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A Synthetic Analogue of the Biomineralization Process: Controlled Crystallization of an Inorganic Phase by a Polymer Matrix

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Abstract: A biomimetic in situ synthesis of CdS in PEO has been devised, which produces composites in which the inorganic phase displays uniformity of size, morphology, phase, and crystallographic orientation. Such regularity is displayed in thin composite films (<300 nm thick); in analogous thick films (≈200 μm thick) only amorphous CdS is produced. Molecular level solvation, matrix preorganization, and strong binding of the inorganic reagents have been shown to be critical for matrix mediation. Solvation or relaxation of the matrix leads to loss of control over crystallization. Addition of a surfactant, AOT, to the reaction system has been shown to effect uniformity of CdS crystal orientation, size, and morphology in thin films.

Introduction

Biological composite materials such as bones, teeth, and shells consist of a polymeric matrix reinforced by an inorganic phase which forms within the matrix.[1–17] These materials are distinguished from synthetic composites by the high degree of organization and regularity displayed by the inorganic phase. Inorganic minerals of uniform size, morphology, and crystallographic orientation can be formed in ordered arrays extracellularly and within living cells. Such a process has not been realized in synthetic systems, although recent strong interest in nanoscience has stimulated much research in the area. We have reported an example of a synthetic process which produces composite materials analogous to those produced by natural biomineralization.[18] The inorganic/organic in situ synthesized composites display controlled inorganic crystal size, morphology, and orientation, which characteristically are determining features of Type II, or matrix-mediated,[8] biocomposites. The synthetic factors which we attempted to optimize in order to give biomimetic properties to synthetic composites were (1) strong binding by the organic matrix of the inorganic reagents (molecular complementarity),[8] (2) good "solvation" of the inorganic reagents by the polymer, and (3) an ordered, regular polymer environment in which to induce nucleation (matrix preorganization).[8] We now report details of this process and analysis of the ways by which some of the variable synthetic factors present in this system affect the organization of the polymer-grown crystals obtained. This report addresses effects of the polymer matrix in influencing controlled crystal growth; subsequent publications will discuss effects of surfactants and ion mobility within the films on the organization of the crystalline inorganic phase. Application of these factors may allow the fabrication of synthetic materials with the control, order, and regularity of biominerals and open many opportunities for accessing unique materials and properties.

Experimental Section

Hexamethyldisilathiane ($(TMS)_2S$), $CdCl_2$, poly(methyl methacrylate) (PMMA), $PbCl_2$, poly(ethyl succinate), poly(ethylene oxide) (PEO) (M_w = 200 000), and AOT (sodium bis(2-ethylhexyl)sulfosuccinate) were purchased from Aldrich and used as received. All synthetic reactions and manipulations, except as noted, were performed under an atmosphere of dry nitrogen or argon using either a Vacuum Atmospheres glovebox or inert atmosphere techniques. Solvents (Aldrich anhydrous grade) were used as received. Ni-TEM grids (3 mm, 200 mesh) were purchased from SPI, Electron Microscopy Supplies, or Ted Pella and were used as received. Scanning electron microscopy was done at 20 kV on a ISI SX-40A equipped with a KEVEX X-ray spectrum analyzer. Transmission electron microscopy was primarily done on a Philips EM420 using a LINK 860 X-ray spectrum analyzer at 120 kV. Additional TEM was done on a JEOL 1200EXII using IMIX X-ray spectrum analysis at 80–120 kV. For electron diffraction, camera length was determined experimentally with a gold standard. UV–vis spectra were taken on a Gilford Response or a Perkin Elmer Lambda 9. X-ray diffraction was performed on a Rigaku Geigerflex using a Cu source, a graphite monochrometer, and a DMAX-B controller.

All films were cast from a solution composed of PEO and $CdCl_2$ in a 9:1 ratio by weight to yield a total weight of 0.50 g, dissolved in 10 mL of distilled water. "Thick" films were formed by applying the solution to one side of a glass slide and allowing the solvent to evaporate. The films were removed from the slide prior to reaction. The approximate thickness of the thick films was 0.2 mm, as determined by optical microscopy. "Thin" films were formed by dip-coating Ni TEM grids with the solution. Excess solution was wicked away with a laboratory tissue to yield films that appeared shiny upon air drying. The approximate thickness of the thin films was <300 nm, as determined by TEM using the method of von Heimendahl[19] on folded film edges. Syntheses of CdS were carried out by immersion of the films or the grids in octane, ether,

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or THF solutions of 0.02 M $(TMS)_2S$ and 0.02 M AOT. The immersed films or grids were allowed to react under dry nitrogen at room temperature for 4–10 days, then rinsed twice with fresh octane, and air dried.

Results and Discussion

General Factors Involved in Biomimetic Synthesis. In designing a process which would produce synthetic composites with the same desirable characteristics as biologically synthesized materials, we chose the in situ synthesis method as the one which most closely approaches biological processes.[7] This method is not new, but without attention to the synthetic factors given above, it does not give composite products with the specified controlled physical properties. Many reports exist of in situ syntheses in which synthetic factors were varied to give inorganic phases of more controlled properties.[7,15,20–33] We show here that application of these factors can change the in situ synthetic process from an uncontrolled precipitation to the synthesis of a well-ordered crystalline phase. We chose CdS as the inorganic phase to be synthesized in preliminary experiments for its combination of a variety of desirable experimental factors. First, the solution precipitation reaction reported for its synthesis in the literature[34] (eq 1) is very thermodynamically favorable, giving a quantitative

$$CdCl_2 + 2S(SiMe_3)_2 \xrightarrow{THF} CdS + 2SiMe_3Cl \qquad (1)$$

precipitate of amorphous CdS instantaneously. The slowness of solid-state reactions makes the choice of one which has a thermodynamic driving force (in this case, the formation of the Si–Cl bond) necessary to achieve completion of the reaction. Second, the only byproduct of the reaction is Me_3SiCl, a volatile liquid which can easily be removed from the film by washing with solvent. Also, the completeness of the CdS synthesis reaction can be monitored in the solid state by energy dispersive X-ray spectroscopy (EDX); the loss of the Si and Cl characteristic peaks in the EDX indicated that the reaction was complete and all of the Me_3SiCl byproduct was removed. Similarly, the product could be characterized by assessing the ratio of Cd to S remaining in the film by EDX. In addition, the particle size-dependent electronic spectrum[35] characteristic of semiconductors provided a spectral method for unambiguously identifying the product as CdS. Finally, the many reports on nanoscale and microcrystalline CdS particles which exist in the literature[24–31,35–43] provide a basis for comparison for differences in properties attained by the solid-state synthesis.

