Textured Materials Templated from Self-Assembling Media

Shirin Eftekharzadeh[†] and Samuel I. Stupp*[,‡]

Department of Materials Science and Engineering and Materials Research Laboratory and Departments of Materials Science and Engineering and Chemistry, Materials Research Laboratory, and Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana−Champaign, Urbana, Illinois 61801

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Mineral crystals with specific surface texture have been grown by a templating mechanism from a lyotropic liquid-crystalline phase. This experimental system is important in understanding mineralization in ordered organic media, a phenomenon of importance in biology and possibly in biomaterials technology as well. The first step in the process involves the doping of a mesophase with precursor ions for the mineral phase with little disruption of the order parameter. Growth of the mineral crystals is then induced by establishing interfacial contact between mesophases doped with different precursor ions. In the system studied here, mineralization occurs at the interface as a result of diffusion of calcium and phosphate ions toward regions of lower concentration. Characterization of the precipitate formed at the interface by X-ray as well as electron diffraction, elemental analysis, and transmission and scanning electron microscopy has revealed the formation of single crystals of brushite ($CaHPO_4{\cdot}2H_2O$) with triangular and platelike morphology. Most importantly, these crystals exhibited longitudinal striations on their surface which are believed to be due a templating effect from the liquid-crystalline phase. The striations are most likely an imprint of the preferred orientation of cylindrical molecular assemblies in the hexagonal mesophase.

Introduction

The formation of structurally unique inorganic minerals in biological tissues has been described as a process that takes place within a highly ordered organic matrix.[1−7] The mechanisms are complex and poorly understood, but it has been suggested that organic matrixes supersaturated with ions provide specific sites for nucleation of mineral and, by virtue of their unique structure, impose constraints on the direction of mineral growth.[3,4,7] Such behavior has been observed in calcified tissues such as bone in which highly ordered collagen fibrils act as heterogeneous nucleation sites for the formation of the mineral phase from a metastable solution of calcium and phosphate ions.[7] These nucleation sites are believed to behave as ion binding agents providing the critical concentration necessary for nucleation.[3,4] The nature of these interactions is such that bound ions remain reactive for the initial nucleation or can add to other nuclei for further growth of mineral phase. Such behavior leads to the composite materials of calcified tissues in which ultimate morphologies are designed by the organic matrix. In some of these composites, mineral particles exhibit a high degree of orientation with respect to one another and with respect to the organic framework within which they are formed.

To understand the role of the organic matrix in the formation of inorganic crystals of such specificity, considerable effort has been devoted to mimic biomineralization processes in the laboratory and various organic/inorganic systems have been investigated.[8−19] Some investigators have used compressed langmuir monolayers of amphiphilic molecules for the oriented nucleation of inorganic minerals.[8−10,13] The crystals grown by this approach are shown to exhibit unique crystallographic orientation given the specific molecular

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[†] Department of Materials Science and Engineering and Materials Research Laboratory.

[‡] Departments of Materials Science and Engineering and Chemistry, Materials Research Laboratory, and Beckman Institute for Advanced Science and Technology.

* To whom correspondence should be addressed.

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interaction of the organic monolayer with the nuclei. A more recent development in this area has taken advantage of surfactants to grow minerals with controlled nanostructures.[14−16] Kresge and co-workers[14,15] reported on the formation of ordered mesoporous molecular sieves via the interaction of inorganic species with surfactants. The ordered mesoporous nanostructure was proposed to form by one of two routes: one in which the interaction of organic and inorganic species facilitate the ordering of an ordered composite system and the other where the inorganic mineral nucleates and grows from a preordered liquid-crystalline phase. The investigation of this system by Chen et al.[19] revealed that the formation of mesoporous structure occurs by the first mechanism and does not follow a templating process by an initially ordered liquid-crystalline phase.

A templating mechanism that uses ordered assemblies as a route to grow minerals with specific morphology has been searched for by a few investigators.[11,17] The first example of *direct* templating by a mesophase was recently reported by our group.[18] The system studied involved the growth of cadmium sulfide particles with hexagonally arranged cavities from a hexagonal lyotropic mesophase.[18] This synthesis involved doping the liquid-crystalline phase with precursor ions without disrupting its order parameter. The observed nanostructure in semiconductor particles was attributed to a templating effect by the hexagonal mesophase. Here, we report on a different templating mechanism for the formation of calcium phosphate-based minerals in the same hexagonal mesophases used to template the nanostructured semiconductors. The growth of mineral in the system studied here was induced by establishing interfacial contact between two mesophases containing different precursor ions. Mineral formed by this technique was characterized by scanning electron microscopy, transmission electron microscopy, and X-ray diffraction.

