A Synthetic Analogue of the Biomineralization Process: Formation of Novel Lead Sulfide Phases

Michael W. Pitcher,[†] Elizabeth Cates,[‡] Louis Raboin,[†] and Patricia A. Bianconi*[,†]

Departments of Chemistry and Polymer Science, The University of Massachusetts at Amherst, Amherst, Massachusetts 01003, and Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802

Received July 22, 1999. Revised Manuscript Received March 8, 2000

A biomimetic in-situ synthesis of PbS in PEO has been devised, which produces composites in which the inorganic phase can display regularity of morphology and crystallographic orientation. This in-situ synthesis of PbS in a PEO film has also produced two previously unknown phases of lead sulfide, one of which can be described as "compressed" galena (PbS), the other is a new form of lead disulfide (PbS_2).

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 in vivo, both intra- and extracellularly. Such a process has not been completely 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, to give the above-mentioned controlled properties, to the inorganic phase of these 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]

In designing a process to synthesize composites with the same desirable characteristics as biologically synthesized materials, we chose in-situ synthesis as the method that most closely approaches biological processes.[7] This method is not new, but without attention to the aforementioned factors does not give composite products with controlled physical properties. To mimic biosynthetic mechanisms as closely as possible, poly(ethylene oxide) (PEO) was chosen as the polymer matrix. This polymer binds metal ions strongly, forming in many cases crystalline complexes,[19] and thus more closely resembles biological systems in which inorganic ions interact strongly with an organic matrix. The molecular-level "solubility" and organization of ions in PEO, again, more closely mimics ordered, molecularly bound ions found in biological matrices, than do inorganics that are occluded particles of various sizes and phase-separated from the organic matrix. The molecular-level dispersion and strong binding of metal ions by PEO, allows the high degree of matrix mediation of the reactions these ions can undergo in the polymer matrix; such control is known to be required for organized crystal growth in biological systems.[8]

[†] University of Massachusetts.

[‡] Pennsylvania State University.

(1) Berman, A.; Addadi, L.; Weiner, S. *Nature* **1988**, *331*, 546.

(2) Berman, A.; Addadi, L.; Kuick, A.; Leiserowitz, L.; Nelson, M. *Science* **1990**, *250*, 664.

(3) Weiner, S. *Biochemistry* **1983**, *22*, 4139.

(4) Traub, W.; Arad, T.; Weiner, S. *Proc. Natl. Acad. Sci. U.S.A.* **1989**, *86*, 9822.

(5) Mann, S.; Sparks, N. H. C. *Proc. R. Soc. London B* **1988**, *234*, 441.

(6) Fink, D.; Caplan, A.; Heuer, A. H. *MRS Bull.* 1992, October, 27.

(7) Calvert, P.; Mann, S. *J. Mater. Sci.* **1988**, *23*, 3801.

(8) Mann, S. *Nature* **1988**, *330*, 119.

(9) *Biomineralization: Chemical and Biological Perspectives*, Mann, S., Webb, J., Williams, R. J. P., Eds.; VCH Publishers: New York, 1989.

(10) Krampitz, G.; Graser, G. *Angew. Chem., Intl. Ed. Eng.* **1988**, *27*, 1145.

(11) Mann, S. *Struct. Bond.* **1983**, *54*, 125.

(12) Weiner, S. *CRC Crit. Rev. Biochem.* **1986**, *20*, 365.

(13) Addadi, L.; Weiner, S. *Angew. Chem., Intl. Ed. Engl.* **1992**, *31*, 153.

(14) Degens, E. T. *Top. Curr. Chem.* **1976**, *64*, 1.

(15) Heuer, A. H.; Fink, D. J.; Laraia, V. J.; Arias, J. L.; Calvert, P. D.; Kendall, K.; Messing, G. L.; Blackwell, J.; Rieke, P. C.; Thompson, D. H.; Wheeler, A. P.; Veis, A.; Caplan, A. I. *Science* **1992**, *255*, 1098.