In order to mimic biosynthetic mechanisms as closely as possible, poly(ethylene oxide) (PEO) was chosen as the polymer matrix. A large body of research demonstrates that this polymer binds a variety of metal ions strongly,[44] and thus more closely resembles biological systems in which inorganic ions interact strongly with an organic matrix.[8] In the specific case of group 12 ions, Blumberg, Pollack, and Hoeve have shown that PEO binds $HgCl_2$ and $CdCl_2$ molecularly in crystalline complexes formed by coordination of oxygen from the polymer chains to the metal ions.[44a] For both Hg and Cd, a characteristic diffraction pattern appears upon casting PEO films from $HgCl_2$ or $CdCl_2$ solutions. The crystal structure of the $HgCl_2$/PEO crystalline complex has been solved by fiber X-ray diffraction:[44a] the contents of the unit cell show that each Hg^{2+} is coordinated by four oxygen atoms from two PEO chains. The $CdCl_2$/PEO complex gives an identical diffraction pattern, showing that the complexes formed with Hg and Cd are isostructural. The molecular-level "solubility" and ordered arrangement of $CdCl_2$ in PEO again more closely mimics the ordered arrays of molecularly-bound inorganic ions which form in biological matrices and give rise to organized composite formation by the process of biomineralization than does an inorganic reagent which is phase separated from the organic matrix and is present as occluded particles of various sizes. The molecular-level dispersion and strong binding of $CdCl_2$ by PEO allows the high degree of matrix mediation of the reactions $CdCl_2$ can undergo in the polymer matrix; such control is known to be required for organized crystal growth in biological systems.

Crystallization in Thick Polymer Films. In a typical CdS synthesis in bulk or "thick" films of PEO, the solution formed by dissolving PEO and $CdCl_2$ in a 9:1 ratio by weight (total weight = 0.50 g) in 10 mL of water is pipeted onto a glass microscope slide, forming a film of PEO/$CdCl_2$ approximately 0.2 mm thick. Films containing higher percentages of $CdCl_2$ ($\approx$40%) show the

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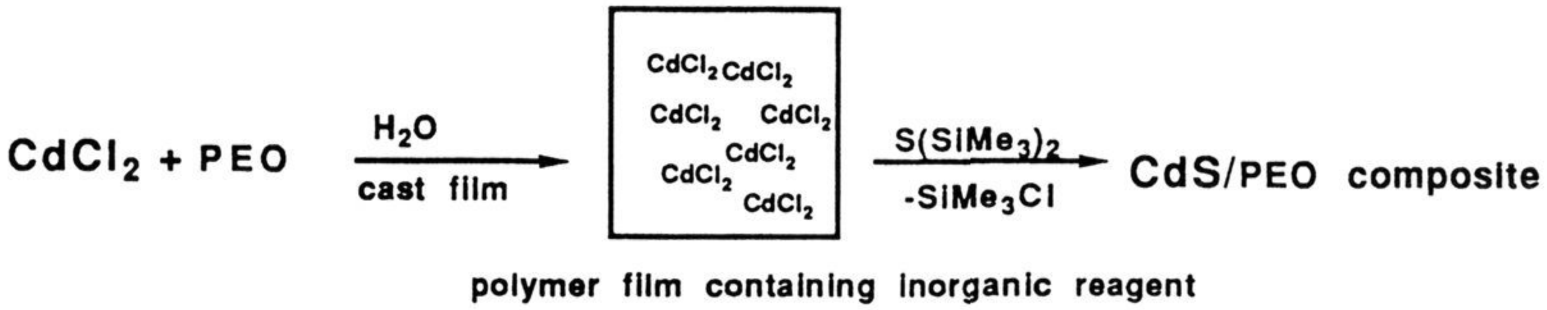
Scheme 1



characteristic lines of crystalline PEO in their X-ray diffraction patterns as well as new peaks arising from the formation of PEO-Cd crystalline complexes. The dried films are then removed from the glass slide and immersed in a solution of 0.02 M $(SiMe_3)_2S$ in an inert atmosphere (Scheme 1). After a period of days (variable, depending on the solvent used: see below), the reaction to form polymer-solvated CdS is complete, as shown by the presence of Cd and S and the absence of Cl and Si in the EDX spectra of the rinsed composite films. The presence of CdS is confirmed by the electronic spectrum of the films, which show, in these cases, an absorption characteristic of the semiconductor.[24-31,35-43]