Experimental Section

The surfactant used in this investigation was obtained from ICI as a 97% oligoethylene oxide $(\overline{10})$ oleyl ether ($C_{18}H_{35}$-$(OCH_2CH_2)_{\overline{10}}OH$) aqueous solution. The water was removed from this solution prior to use by exposure to vacuum for 24 h. Solutions of the surfactant containing calcium ions were prepared by the addition of a calcium acetate solution of the desired concentration to the neat surfactant but keeping the weight ratio of surfactant to water equal to 1. This composition was found to ensure the formation of a hexagonal mesophase at room temperature (25 °C). The homogeneity of the solution was achieved by stirring the mixture above the isotropization temperature for approximately 5 min prior to cooling to room temperature. Solutions of the surfactant containing phosphate ions were prepared using an identical procedure by the addition of phosphoric acid solution of varying concentrations to the surfactant. Both solutions were allowed to cool to room temperature for approximately 15 min after stirring in the isotropic state. An interfacial contact between the two hexagonal mesophases was created by first heating the surfactant/calcium acetate mixture to its isotropic state, pouring this solution on the top surface of the surfactant/phosphoric acid mesophase kept at room temperature, and then letting the entire system cool to room temperature. This procedure was carried out with mesophases containing calcium acetate and phosphoric acid solutions with molar concentrations in the range 0.1−0.4 and an atomic Ca/P ratio of unity. The precipitate formed at the interface was isolated by dissolving the organic components in 50/50 by volume diethyl ether/ethanol using sonication and then centrifuging the mixture. The isolated precipitate was washed twice in ethanol, and the solvent was removed by further centrifugation. The powder was dried in air at room temperature and characterized by X-ray diffraction (Rigaku 2DMAX), elemental analysis, scanning electron microscopy (Hitachi S-800), and transmission electron microscopy (Philips CM-12).

Results and Discussion

Addition of 50 wt % water to the surfactant studied in this work led to the formation of a clear and viscous gel. This gel when observed at room temperature between crossed polars in an optical microscope reveals birefringence (see Figure 1a) with a texture that is characteristic of hexagonal lyotropic mesophases.[20] The addition of 0.1−0.4 M calcium acetate solutions or 0.1−0.4 M phosphoric acid solutions to the surfactant as opposed to pure water also led to the formation of a clear and birefringent gel at room temperature. The optical texture of ion-doped surfactant at room temperature was also consistent with the formation of lyotropic hexagonal mesophases (Figure 2a,b).

The X-ray diffraction pattern of hexagonal mesophases is characterized by three Bragg peaks corresponding to (100), (110), and (200) planes with their respective *d* spacings in the ratio $1{:}1/\sqrt{3}{:}1/\sqrt{4}$.[21] However, most hexagonal mesophases often show only the first two reflections because of lower intensity in higher order peaks. The X-ray diffraction of the surfactant/water system at room temperature exhibited two Bragg peaks with *d* spacings in the ratio $1{:}\ 1/\sqrt{3}$ (see Figure 1b). The same *d* spacings were observed when the mesophases were prepared with calcium acetate or phosphoric acid solutions in the concentration range 0.1−0.4 M (see Figure 3). The optical microscopy texture along with the X-ray diffraction scans of the surfactant mesophases, in the presence or absence of ionic species, confirmed their hexagonal nature at room temperature. This liquid-crystalline state consists of close-packed arrays of cylindrical aggregates with the polar ethylene oxide units of the surfactant pointing to the outside and the nonpolar alkyl chains to the inside. With this arrangement, water can exist in the hydrophilic region and in the spaces between cylindrical assemblies. The hexagonal mesophase for all systems studied in this work was stable at room temperature as long as the water composition was kept at approximately 50 wt %.

The hexagonal to isotropic transition for the surfactant/water system was found to occur within the range 50−55 °C. Doping of the mesophases with phosphoric acid solution did not have any significant effect on the hexagonal-to-isotropic phase transition temperature. Interestingly, however, doping with calcium acetate solution decreased this temperature range as the concentration was increased. The viscosity of the calcium-doped mesophase was also found to decrease slightly at room temperature when the calcium acetate concentration was increased. The data describing the effect of ion concentration on phase transition temperatures are shown in Figure 4.

