

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

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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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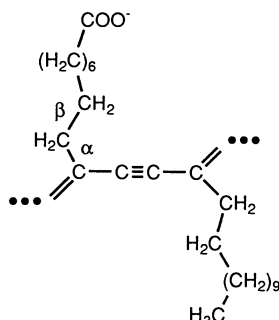
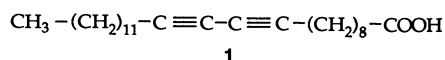
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matic transition in the polydiacetylene film. A more detailed analysis with Fourier transform infrared (FTIR) spectroscopy under mineralizing conditions indicates that rotation of the alkyl side chain about the single bond ( $C_8-C_9$ ),  $\beta$  to the polydiacetylene backbone, may be responsible for the observed color transition (Scheme 1).

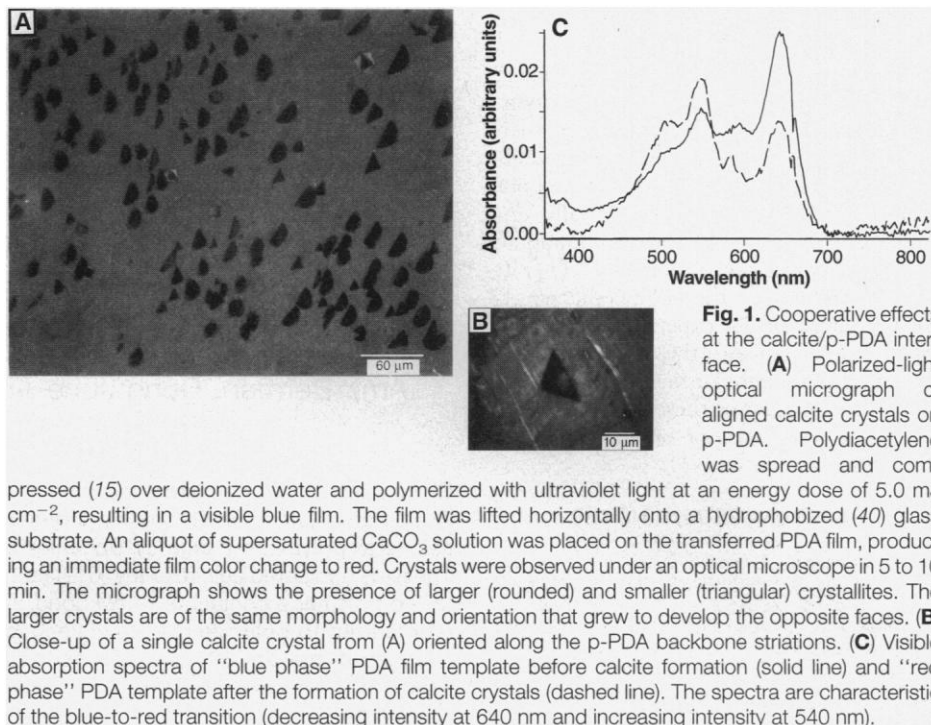
We spread and compressed (15) 10,12-pentacosadiynoic acid (PDA, 1) on the surface of a standard trough. Topochemical polymerization of the diacetylene monomers to the polydiacetylene (p-PDA, 2) was carried out by ultraviolet irradiation (16, 17).

The polymerization mechanism is well characterized and proceeds as a radical stepwise 1,4 addition. The solid-state or topochemical reaction requires that the molecules are regularly packed in a very specific arrangement producing a highly crystalline material with long-range two-dimensional order (17). The crystalline morphology can be readily observed between crossed polarizers in an optical microscope. The p-PDA domain size varied up to 1 mm, although some reports indicate that domains as large as 3 mm can be grown (18). The conjugated backbone of alternating double and triple bonds (ene-yne) gives rise to intense absorptions in the visible spectrum.