Examination of the CdS formed in these experiments demonstrates that one of the most important effects exerted by the polymer crystallization matrix is indeed control of the synthetic reaction by both strong binding of the reagents and matrix organization. In these composite material syntheses, the organic polymer matrix mediates the inorganic synthetic reaction and determines the product's morphology. In the above-described reactions no crystallization control is seen: only amorphous CdS results (addition of surfactants to the reaction mixture does not produce crystallization: see below). Scanning electron microscopy (SEM) shows the spongy surface of one such film in which the carrier solvent was THF, which swells but does not dissolve the polymer (Figure 1a). Significant amounts of CdS were found in the THF solution in which the reaction was carried out. EDX of a cross section of the film shows that CdS is evenly distributed throughout, although it is slightly more concentrated at the film surfaces. In this film, although UV–visible spectroscopy and EDX show that CdS is present, no definite CdS particles can be detected, and XRD of the composite indicates an absence of observed crystallinity in the CdS. The PEO film is no longer soluble in water, indicating that it has been cross-linked, presumably through binding of multiple polymer chains to CdS particles which effectively cross-links the polymer to a high enough degree that it becomes insoluble. This coordination cross-linking is not seen when $CdCl_2$ is dissolved in the matrix; the $CdCl_2$ is molecularly dispersed and each Cd cannot coordinate a large enough number of polymer chains to affect polymer solubility. The CdS must be present in particle sizes large enough to coordinate multiple polymer chains; this is also indicated by the electronic spectra of the films, which indicate that the CdS particles are large enough not to display the absorption characteristics of quantum-dot semiconductors. The CdS is therefore present in these composites in particles which are strongly bound to the matrix and dispersed throughout the thickness of the film, and which are either amorphous or too small to give rise to identifiable X-ray powder diffraction patterns. The particles are too small to visualize easily with SEM but are over the "quantum-dot" size limit.[24-31,35-43]

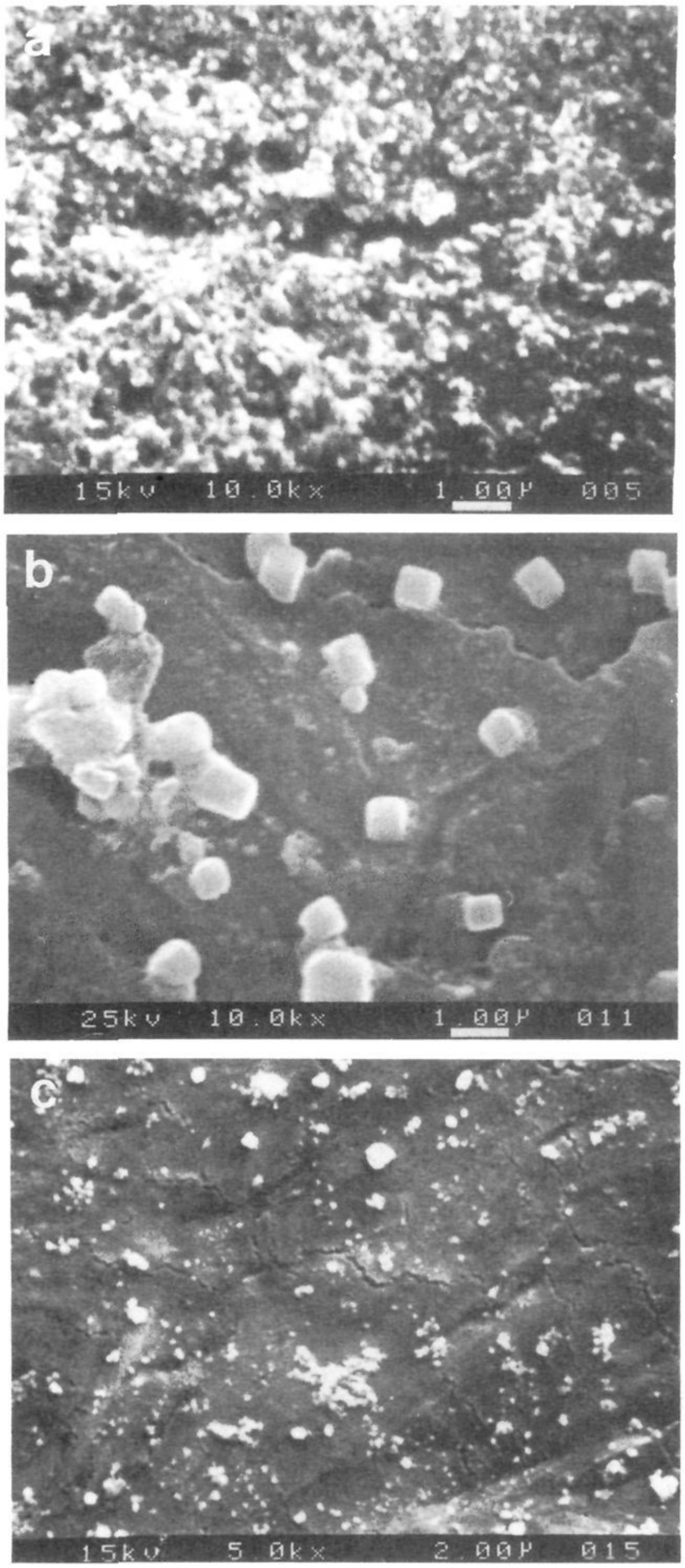


Figure 1. (a) Scanning electron micrograph of PEO film after in situ synthesis of CdS at room temperature, THF carrier solvent. (b) Same film after annealing at 120 °C. (c) Scanning electron micrograph of PEO film after in situ synthesis of CdS at 120 °C, octane carrier solvent (ref 18).