The decrease in isotropization temperature with increasing calcium acetate concentration and the lower viscosity of calcium-doped mesophase must be due to the combined interaction of cations and anions with the

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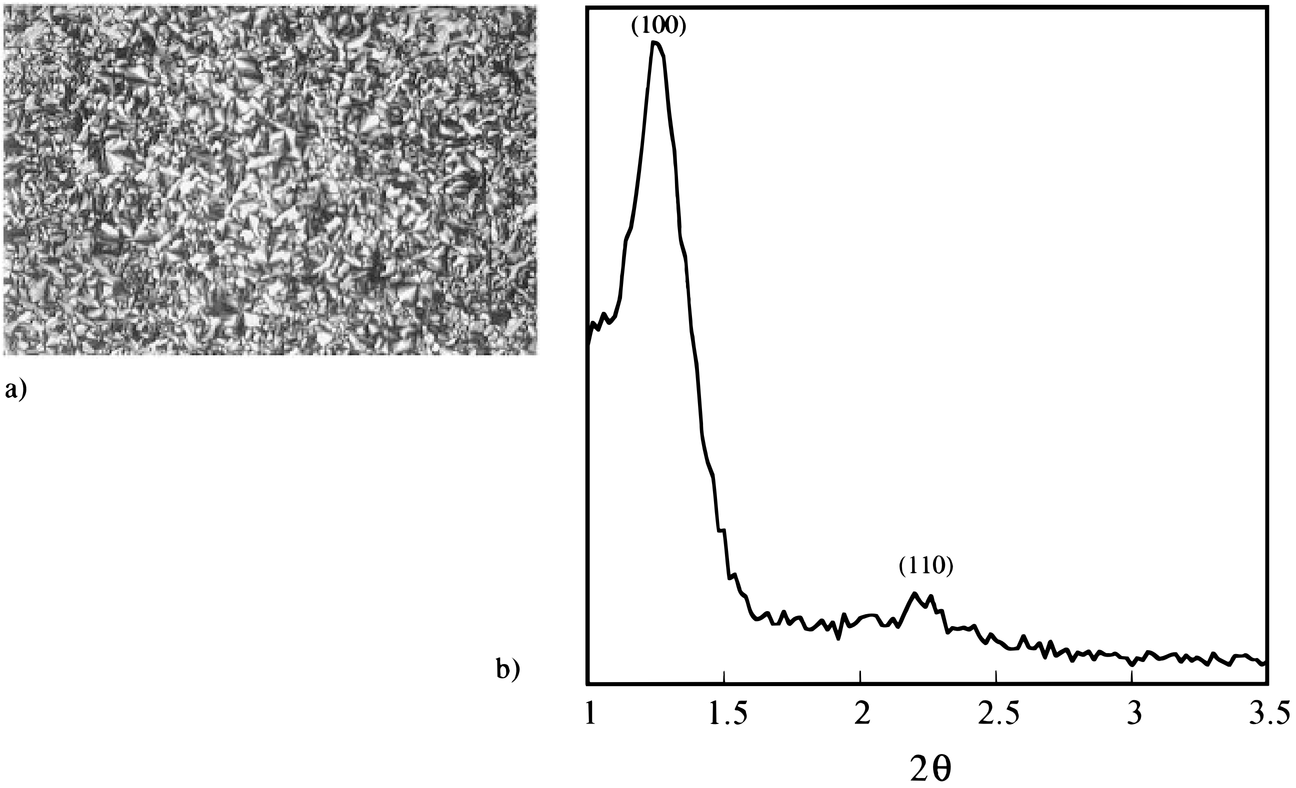

Figure 1. (a) Optical texture under crossed polars and (b) X-ray scan of surfactant mesophases formed with 50 wt % oligoethylene oxide $(\overline{10})$ oleyl ether and 50 wt % water at room temperature revealing the formation of a hexagonal mesophase.

