, 12). The concentration was 120 ppm in the upper two and 600 ppm in the lower two samples. Note the 'Swiss cheese' morphology of the single crystals in the upper right micrograph.

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