When the CdS/PEO composite films are heated, however, to 120 °C for 1 h under inert atmosphere and then cooled, their electronic absorption bands shift toward the red, indicating that the CdS particles within the film are growing larger, and peaks characteristic of both common forms of CdS, the wurtzite and the zinc blende structures, appear in the XRD. SEM now reveals that large (1 μm on an edge) regular cubic crystals of CdS have formed (Figure 1b), presumably by the ordered aggregation of smaller particles preformed during the room temperature reaction. Such ordered aggregation of mineral particles is postulated as one of the processes by which natural biomineralization may occur.[11] The PEO films are again water soluble, indicating that the strong binding of the polymer chains to the CdS particles has been relaxed, allowing the particles to assemble into the larger crystals which are not molecularly bound to the PEO and which therefore phase separate from the polymer, rising toward the film's surface (Figure 1b). In confirmation of this mechanism, a synthetic pathway which bypasses the intermediate stage, the reaction of a 10% $CdCl_2$/PEO film with $(SiMe_3)_2S$ in octane at 120 °C gives CdS crystalline product of merely random morphology (Figure 1c), demonstrating that initial formation of the CdS particles in an ordered, strongly binding environment is necessary to their ordered aggregation into regularly shaped crystals. By heating the polymer matrix above its melting point (PEO mp 67 °C) the matrix's strong binding and crystallinity, and therefore its preorganization, are destroyed or greatly diminished, and only random-morphology product is produced (Figure 1c). These results suggest that it was the regularity of the CdS particles formed in the room-temperature, ordered film which allowed their later assembly into regular crystals; in no case are regular crystals of controlled size and habit formed unless the initial synthesis takes place within an ordered, crystalline environment which binds the reagents well. However, if the initial particles are formed in the ordered polymer matrix, they agglomerate upon heating into larger crystals of regular size and habit.

In confirmation of this hypothesis, we found that any synthesis of CdS in a noncrystalline, nonbinding environment produces no control over the crystallinity and morphology of the products formed. For example, reaction of $CdCl_2$ and $(SiMe_3)_2S$ in an amorphous, nonbinding polymer such as poly(methyl methacrylate) (PMMA) gives spherical crystalline particles (Figure 2a). The amorphous, essentially isotropic environment of the Cd reagent in this polymer, in which no directional control is imposed by binding to the polymer matrix or by any regularity in the ordering of the polymer chains, also confers no directional control on the morphology of the product. In contrast, all crystalline polymers used as matrices confer some morphological control on the CdS product. One example is poly(ethyl succinate), shown in Figure 2b, in which a platelike habit is seen for the CdS.

Strong binding of the inorganic reagents by the matrix on a molecular level controls the homogeneous dispersion of the inorganic phase, as well as molecular-level structural modifications analogous to those seen in biological systems. Composite films of CdS and nonbinding polymer matrices [poly(methyl methacrylate), poly(ethyl succinate), and poly(styrene)] give phase-separated inorganic/organic composites, with the inorganic phase often forming a network on the surface of the film (Figure 2c). When a copolymer containing both binding and nonbinding groups (70:30 poly[2-vinylpyridine]-co-poly[styrene]) is used as a crystallization matrix, the CdS is homogeneously dispersed throughout the film in isolated particles organized into the binding regions.[24,25,36-40] No surface inorganic layer is formed. Analogous results are obtained when HgS is synthesized in polymer films containing binding and nonbinding groups in a manner similar to that shown in Scheme 1, using $HgPh_2$ as the inorganic reagent.

That molecular level dispersion of the inorganic regents is necessary to matrix mediation of their reaction products was demonstrated by the in situ synthesis of PbS in PEO. The inorganic reagent chosen for this synthesis was $PbCl_2$, specifically because, unlike $CdCl_2$ and $HgPh_2$, it does not "dissolve" in the polymer matrix, but rather forms nanometer-sized crystalline aggregates which can be observed by electron microscopy and X-ray diffraction. The resulting PbS is formed in similar nanometer-sized aggregate crystals, with no structural mediation by the matrix; addition of the surfactant AOT (see below) did not alter this result. These results demonstrate that molecular-level solvation and binding by the polymer matrix is required for any molecular-level matrix mediation of these in situ reactions.