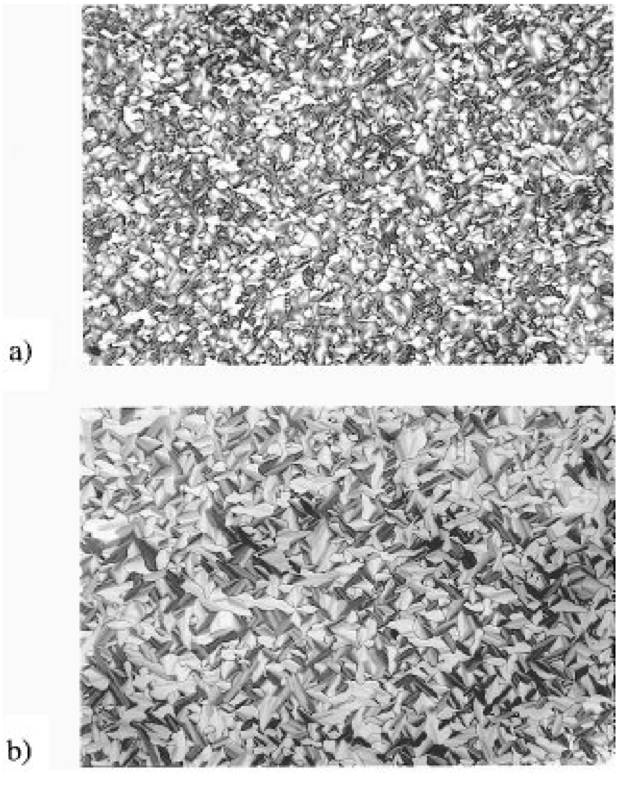

Figure 2. Optical textures under crossed polars of mesophases doped with (a) calcium acetate (b) phosphoric acid.

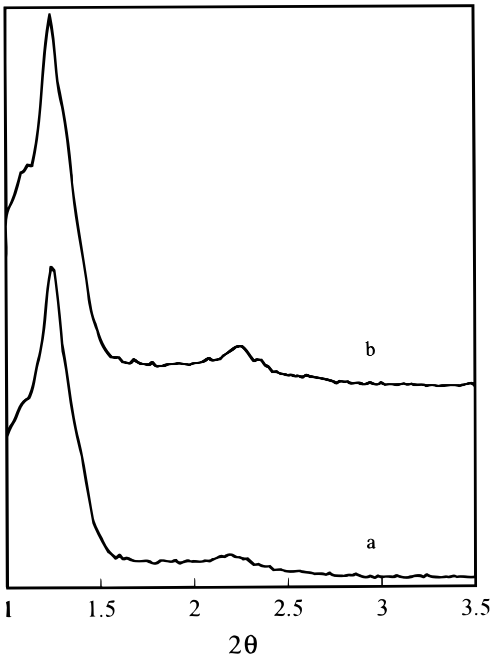

Figure 3. X-ray diffraction scans of mesophases prepared by mixing oligoethylene oxide $(\overline{10})$ oleyl ether with (a) 0.4 M calcium acetate solution and (b) 0.4 M phosphoric acid solution at room temperature. The surfactant to water ratio in each case was kept equal to one.

polar ethylene oxide sequences of the surfactant. When surfactant molecules self-order into a mesophase, the total free energy of the system is lowered of course by allowing only the energetically favorable interaction of water with polar sequences (oligo(ethylene oxide) in this case). Within a certain range of water content and a specific cross-sectional area of the polar ends, this can lead to the formation of cylindrical assemblies arranged in a hexagonal manner with hydrophilic groups facing the aqueous region. When calcium ions are added to the mesophase, they are expected to interact strongly with ethylene oxide units due to the polar nature of C−O bonds. This is also inferred on the basis that

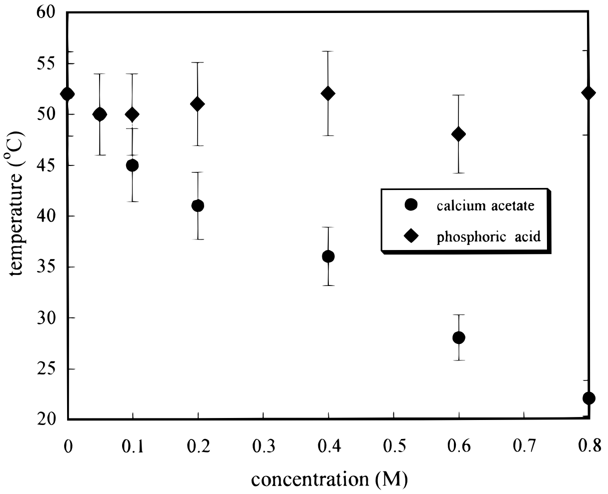

Figure 4. Variation of hexagonal to isotropic transition temperature with concentration of surfactant mesophases doped with calcium acetate or phosphoric acid.

metal ions are known to form complexes with the repeating units of poly(ethylene oxide).[22−25] The interaction between calcium ions with $-CH_2CH_2O-$ repeats can induce changes in the conformation of these segments. This behavior could have the effect of changing the cross-sectional area of polar units or altering the overall polarity of these hydrophilic segments.[24,26] Both these effects could reduce the energetic driving force for hexagonal packing and give rise to geometrical distortions in the cylindrical assemblies. The assemblies in this case should also exhibit greater flexibility, and thus one would expect lower isotropization temperatures and mesophase viscosities with increasing calcium ion concentration.