The visibly blue films were transferred to hydrophobized solid supports in a horizontal manner, such that the carboxylic acid head groups were exposed at the film–ambient interface (19). Linear striations typical of p-PDA films (18) were observed in the polarizing optical microscope. Calcite crystallization was initiated simply by placing an aliquot of supersaturated  $CaCO_3$  solution on the p-PDA film. The supersaturated solution was prepared by purging stirred aqueous suspensions of  $CaCO_3$  with  $CO_2$  followed by filtration. Two significant phenomena were observed upon calcite formation at the p-PDA films. First, in the regions where calcite crystals were formed, the crystals were all aligned in the same



**Scheme 1.**

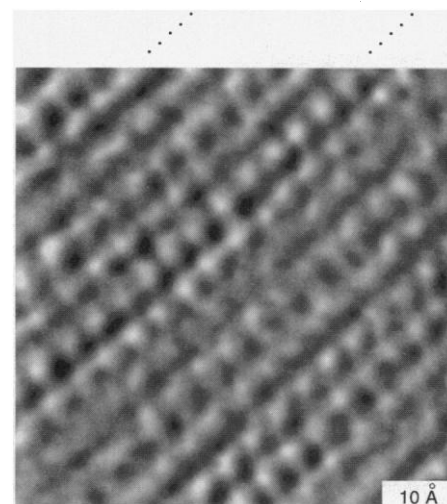


direction within the p-PDA domain boundary (Fig. 1A) (20). The morphological symmetry axis of the crystals were perpendicular to and asymmetrically oriented with respect to the linear striations (Fig. 1B). Second, the initially blue film changed color to red-phase polydiacetylene immediately after the onset of calcite growth (Fig. 1C).

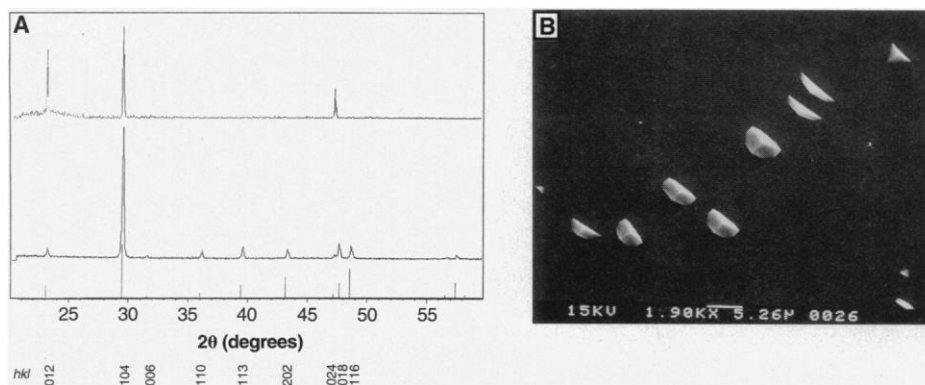
We identified the structural features of the p-PDA film that induce the calcite alignment by atomic force microscopy (AFM). By progressively increasing the magnification (21), we found that the fibrous structures of the p-PDA observed in the optical micrographs (Fig. 1B) persisted down to the molecular scale and correspond to the direction of the conjugated ene-yne polymer backbone (Fig. 2). The asymmetry in the crystal alignment is therefore about the polymer backbone axis. The average periodicity along a given polymer backbone (intrabackbone), as measured from a large number of images (22), was  $4.9 \pm 0.3$  Å, in agreement with reported diffraction data (16, 23) and previous AFM results (24). The interbackbone distance was  $5.1 \pm 0.5$  Å.

For identification of the nucleation face and the absolute orientation of the calcite crystals with respect to the previously defined p-PDA backbone direction, x-ray diffraction and scanning electron microscopy (SEM) were carried out. In the oriented calcite/p-PDA system, reflections of the type (012) were unproportionably intense relative to randomly oriented calcite (Fig. 3A). All other reflections were absent [except for the (104) reflection, which was relatively weak compared to randomly oriented cal-

cite]. Hence, the (012) plane was oriented parallel to the p-PDA membrane plane. The calcite (012) direction consists of alternating layers of calcium and tilted carbonate molecules. The exact angle that the crystal faces were inclined with respect to the film plane was determined by changing the SEM microscope stage tilt (Fig. 3B). The micrographs also enabled identification of the cleavage rhombohedron dihedral angles that determine the direction of the calcite symmetry (c) axis (Fig. 4). Tilt angle measure-



**Fig. 2.** Identification of the polymer backbone direction by atomic force microscopy. Image size: 60 Å by 60 Å. Total load  $F_{tot} = 1.5$  nN with a  $Si_3N_4$  cantilever (spring constant  $k = 0.1$  N m<sup>-1</sup>). The dotted lines indicate the direction of the p-PDA polymer backbone.