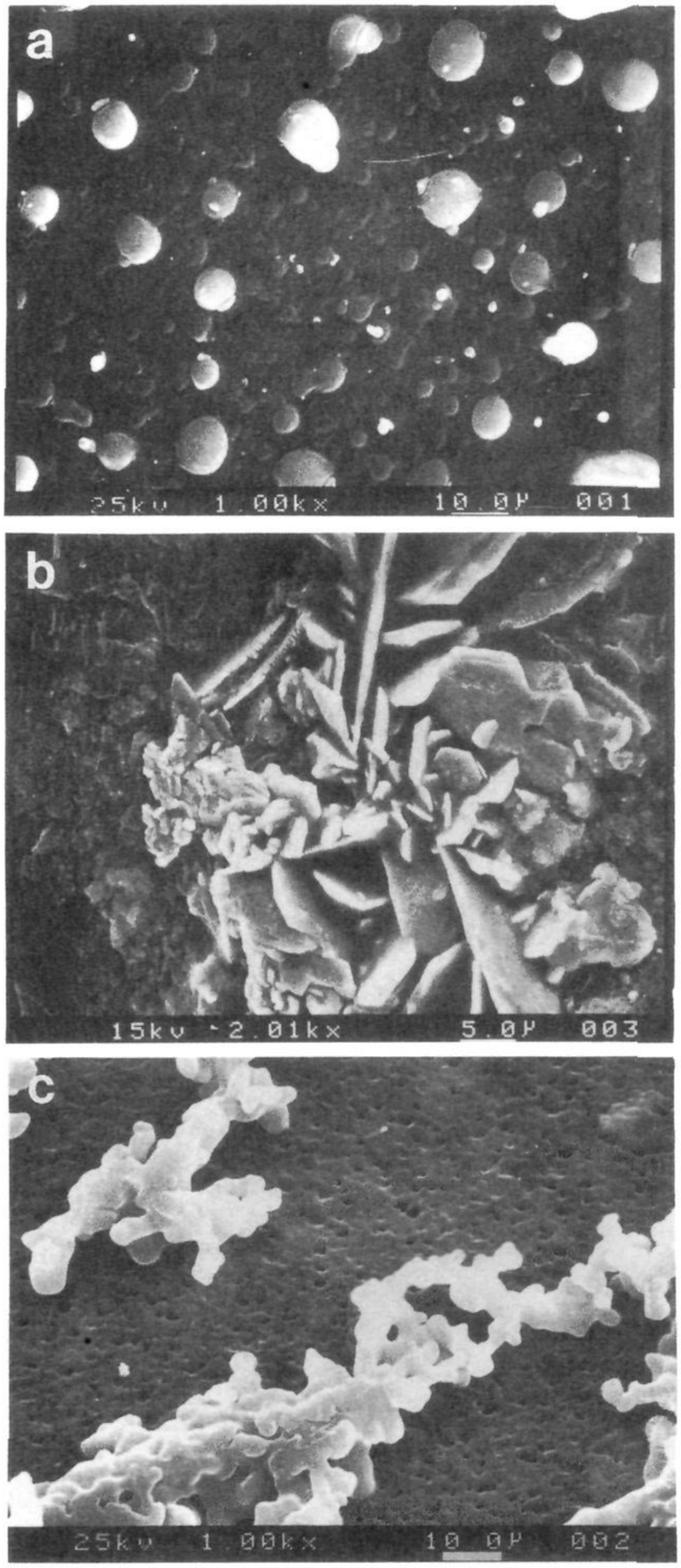


Figure 2. (a) Scanning electron micrograph of PMMA film after in situ synthesis of CdS at 120 °C, octane carrier solvent. (b) Scanning electron micrograph of poly(ethyl succinate) film after in situ synthesis of CdS at 56 °C, THF carrier solvent. (c) Scanning electron micrograph of PMMA film after in situ synthesis of CdS at 120 °C, octane carrier solvent (ref 18).

Crystallization in Thin Polymer Films in the Presence of a Surfactant. Although the in situ syntheses of CdS in the "thick" films discussed above were successful in producing crystals which had some characteristics of organized biomineralized tissues (uniformity of size and morphology), other characteristics of biomaterials (such as crystallographic orientation and control of crystalline phase) were not reproduced by our synthetic system. We determined to study the nature of the initial CdS particles produced at room temperature in the thick films, since our experiments indicated that these particles had some unique characteristics which allowed their assembly into regular crystals when they were released from binding to the polymer by heating

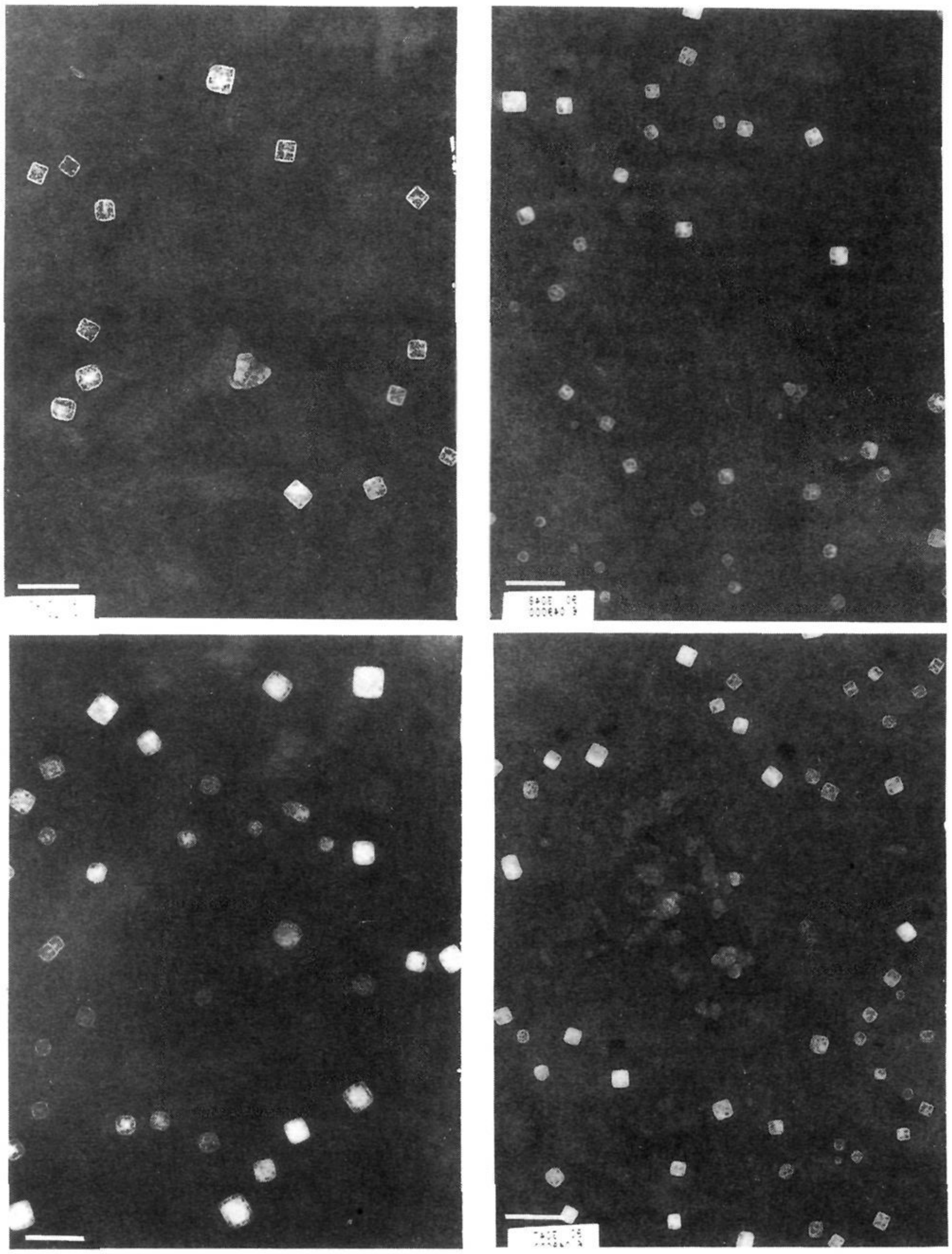


Figure 3. Transmission electron micrographs of PEO films after in situ synthesis of CdS at room temperature, octane carrier solvent, in the presence of AOT. Scale bar = 200 nm.

