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A Shape-Persistent Polymeric Crystallization Template for $CaCO_3$

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The formation of biominerals is controlled by organic template molecules resulting in materials with unique shapes and properties. It is believed that the template molecules act as nucleators for the inorganic material and that the surface chemistry of the template induces oriented nucleation of the complementary crystal face.[1] It is easily understood that in such a mechanism the spatial distribution and nature of the charged groups on the template are of great importance. Moreover, the template must be shape-persistent under crystal growth conditions to be invariant during the nucleation stage.[2] Oriented nucleation in synthetic systems has been achieved using monolayers,[3] micelles,[4] vesicles,[5] inverted micelles,[6] and lyotropic liquid crystalline systems.[7] For synthetic polymers, however, it has been difficult to achieve oriented nucleation and to correlate their activity in crystallization assays to the polymer structure since they mostly occur in random-coil conformations.

In a previous contribution we demonstrated that the helical conformation of poly(isocyanides) in solution can be stabilized and rigidified by the presence of secondary interactions, e.g., hydrogen bonds, between the side chains.[8] We reported that for alanyl-alanine-derived poly(isocyanide)s **1** and **2** (Figure 1a) the helical structure persists even in aqueous media. These rigid macromolecules possess a regular distribution of carboxylic acid-terminated side chains which allows the study of the templating processes involved in calcium carbonate mineralization using a shape-persistent polymeric template.[9]

SAXS measurements revealed that in aqueous solution the sodium salt of poly(L-isocyanoalanyl-D-alanine) **1** is present as single macromolecular rods with lengths >100 Å. In the presence of calcium ions, an additional maximum is observed at $\sim s = 2.5 \times 10^{-2}$, indicating that under these conditions the polymer molecules form aggregates with a cross-section of 40 Å. Nevertheless, the addition of Ca^{2+} up to a concentration of 10 mM had no effect on the CD spectrum of the polymer (Figure 1b), indicating the persistence of the rigid helical structure under the conditions used for crystallization experiments (vide infra).[10]

Moreover, whereas in the absence of Ca^{2+} the intensity of the Cotton band at 290 nm over a period of 24 h gradually decreased, indicating a slow unwinding of the helix, in the presence of the calcium ions no such effect was observed. Thus, the presence of Ca^{2+} ions even stabilizes the polymer architecture, probably because complexed calcium ions screen the peptide bonds in the polymer side chains from water molecules, thereby prohibiting the slow, but gradual disruption of the hydrogen bonds.

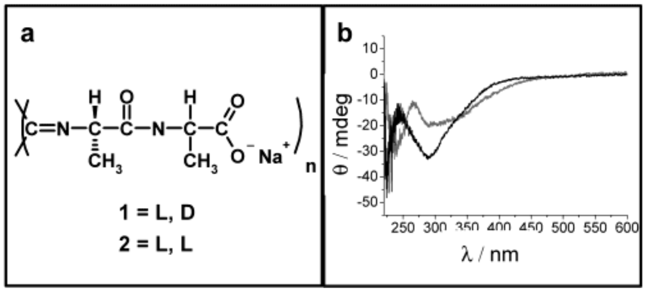

Figure 1. (a) Chemical structures of polymers **1**, and **2**. (b) CD spectra of aqueous solutions of **1**/Ca^{2+}, (black) and **2**/Ca^{2+} (gray); Ca^{2+}/repeat unit = 1:1, [polymer] = 1.3 mM (in repeat units).

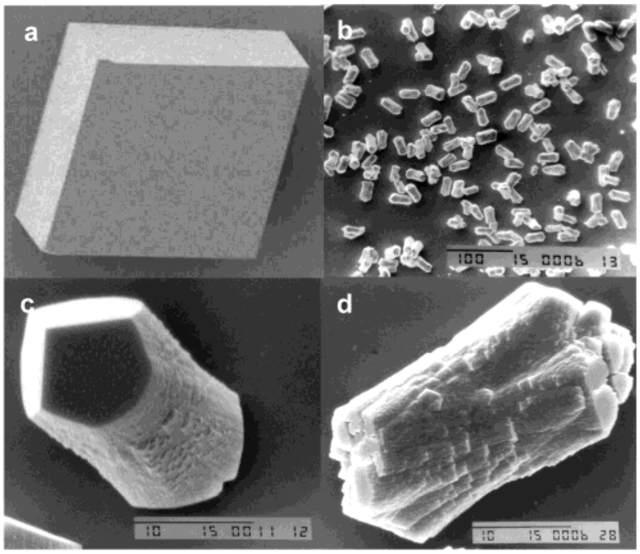

Figure 2. Scanning electromicrographs of (a) calcite grown in the absence of polymer, (b−c) calcite grown in the presence of **1**, and (d) crystals grown in the presence of **2**.

The introduction of polymer **1** into a crystallization solution (Ca^{2+}/repeat unit = 2000/1) resulted in the formation of crystals with apple core-type morphology [dimensions: 28 (± 2) μm × 15 (± 1) μm] which according to FT-IR and PXRD (see Supporting Information) consisted of the calcite polymorph (Figure 2). A nucleation density of approximately 600 mm^{-2} was determined, which is in the range normally observed for Langmuir monolayer templates[11] but significantly higher than nucleation densities found for templates in bulk solution.[12] In addition, no rhombohedral calcite crystals were observed (Figure 2b), demonstrating the effectiveness of the poly(isocyanide) templates in affecting the formation of calcium carbonate. Notably, no effect of molecular weight and polydispersity of the template on the resulting crystals was observed.