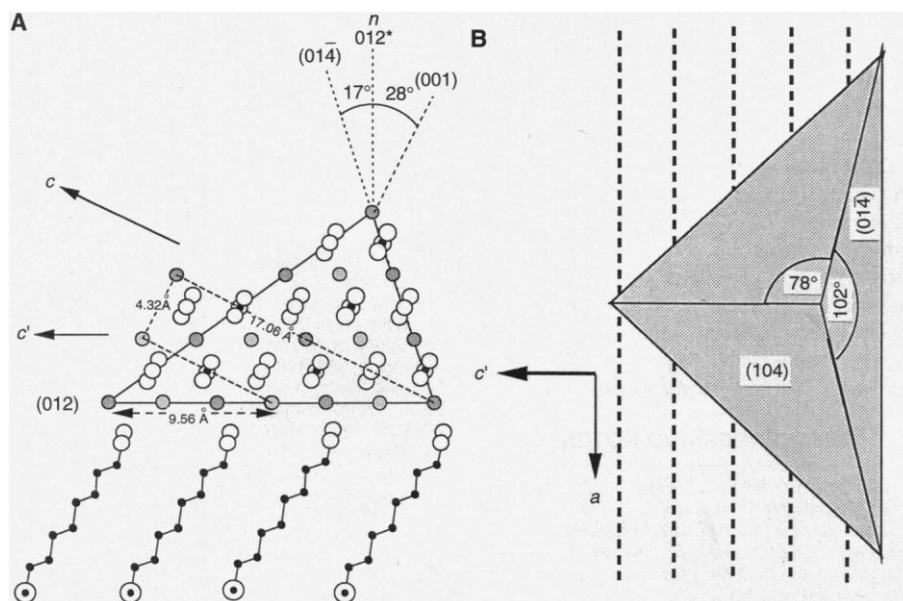
**Fig. 3.** Identification of nucleation face and orientation of calcite with respect to the p-PDA polymer backbone. **(A)** Powder x-ray diffraction was collected on a Siemens powder diffractometer ( $\text{CuK}\alpha$  line; wavelength  $\lambda = 1.54 \text{ \AA}$ ). Axes depict relative intensity versus Bragg diffraction angle ( $2\theta$ ). The Miller indices  $hkl$  of crystal planes associated with the diffraction lines are indicated below each line. Top: Diffraction from (012) uniformly oriented calcite crystals grown on p-PDA template. Middle: Diffraction pattern from randomly oriented calcite powder. Bottom: Calculated positions and relative intensities of calcite powder diffraction pattern. **(B)** Scanning electron micrograph of the (012) uniformly co-aligned calcite crystals. Larger crystals develop opposite faces yielding the rounded shapes seen in the optical micrograph of Fig. 1A.

ments yielded a  $17^\circ \pm 1^\circ$  inclination between the film normal and the (014) face, which confirms the assignment of the (012) basal plane, on the basis of the known structure of calcite (25). The crystal's  $a$  axis [long direction of the (014) face] was perpendicular to the projected symmetry axis ( $c'$ ) and parallel to the polymer backbone direction (Fig. 4B). Both the crystal and the p-PDA polymer had a periodicity  $\approx 5 \text{ \AA}$  along this

direction. The carboxylate head groups of the p-PDA film, therefore, fit closely to the calcite crystal structure along the polymer backbone, completing the coordination sphere around the calcium ions, which would otherwise be occupied by carbonate.