and were allowed to aggregate. We therefore began in situ syntheses of CdS in polymer films which were thin enough (<300 nm) to examine by transmission electron microscopy (TEM), since this technique would allow visualization and examination of the initial CdS particles. In addition, we introduced the surfactant sodium di(2-ethylhexyl)sulfosuccinate) (AOT) into the solvent in which the polymer films were immersed during the in situ reaction. This surfactant was added as an analogue or mimic of the soluble molecules (often glycoproteins) typically found within the polymer matrix in biological systems, which are thought to influence crystal growth and habit modification by selective binding to specific crystal faces.[1,2,13,45–49] This method of chemically controlling crystal orientation and growth by specific molecular interactions with organic molecules has been mimicked in synthetic systems by Langmuir mono- or bilayers of surfactants on the air/water interfaces of crystallizing solutions.[50–63] The charged polar head groups of the surfactant molecules interact

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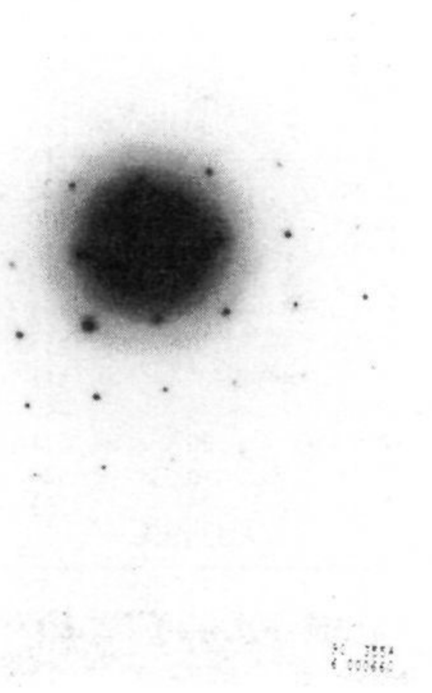

Figure 4. Single-crystal electron diffraction pattern of a crystal in a film shown in Figure 3.

with, concentrate, and nucleate inorganic ions from solution, while the organized nature of the structured monolayer film provides the means of controlling orientation, phase, and habit.[61] In our in situ CdS synthetic system, in which inorganic reagents react within a PEO film immersed in octane, the surface of the PEO film presents the most polar environment, and should therefore attract and bind the negatively charged sulfonate head groups of AOT, while the long alkyl tails of the surfactant molecules would remain in the octane solution. The AOT should assemble on the PEO film's surface, forming a layer analogous to a Langmuir–Blodgett layer at an air/water interface, and the sulfonate head groups could therefore interact with, concentrate, and nucleate polymer-bound Cd ions, while the organized nature of the structured surfactant film provided control of orientation, phase, and habit, as is seen in crystal growth from solutions exposed to surface monolayers. This biomimetic synthetic strategy proved successful. Thin films of 10% $CdCl_2$/PEO were dip-coated directly onto nickel TEM sample grids, which were then immersed in octane solutions of $(SiMe_3)_2S$ and AOT at room temperature. After 4 days reaction time, examination of the films by TEM revealed that square single crystals had formed throughout the film (Figure 3) of approximately 100 nm on an edge. The crystals are oriented within the film in that all display the allowed $hk0$ reflections in their electron diffraction patterns, but no trace of the allowed reflections with $l \neq 0$ is seen, showing that all the crystals are aligned with a 4-fold axis perpendicular to the plane of the organic film (Figure 4). The crystals also all occur in the rock salt structure, a phase previously seen in CdS only at high pressures,[64] in CdS nanoparticles which had been biosynthesized *in vivo* by yeast cells,[65] and in one report of CdS synthesized within a biomimetic membrane.[27] This synthetic approach has therefore produced all of the characteristics (uniform size, morphology, and phase, and crystallographic orientation) seen in the crystalline arrays found in organized biological composites.

XPS of the rinsed films shows a mono- or multilayer assembly of the surfactant on the polymer film's surface. EDX of the films shows the presence of Cd and S in equal amounts and negligible amounts of sodium, chlorine, and silicon. Electron diffraction studies of crystals such as those shown in Figure 3 show that they are single crystals (Figure 4); the diffraction patterns of the crystals are identical throughout the films, indicating that all crystals are of the same phase. The diffraction pattern obtained shows d-spacings at 2.73, 1.94, 1.37, 1.23, and 0.963 Å characteristic of the rock salt structure of CdS (Table 1) oriented on (001). Characteristic d-spacings of CdO and the zinc blende phase of CdS are also shown in Table 1; the diffraction pattern of the crystals obtained in the in situ synthesis is distinguishable from that of these two phases within the error limits of the electron diffraction technique, demonstrating that the crystals are not either of these two phases. The lattice parameter calculated for the in situ synthesized crystals (5.48 Å) is also distinguishable from that of CdO (4.96 Å) and zinc blende CdS (5.82 Å), again confirming the identification of these crystals as rock salt CdS. The nucleation and growth of this metastable phase of CdS by this synthetic system is presumed to arise from binding of polymer and/or surfactant molecules to the crystal faces, thus lowering their surface energy and raising kinetic activation energy barriers for transformation to the thermodynamic phases.[66]