The effect of phosphate ions (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$) on mesophase stability is very different given their negative charge. Phosphate ions must reside in hydrophilic regions between cylindrical assemblies as free or hydrated ions with no specific interaction with surfactant molecules that would lead to a change in the polarity of hydrophilic segments. Hence, as long as the aqueous space accommodates these ions, the hexagonal mesophase is not disrupted and the hexagonal-to-isotropic transition temperature remains constant with an increase in the phosphoric acid concentration. This is indeed what we found experimentally.

The stability of the mesophase is also affected by the nature of counterions. When mesophases were prepared with $Ca(NO_3)_2$ or $CaCl_2$ as opposed to calcium acetate, the isotropization temperature was found to stay relatively constant. One might expect that an organic counterion such as acetate could penetrate the surfactant assemblies more readily that either Cl^- or NO_3^-. A greater distortion of the cylindrical objects will therefore be expected in the presence of acetate counterions and consequently a lower viscosity and isotropization temperature. We also found that the mesophase prepared with $NH_4H_2PO_4$ exhibits a lower isotropization temperature than the mesophase formed with phosphoric acid possibly due to the bulkier nature of NH_4^+ counterions. Compared to hydrogen ions, the interactions of NH_4^+ counterions with ethylene oxide units can cause a greater change in the cross-sectional area of the hydrophilic compartments thus leading to a more distorted hexagonal mesophase.

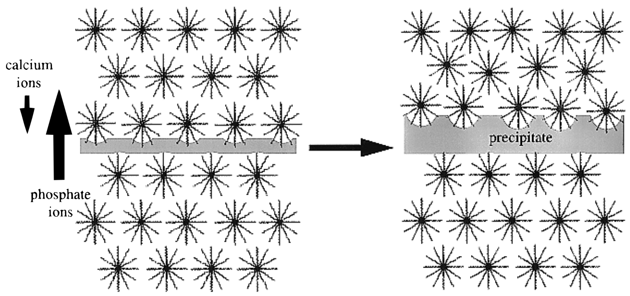

Figure 5. Schematic diagram representing the growth of mineral at the interface between two hexagonal mesophases doped with calcium acetate in one mesophase and phosphoric acid in the other. Crystal growth at the diffusion front and outside cylindrical assemblies should result in longitudinal striations on the surface reflecting the orientation of molecular assemblies in the mesophase.

Precipitation of mineral could occur within the aqueous regions of the hexagonal mesophase as a result of diffusion of oppositely charged ions toward regions of lower concentrations (see Figure 5). Precipitation could also occur within the volume of mesophase defects or within hydrophilic compartments of the mesophase. Macroscopically, precipitation was found to occur mostly near the interface between both mesophases but within the calcium-doped region. This behavior has also been observed for various molar ratios of calcium to phosphate in the two mesophases. The consistency in the occurrence of precipitation in the surfactant/calcium acetate mesophase for various Ca/P molar ratios is an indication of the greater rate of diffusion of phosphate ions compared to that of calcium ions. In a calcium-doped hexagonal mesophase, the interaction of calcium ions with the polar ethylene oxide groups of the surfactant should limit their freedom of movement in the aqueous region, making their diffusion even slower, whereas phosphate ions with no specific interaction with the surfactant should be able to diffuse more freely into the calcium-doped mesophase. Mineralization is therefore initiated mostly at the interface where the two oppositely charged ions first meet and proceeds into the surfactant/calcium acetate mesophase upon further diffusion of phosphate ions. This is in agreement with our previous assumption that strong interactions occur between surfactant molecules and calcium ions but not with phosphate ions.

The isolated precipitate was a white powder which based on X-ray diffraction scans and Ca/P ratios equal to 1 from elemental analysis was identified as calcium hydrogen orthophosphate dihydrate or brushite. The stoichiometry of this mineral is $CaHPO_4{\cdot}2H_2O$. Brushite occurs in a number of different biological systems[27] and has been described as one of the precursors in the