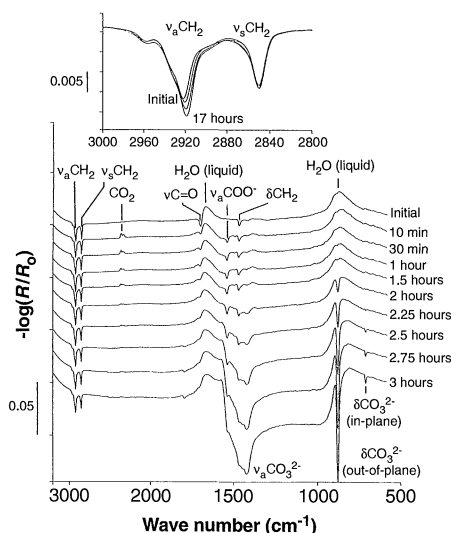
This analysis alone is insufficient to explain the asymmetric orientation of the crystals relative to the polymer backbone. If lattice match alone were important, the cal-

cite crystals would orient symmetrically about this axis. We postulate that reduction of symmetry in the p-PDA film structure induces the observed orientation of the calcite crystals. One such possibility is that the polymer alkyl side chains are parallel to each other and tilted with respect to the polymer backbone axis, resulting in a stereochemical match between the tilted carboxylates of the film and the carbonate of the crystal (Fig. 4A). Previous scanning tunneling microscopy studies of the carboxylate polar head groups of p-PDA on graphite indicate a non-symmetric electron density distribution about the polymer backbone axes (26). The average thickness of a large number of the p-PDA trilayer films used in this study, as measured by AFM, was  $78 \pm 8 \text{ \AA}$ . Given the molecular length of  $30 \text{ \AA}$ , a tilt of  $30^\circ$  from the film normal was calculated, in agreement with previous diffraction studies (16). The  $30^\circ$  tilt of the p-PDA alkyl side chain closely matches the  $28^\circ$  tilt of the carbonate in the (012) direction (Fig. 4A), indicating good stereochemical match between calcite and p-PDA (27). These results are consistent with the absence of the (001)-oriented calcite on p-PDA. Although the chemistry of the (001) face was similar to that of (012) (alternating layers of calcium and carbonate), the carbonate in the (001) direction is parallel to the plane and therefore stereochemically mismatched to the p-PDA structure. The data indicate that lattice match dominates along the  $a$  direction. Stereochemical registry coupled to symmetry reduction in the p-PDA template dominates the interactions in the  $c'$  direction and appears to ultimately be responsible for the co-alignment and unidirectionality of the crystals with respect to the polymer backbone. The color changes observed upon calcite mineralization suggest that while the p-PDA may be preorganized into the  $30^\circ$  tilted structures, further reorganization of p-PDA occurs, most likely to optimize the specific stereochemistry of the carboxyl group. Color changes in polydiacetylenes have been shown experimentally (28) and theoretically (29) to be coupled to side-chain conformation and can be induced by high temperature (30, 31), mechanical stress (32), or specific viral binding (19). To ascertain the role of side-chain reorganization with respect to calcite nucleation, we did an in situ analysis (33) by Fourier transform infrared spectroscopy. Vibrational bands arising from both the growing crystal and the p-PDA film were observed (Fig. 5). In concurrence with the onset of calcite deposition, a significant increase in intensity of  $\sim 26\%$  occurred in the asymmetric  $\text{CH}_2$  vibrational band (Fig. 5, inset). One explanation for this observation is a rotation about the single bond (C8–C9),  $\beta$  to the p-PDA backbone, bringing the C–C–C plane toward orthogo-



**Fig. 4.** Schematic showing the potential geometric relation between the (012) face of calcite and the p-PDA template. **(A)** View along the calcite  $a$  axis, down the polymer backbone direction, and edge-on the (012) basal plane. The alternating calcium (gray circles; dark in front, lighter toward the back) and the tilted carbonate layers characteristic of the (012) plane are depicted. The calcite unit cell is shown as a dashed, truncated rectangle. The partial structure of the p-PDA film is shown. The polymer backbone axis is symbolized as  $\odot$ . The tilt angle of the polymer alkyl chains and head groups ( $\odot$ ) emulate the carbonate stereochemistry and are implicated in the alignment of the crystal about the backbone axis. **(B)** Top view schematic of a single calcite crystal with respect to the polymer backbone direction, indicating the dihedral angles. The (014) face corresponds to that viewed edge on in (A).