The formation of these organized crystals in the polymer films is critically dependent on a number of synthetic variables; without optimization of these factors, amorphous aggregates, other crystalline phases of CdS, or mixtures of all types of mineralization in the same film are the principal products of the in situ syntheses. One of the most important factors is the "solid-state" effect, or that, in order to obtain significant matrix mediation, the polymer must be a (relatively) dense solid. Any sort of solvation or relaxation of the matrix results in loss of control over crystallization. For example, when THF or any solvent capable of dissolving or swelling the PEO matrix is used as the reaction medium (or "carrier solvent") in the in situ reaction (without AOT), significant amounts of Cd diffuse out of the polymer, forming CdS in solution (as was also seen in the thick film syntheses). TEM examination of these films shows the formation of highly dendritic aggregates, not single crystals, which is characteristic of very rapid crystal growth.[67] In contrast, identical reactions in octane, an inert solvent for PEO, produce no loss of Cd from the polymer, and result in more regular and better-crystallized CdS (Figure 5). These results suggest that the mineralization may occur within the polymer matrix, not on the surface with the polymer acting solely as a template (a mechanism which is thought to be operative in many biological crystallizations), and suggest that such a mineralization mechanism may also be important in some biological mineralization systems.

Strong binding of the inorganic reagents by the matrix on a molecular level by the polymer matrix was again found to be necessary for control of crystallization; no organized single crystals have yet been obtained from nonbinding polymer matrices, even in the presence of AOT. Our results also suggest that a *crystalline* polymer matrix, while indeed necessary for the production of

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Table 1. Comparison of Experimental and JCPDS Preference Diffraction Reflections of CdS Crystals in a PEO Matrix

experimental		JCPDS						
CdS rock salt	CdS zinc blende	CdS rock salt			CdS zinc blende			CdO
d (Å)	*d* (Å)	*d* (Å)	*I*	(*hkl*)	*d* (Å)	*I*	(*hkl*)	*d* (Å)
		3.16	100	111	3.36	100	111	2.712
2.73	2.88	2.73	70	200	2.90	40	200	2.349
1.94	2.05	1.93	60	220	2.058	80	220	1.661
		1.64	20	311	1.753	60	311	1.416
		1.57	20	222	1.680	10	222	1.355
1.37	1.43	1.36	10	400	1.453	20	400	1.1742
1.23		1.22	15	420	1.337	30	331	1.0772
	1.29	1.11	10	422	1.298	10	420	1.0499
0.963		0.963		440	1.186	30	422	0.9584
					1.120	30	333 511	0.9036
					1.028	5	440	0.8300
					0.985	20	531	
					0.918	5	620	
					0.887	5	533	
a = 5.48 Å	*a* = 5.76 Å	*a* = 5.45 Å			*a* = 5.818 Å			*a* = 4.6953 Å

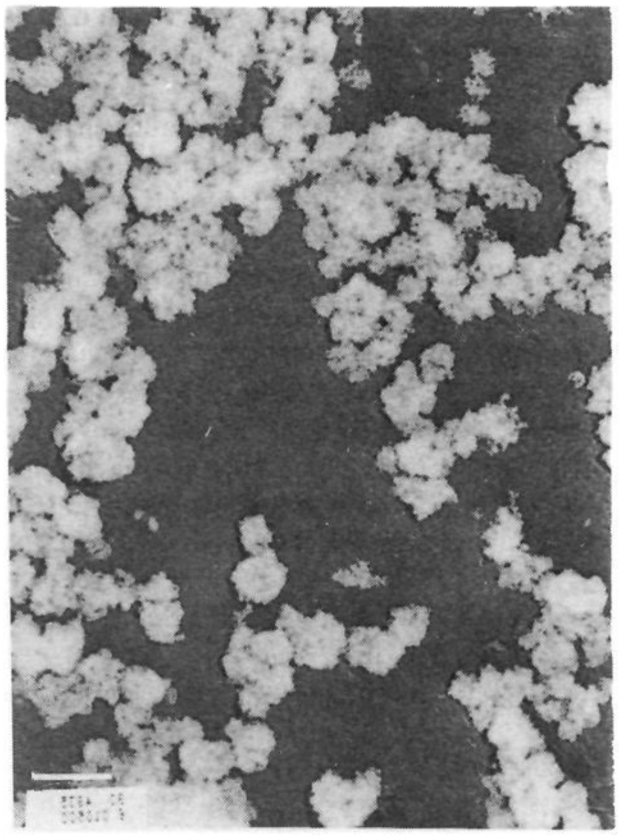

Figure 5. *Transmission electron micrographs of PEO film after in situ* synthesis of CdS at room temperature, octane carrier solvent. Scale bar = 0.95 μm.

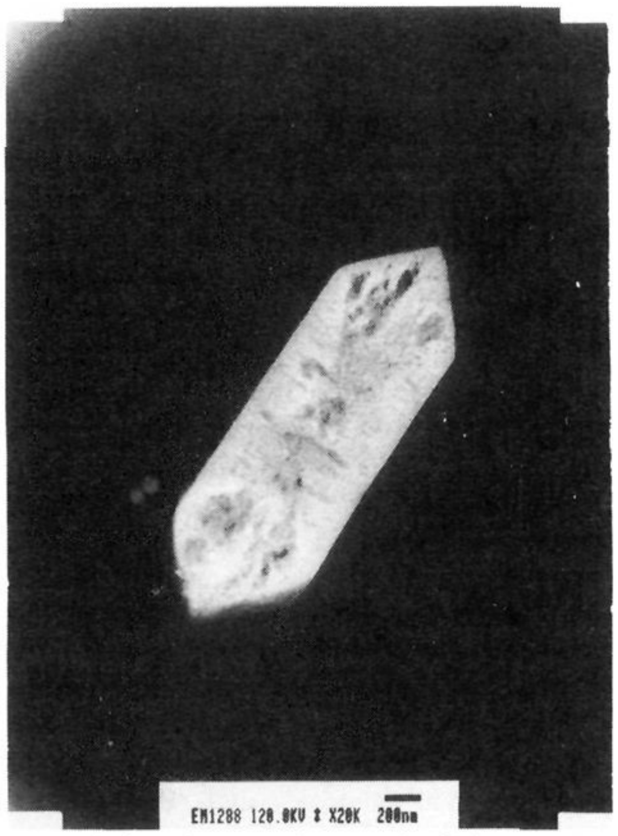

Figure 6. *Transmission electron micrograph of bipyramidal formed in* PEO film in the presence of AOT.