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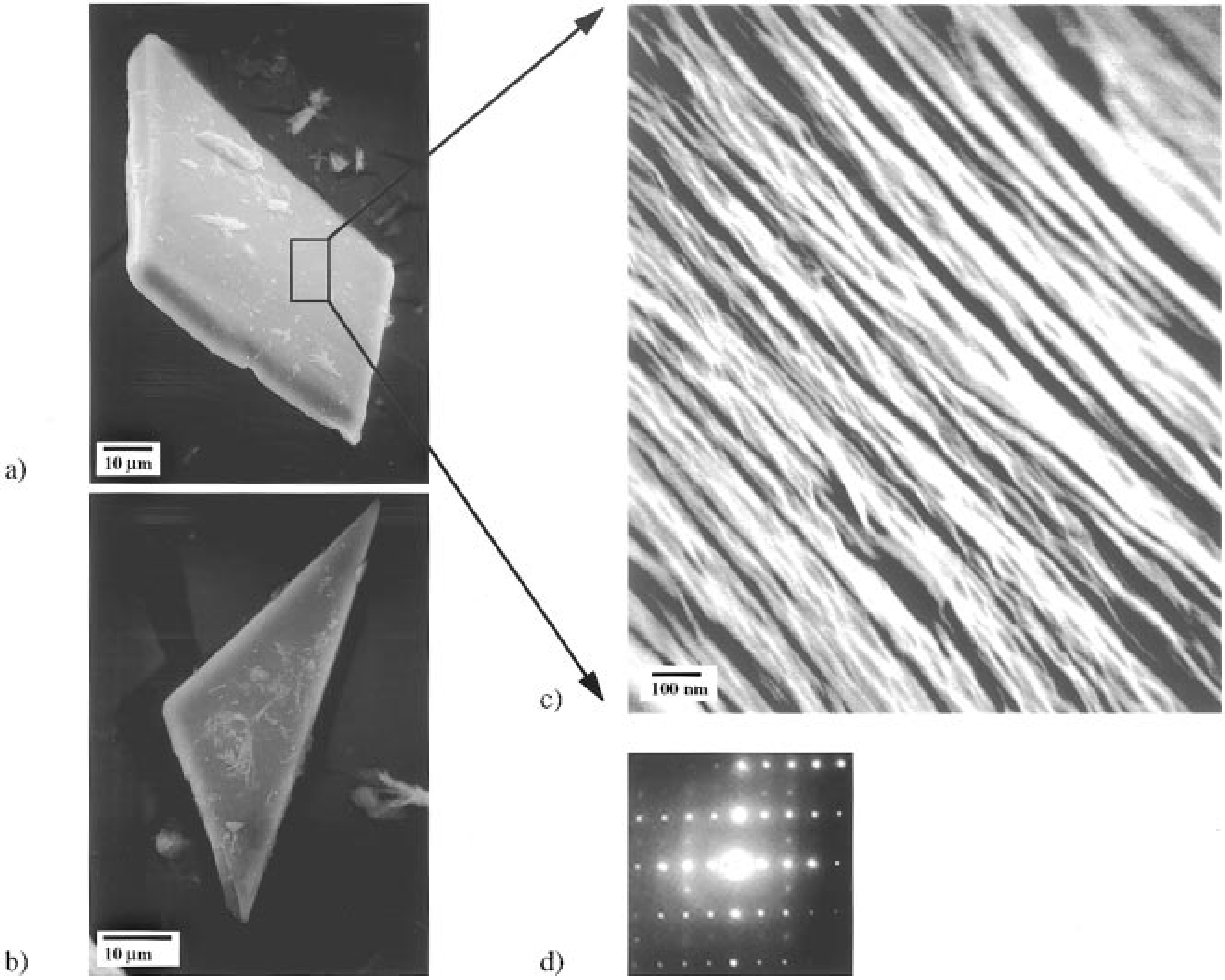

Figure 6. Scanning electron micrograph of the precipitate formed at the interface between two mesophases doped with 0.4 M aqueous solutions of calcium acetate and phosphoric acid: (a) platelike crystal, (b) triangular crystal, (c) surface texture, and (d) electron diffraction pattern.