**Fig. 5.** In situ FTIR spectra of the polydiacetylene template and the growing crystal during the course of mineralization. A small Langmuir trough was fitted into an FTIR sample chamber. Each spectrum was taken by external reflection method (33) from ambient gas with a plane-polarized beam irradiating at  $10^\circ$  from the surface normal. The reflected signal  $R$  was divided by the background signal  $R_0$  from a bare water surface. After polymerization of the film, the subphase was replaced by supersaturated  $\text{CaCO}_3$  solution and the blue-to-red color transition was observed. Upon calcium ion binding to the carboxylic acid head group, the frequency of the carbonyl band ( $\nu \text{C=O}$ ) at  $1698 \text{ cm}^{-1}$  shifted to  $1538 \text{ cm}^{-1}$  ( $\nu_a \text{COO}^-$ ), typical of the salt form of the acid. Calcite crystal formation is identified by increasing carbonate bands (broad asymmetric stretching  $\nu_a$  peaked at  $1423 \text{ cm}^{-1}$  and out-of-plane and in-plane deformation  $\delta$  bands at  $880$  and  $712 \text{ cm}^{-1}$ , respectively). The observation of these bands indicate that the carbonate lies at an intermediate angle with respect to the film plane, as expected for the (012) plane (41). In concurrence with the onset of calcite deposition, the p-PDA membrane film undergoes reorganization as observed in the methylene stretching bands. Elapsed time after subphase replacement is indicated in the figure. (Inset) The CH stretching region after baseline correction of the symmetric (s) and asymmetric (a) vibrations.



nality with respect to the polymer backbone. Rotations about this bond have been implicated in the thermally induced blue-to-red color transition of polydiacetylenes (thermochromism) (28). Because the plane of the carboxylate lies perpendicular to the C-C-C plane upon calcium binding (34), this rotation would bring the carboxylate into the optimal position for stereochemical match (Fig. 4A). Calcium binding alone is insufficient to induce the color change as evidenced by the negative response of the films to calcium chloride solutions (35).

The morphology of most of the calcite crystals nucleated at p-PDA (Fig. 3B) indicates faster growth along the  $a$  direction compared with that along  $c'$ , suggesting different kinetics for growth along the lattice matched direction ( $a$ ) compared to the mismatched (and therefore inhibiting) direction ( $c'$ ). This observation is in keeping with the stereochemical rule that relates crystal morphology to different growth rates arising from growth inhibition at specific crystallographic directions (36).

The extended range of the co-aligned crystals (up to 1 mm) and the total control exerted over their orientation is to our knowledge unprecedented in crystal growth at the in vitro organic-inorganic interface. This degree of three-dimensional control is observed in many living systems where organisms control crystallographic orientation as well as crystal size and morphology. For example, large arrays of distinct crystallites are co-aligned in certain forms of nacre (37) and in the radial segments of coccolith (38). Interestingly, reduction of calcite crystal symmetry in calcareous sponge spicules presumably also occurs through oriented nucleation on the (012) calcite plane (39). Al-

though simplified, this polymeric model system suggests that symmetry reduction of the organic matrix is a mechanism by which organisms control the co-alignment and the precise crystallographic orientation of the deposited crystals. This mechanism is in addition to previously recognized mechanisms such as charge distribution, lattice match, and stereochemical registry.

Control over the molecular orientation in material fabrication is a goal of many studies and research efforts. Polymerized synthetic membranes may provide new models for biomineralization and new crystalline materials. By this approach, a variety of oriented crystalline materials may be realized for technological applications, as well as for basic scientific understanding of the fundamental properties of oriented particulate or dense crystalline films. This method demonstrates that new crystalline materials can be synthesized by taking some cues from Nature. In turn, materials design and synthesis can also "feed back" into a better understanding of Nature's biomineralization.

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