regularly-shaped crystals by the vectorial aggregation of amorphous particles, may not be needed for the direct synthesis of organized arrays of single crystals in thin films. Other mechanisms of matrix mediation, primarily the interaction of the Cd^{2+} ions with the surface surfactant layer and the regulation of ion mobility within the films, appear to be more important in the nucleation, morphology control, and orientation of single crystals in this system than the crystallinity or regularity of the matrix environment.[68] Organization of the matrix appears to be more influential in achieving spatial organization of crystalline arrays than in achieving regularity in the properties of the single crystals: in our system, though the matrix is semicrystalline and therefore organized on one level, it is not spatially organized, and so the CdS crystals appear at seemingly random locations throughout the film (Figure 3). In contrast, reports of in situ syntheses of various inorganic phases within copolymer matrices which are phase separated into spatially well-organized domains of metal ion binding and nonbinding regions show highly spatially organized mineralization, although biomimetic control of the inorganic phases' properties is not reported.[69]

Although use of AOT with thin PEO films in this in situ synthesis of CdS does produce the organized single crystals discussed above, another form of CdS is invariably found in these composite films. Large ($\approx$3 μm × 1 μm), very regular bipyramidal-shaped assemblies of CdS are seen in every thin film which has been exposed to AOT (Figure 6). The number of these structures increases almost linearly with increasing AOT concentration. Although perfectly regular in shape, these assemblies do not appear to be crystalline, producing only faint rings in electron diffraction studies. They appear to be formed of very small crystallites or amorphous particles assembled into regular bipyramidal shapes selected by the AOT. The bipyramidals' apparent lack of crystallinity, however, may be produced by rapid deterioration on exposure to the electron beam, or by the structures being so thin in the third dimension that they do not present enough CdS to the beam to give a detectable diffraction pattern. Experiments designed to distinguish among these possibilities are now in progress. Upon long exposure to AOT, PEO films containing only $CdCl_2$ also form identically-shaped, apparently noncrystalline bipyramidal assemblies, demonstrating that it is

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the surfactant which is responsible for these assemblies and not some feature of the CdS synthetic reaction. This appears to be an example of the vectorial aggregation of amorphous or microcrystalline particles which, in biological systems, is responsible for the formation of macroscale organized composite structures, as for example, the spines of sea urchins.[1,2,11,47] We are currently investigating by SIMS whether high AOT coverage on regions of the films' surfaces correlates to production of bipyramidals in these areas.

Studies of the composite films produced in the presence of AOT have virtually ruled out a possible crystallization mechanism—that rock salt CdS is selectively nucleated under a thin template crystal of NaCl formed on the polymer surface during the reaction shown in Scheme 1. No NaCl has been seen in the films by any spectroscopic technique; its absence is attributed to the excellent chloride-scavenging ability of the silicon reagent used and the high solubility of NaCl in PEO, which would prevent crystal formation. Also, we have now synthesized crystallographically oriented CdS in the zinc blende structure by the in situ method in the presence of AOT.[68] Since NaCl cannot adopt the zinc blende structure, a surface layer of NaCl could not be responsible for templating the growth of CdS crystals with this structure. The template mechanism could possibly be realized in our synthetic system by using a weaker silicon-binding halide ion (for example, Br^-) as the counterion of the Cd^{2+}, or by forming a less soluble alkali metal halide upon addition of the surfactant (for example, KBr rather than NaCl). Research into realization of this crystallization mechanism continues.

Conclusions

A biomimetic in situ synthesis of ordered crystalline arrays has been devised, which produces inorganic/organic composites in which the inorganic phase displays the characteristics of highly organized biocomposites, namely uniformity of size, morphology, phase, and crystallographic orientation. The formation of these organized crystals in the polymer films is critically dependent on a number of synthetic variables. Molecular-level solvation and strong binding of inorganic reagents by the polymer matrix has been found to be required for any molecular-level matrix mediation of in situ reactions and for control of the homogeneous dispersion of the inorganic phase within the organic matrix. In addition, any solvation or relaxation of the matrix during the in situ synthesis results in loss of control over crystallization. In thick polymer films ($\approx$200 μm), only amorphous mineralization is seen at room temperature, even upon addition of surfactants. In these films, synthesis in a well-ordered, strongly binding environment produces CdS particles which can assemble via aggregation into crystals of uniform size and morphology. Conversely, no regulation of crystal properties is seen when the initial mineralization occurs in a disorganized or nonbinding environment.

In thin (<300 nm) polymer films, addition of the surfactant AOT to the reaction system produces single crystals of CdS which are uniform in size and morphology, crystallographically oriented on (001), and which adopt primarily the rock salt phase. Mineralization appears to occur within the polymer film, not on the surface with the polymer acting as a template. The surfactant also produces, in thin films containing CdS or $CdCl_2$, regular, bipyramidal-shaped assemblies of the inorganic phase which are possibly noncrystalline. These increase in number with increasing concentration of surfactant and appear to result from the assembly of mineralized particles into regular shapes selected by the structure of the surfactant layer covering the films' surfaces. Formation of rock salt crystals of CdS in this in situ synthetic system does not appear to be the result of templated growth from a surface layer of crystalline NaCl. Control over nucleation, morphology, and orientation of single crystals in the thin film synthetic system appears to be primarily the result of the interaction of the Cd^{2+} ions with the surface surfactant layer and the regulation of ion mobility within the films. The effects of these synthetic factors will be reported in subsequent publications.

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