formation of bone and dental tissues.[28,29] The brushite precipitate, as observed by scanning electron microscopy, contained platelike and triangular single crystals (see Figure 6a,b,d) and the surface texture of these crystals exhibited a preferential orientation (see Figure 6c). The preferred orientation in the surface texture of the precipitate, as revealed by scanning electron microscopy, could reflect the restrictions imposed by the liquid-crystalline phase on crystal growth. This texture could also be the result of a particular polymorph of brushite whose growth is favored in the mesophase. Thus, we have conducted a number of different control samples with conditions similar to those of the mesophase, for example, concentration and viscosity, but without molecular ordering. Morphological analysis of these crystals indicates the absence of any surface striations (see Figure 7). This brushite crystal was formed by mixing 0.4 M aqueous solutions of calcium acetate and phosphoric acid. Precipitation occurred instantaneously, and the solution was allowed to stir for several hours before centrifugation. Similar surface textures were observed when crystal formation was carried out by mixing dilute solutions of surfactant containing precursor ions, and by interfacial contact between two isotropic viscous gels of poly(ethylene oxide) containing calcium acetate and phosphoric acid. This would stimulate the slow growth of crystals in the mesophase. The striated texture was found only in crystals grown in the hexagonal mesophase and thus must reflect its role in mediating nucleation and growth of the crystals. During mineralization in ion-doped hexagonal mesophases, it is possible for the mineral to grow around cylindrical assemblies when there is strong interaction between mineral precursor ions and hydrophilic segments. Under these circumstances, bound cations can provide a structural framework for nucleation and growth of mineral as long as they maintain their reactivity. As observed previously in our group,[18] this can lead to mineral morphology that copies exactly the symmetry and nanoscopic dimensions of hydrophobic and hydrophilic compartments in the lyotropic template. In our previuos work, mineralization of CdS occurred only within the hydrophilic compartments of cylindrical assemblies, thus forming in the product periodic nanoscale cavities representing the hydrophobic region where precipitation did not occur. The brushite crystals grown in this work did not exhibit this nanostructure. However, the oriented surface texture, which is observed only when crystals are grown in the mesophase, appears to be an imprint of cylindrical assemblies at the mineral growth front (see Figure 5).

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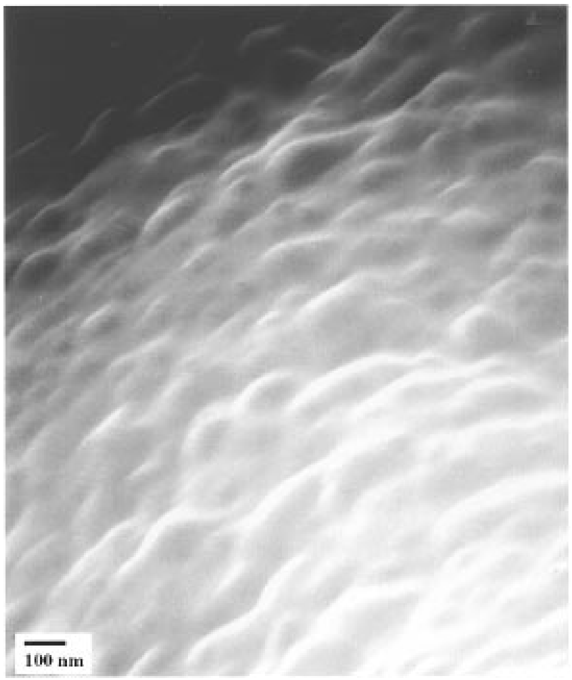

Figure 7. Scanning electron micrograph of the surface texture of crystals formed in isotropic aqueous solution.

We believe the interaction of calcium ions with polar ethylene oxide sequences, though sufficient to slow their diffusion in the aqueous region, does not lead to precipitation of phosphate-containing mineral within the molecular assemblies. This is supported by results from elemental analysis and EDAX, which shows an insignificant amount of carbon (less than 5 vol %) associated with the precipitate. To obtain a nanostructured precipitate as a result of direct templating, mineralization needs to occur within hydrophilic compartments of the mesophase. In the case of CdS reported earlier,[18] precipitation within these compartments is supported by the observation of a much higher content of carbon in the product (~15% by volume). For the calcium doped mesophase, the strength of the interaction of this cation and the surfactant should be sufficient to cause an increase in the local concentration of calcium ions and facilitate the critical concentration for nucleation. This is inferred on the basis that direct mixing of calcium acetate and phosphoric acid solutions with concentrations of 0.05 and 0.1 M did not result in any precipitation but significant amount of precipitate was formed in the mesophases prepared with the same concentration of ions. However, results from elemental analysis indicate that calcium ions do not remain bound to surfactant assemblies during precipitation. The absence of a bulk nanostructure with mineral could be explained by an extremely low diffusivity of phosphate ions into the molecular assemblies of the mesophase. As mentioned earlier, this is supported by the insensitivity of the isotropization temperature to phosphate ion concentration. Mineral crystals may not grow around cylindrical assemblies because phosphate ions do not penetrate the hydrophilic compartments and therefore crystals only grow at an interface. During this process, the growing mineral can displace the cylindrical assemblies along the direction of crystal growth and cause some distortion in hexagonal packing (see Figure 5). The preferred oriented surface morphology of crystals is therefore believed to reflect the orientation of cylindrical aggregates in contact with growing crystals.