The formed crystals were elongated along the crystallographic *c*-axis with three {10.4} end faces expressed on each side of the crystal (Figure 2c). The development of {*hk*.0} growth faces in addition to the end faces is attributed to the nonspecific adsorption of polymer molecules onto these faces, thereby effectively blocking

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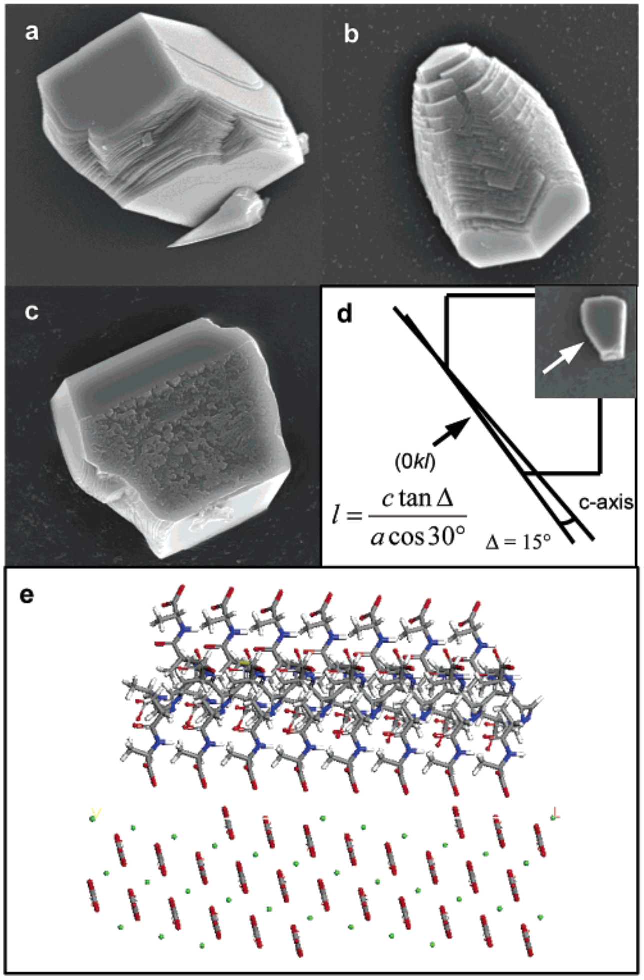

Figure 3. (a−c) Scanning electron micrographs of crystals grown on **1** physisorbed at a glass microscope cover slip. (a) Crystal isolated after 24 h; (b) crystal isolated after 96 h; (c) crystal with exposed nucleated face; (d) indexing of the nucleated face; (e) model of **1** adsorbed to (01.1) calcite showing the orientational match between the carboxylate groups of the template and the carbonate ions in the nucleated crystal face.

growth in these directions and allowing growth only along the *c*-axis. The high nucleation densities, the low spread in size, and the absence of rhombohedral crystals suggest that **1** also acts as an efficient nucleator.

To demonstrate nucleation, glass microscope cover slips were immersed in a polymer solution for 16 h and after rinsing with water placed in a supersaturated $CaCO_3$ solution. Since only polymer physisorbed on the cover slip was present, nucleation was expected to take place at the glass surface. Initially, crystals that still exhibited rhombohedral morphology were formed (Figure 3a). In time, however, the morphologies of the growing crystals changed to resemble those found in bulk solution (Figure 3b), suggesting desorption of the polymer molecules and subsequent resorption onto the growing crystal, thereby affecting its morphology. SEM examination of the crystals revealed a unique roughened nucleating plane that had been attached to the glass slide containing the physisorbed polymer (Figure 3c). This plane was identified by determining the angle between the projection of the *c*-axis and the nucleated plane when viewing the latter and a {10.4} face edge-on (Figure 3d).[13] This angle was determined to be 15°, identifying this nucleating plane to be the (01.1) face of calcite. The expression of this face which has carbonate spacings of 4.05 and 4.99 Å is unusual. Data from molecular modeling calculations suggest that it is unlikely that there is a match between the spacings of the carbonate ions in this crystal face and the spacings between the carboxylate end groups of the polymer. However, models (Figure 3e) suggest that a match between the orientation of the carboxylate groups and the carbonate ions in the (01.1) face is well possible.[14] Attempts to isolate crystals from bulk solution containing nucleated faces were yet unsuccessful.

The specificity of the interaction between **1** and the growing crystal was demonstrated by comparison of the above results with those obtained with L,L-isomer **2**. Polymer **2** has a less well-defined structure as evidenced by its CD spectrum which consists of the superposition of a band at 290 nm and an additional band at 330 nm (Figure 1b). Indeed, crystals grown in the presence of **2**, were less well-defined, both in shape (Figure 2d) and in size [dimensions: 31 (± 4) μm × 14 (± 2) μm]. The PXRD pattern of these crystals contained four additional reflections compared to patterns obtained from crystals grown in the presence of **1** which only exhibited a {10.4} reflection (Figure 2d).

In summary the well-defined structure of poly(L-isocyanoalanyl-D-alanine) **1** has allowed for the first time the investigation of the relation between the structure of a polymeric template and a developing inorganic phase. In this case the formation of calcite is controlled both by nucleation and adsorption processes. The small disturbance of the secondary structure of the polymeric template resulting from a change in the chirality of the polymer is directly reflected in the degree of control over the crystallization process.

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Supporting Information Available: SAXS and PXRD data, CD and IR spectra, pH titrations of **1** and **2**, and experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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