Total Alignment of Calcite at Acidic Polydiacetylene Films: Cooperativity at the Organic-Inorganic Interface

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the main qualitative features of the force distribution at large *v*.

Our results indicate that very strong contact forces in bead packs are exponentially rare. We do not know whether such rare fluctuations could account for the heterogeneous phenomena that motivated our study (*3, 4*), although exponentially uncommon processes are known to dominate certain other stochastic phenomena (*14*). It is also possible that the large boundary effects apparent in our experiments are intimately connected with the unusual dynamic properties of granular media. Further experiments can address these issues and may provide a new level of understanding of these heterogeneities.

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Biological matrices can direct the absolute alignment of inorganic crystals such as calcite. Cooperative effects at an organic-inorganic interface resulted in similar co-alignment of calcite at polymeric Langmuir-Schaefer films of 10,12-pentacosadiynoic acid (p-PDA). The films nucleated calcite at the (012) face, and the crystals were co-aligned with respect to the polymer's conjugated backbone. At the same time, the p-PDA alkyl side chains reorganized to optimize the stereochemical fit to the calcite structure, as visualized by changes in the optical spectrum of the polymer. These results indicate the kinds of interactions that may occur in biological systems where large arrays of crystals are co-aligned.

Biological organisms are capable of controlling inorganic crystal growth to a remarkable degree (*1, 2*). This exquisite control is usually achieved with the use of an organic polymeric "matrix" of highly acidic macromolecules. In certain cases, the minerals that are formed by biological organisms are uniquely oriented or co-aligned relative to the organic matrix (*3*). The in vitro synthesis of novel organic-inorganic composites with properties analogous to those produced by Nature continues to challenge the materials scientist. The use of simplified surfactant molecular assemblies (*4, 5*) resembling biological membranes (for example, monolayers, multilayers, or vesicles) is one approach toward achieving this goal. These structures provide modifiable interfacial functionalization and well-defined spatial organization. A number of elegant examples demonstrate the nucleation and growth of organic (*6*) and inorganic crystals at monolayer assemblies (*7–9*). To our knowledge, the crystals produced by these methods are oriented only in the direction normal to the membrane plane (*8, 9*). The crystal axes in the plane of nucleation do not appear to be aligned with a structural parameter of the nucleation surface.

Previous studies have indicated that stereochemical match between the organic and inorganic interfaces is a predominant factor in determining the specific nucleation face type, in addition to lattice match and electrostatic interactions (*10–12*). One difficulty is that structural information regarding the organic template has so far been obtained in the absence of mineralization at the monolayer [for example, from grazing incidence x-ray diffraction, electron diffraction, and x-ray reflectivity (*13, 14*)], yielding the average spacing between organic functional groups and the two-dimensional unit cell dimensions. Furthermore, it has been suggested that synergistic changes in the organic template structure occur upon interaction with solid interfaces, as is the case when crystals are forming at the hydrophilic head-group region (*12*). In such cases, in situ structural information regarding the organic template is even more elusive as dynamic changes in monolayer organization may occur.

In this report, we demonstrate that cooperativity at the organic-inorganic interface can result in complete alignment of calcite crystals along an identifiable structural feature of the acidic p-PDA matrix. Lattice match between calcite and p-PDA dominates along the *a* axis of the calcite crystal. Symmetry reduction in the p-PDA template coupled with proper stereochemical match ultimately controls the co-alignment of the crystals and determines the nucleation face type. Structural reorientation of the p-PDA matrix occurs upon calcite mineralization to optimize the stereochemical fit. The reorientation is readily observed in p-PDA as a blue-to-red chro-

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