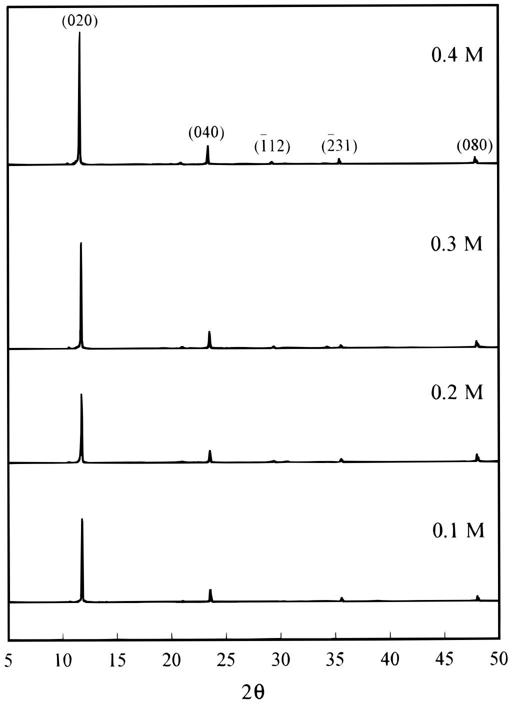

Figure 8. X-ray diffraction patterns of the precipitates formed after 11 days of interfacial contact between two mesophases doped with different concentrations of calcium acetate and phosphoric acid solutions. The concentration shown in each case indicates the concentration of calcium acetate solution as well as phosphoric acid solution used in preparing the mesophase. The Ca/P in each case was kept at unity.

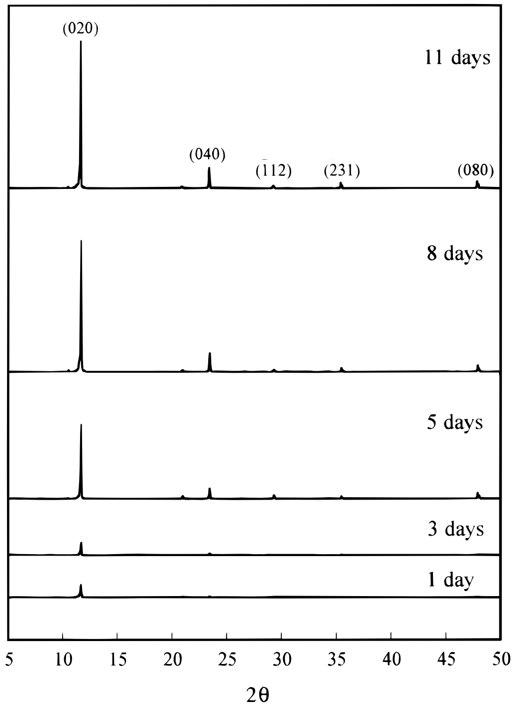

Figure 9. X-ray diffraction patterns of the precipitates formed at the interface between two mesophases doped with 0.4 M solution of calcium acetate and 0.4 M solution of phosphoric acid at different times.

X-ray diffraction scans of precipitates indicated a highly crystalline nature (see Figures 8 and 9). Crystals formed at different concentrations of calcium acetate and phosphoric acid solutions but Ca/P ratios of 1 were found to give rise to similar X-ray scans (Figure 8). The scans were also similar in crystals obtained after longer periods of time, up to 11 days, but higher order reflections were also present (Figure 9). The existence of the same X-ray reflections in the precipitates formed with different concentrations of ionic species suggests that conditions for crystallization are not altered significantly with changing ionic concentrations. However, more crystals are expected to nucleate initially when the mesophase contains higher concentrations of ions. This may affect the ultimate dimensions of crystals, but specific conclusions on this issue cannot be drawn at this time. At longer periods of time, as more ions diffuse across the interface, crystals are expected to grow in average size and degree of perfection. This may explain the higher order reflections observed at longer times (Figure 9).

Conclusions

We have studied the growth of calcium phosphate based minerals from lyotropic liquid-crystalline phases. The experimental system involved creating interfacial contact between hexagonal mesophases of a nonionic surfactant doped with precursor cations in one layer and precursor anions in the other. Mineral formation occurred at the interface as a result of diffusion of ions and the crystals obtained at the interface revealed a surface texture with preferred orientation. The observed surface texture is believed to be an orientational imprint of molecular assemblies in the mesophase.

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