(16) Materials Synthesis Based On Biological Processes. Alper, M., Calvert, P., Frankel, R., Rieke, P., Tirrell, D., Eds. *Mater. Res. Soc. Symp. Proc.* **1991**, *218*.

(17) Materials Synthesis Utilizing Biological Processes. Alper, M., Calvert, P. D., Rieke, P. C., Eds. *Mater. Res. Soc. Symp. Proc.* **1989**, *174*.

(18) (a) Bianconi, P. A.; Lin, J.; Strzelecki, A. *Nature* **1991**, *349*, 315. (b) Lin, J.; Cates, E.; Bianconi, P. A. *J. Am. Chem. Soc.* **1994**, *116*, 4738.

(19) (a) Blumberg, A. A.; Pollack, S. S.; Hoeve, C. A. J. *J. Polym. Sci.: A-2* **1964**, *2*, 2499. (b) Iwamoto, R.; Saito, Y.; Ishihara, H.; Tadokoro, H. *J. Polym. Sci.: A-2* **1968**, *6*, 1509. (c) Radhakrishnan, S.; Schultz, J. M. *J. Crystal Growth* **1992**, *116*, 378. (d) Radhakrishnan, S.; Saini, D. R. *J. Crystal Growth* **1993**, *129*, 191.

10.1021/cm990465s CCC: $19.00

Besides matrix mediation of nucleation, two other key features of biomineralization are control of ion flux at the matrix interface and growth and habit modification by soluble molecules within the matrix.[11] In our synthetic system, ion flux is controlled by optimizing reaction rates and concentration of metal ion reagents. We chose the surfactant sodium di(2-ethylhexyl)sulfosuccinate (AOT) as an analogue of the soluble molecules (often glycoproteins) typically found within the polymer matrix in biological systems, which are thought to influence crystal growth and habit by selective binding to specific crystal faces.[1,2,13,20–23] This method of chemically controlling crystal orientation and growth, by specific molecular interactions with organic molecules, has been mimicked in synthetic systems by Langmuir films of surfactants on the air/water interfaces of crystallizing solutions.[24–37] The charged polar headgroups of the surfactant molecules interact 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 of the growing crystals.[35] In our in-situ 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 headgroups 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 headgroups can then interact with, concentrate, and nucleate polymer-bound metal ions. The organized nature of the structured surfactant film provides control of orientation, phase, and habit, as is seen in crystal growth from solutions exposed to surface monolayers. The combination of these various biomimetic synthetic strategies proved successful in producing arrays of crystals within polymer matrices that were uniform in their morphology, phase, size, and crystallographic orientation.[18]

Many inorganic materials have high-pressure or metastable phases that have interesting properties or which may be technologically useful, as, for example, cubic boron nitride. However, standard methods of synthesis for these materials are often difficult, and simpler alternative synthetic routes are needed to access these potentially useful phases. In nature, many metastable inorganic phases are synthesized biologically, such as the aragonite and vaterite polymorphs of calcium carbonate. Therefore, by mimicking biological methods of synthesis, it might be possible to produce metastable phases of inorganic materials of our choice under more mild conditions. For example, Dameron and co-workers have shown that yeast exposed to cadmium salts will excrete the toxic metal as CdS crystals.[38] These yeast-mineralized CdS crystals were reported to adopt the rock salt structure, which is the high-pressure phase, and are coated with sulfur-containing proteins. By a biomimetic synthesis, we have also been able to produce rock salt CdS as oriented single crystals within polymer films, using a solid solution in-situ method.[18] Galena, the only known phase of PbS, which crystallizes in the rock salt structure, and other lead chalcogenides have been crystallized and oriented at biomimetic interfaces by several different workers.[37] We report here that solid solution in-situ synthesis can be used to produce novel oriented crystalline phases of PbS and PbS_2 within polymer films. This biomimetic synthetic approach appears to be general for the production of high pressure or other novel phases within polymer matrices.

Experimental Section

Hexamethyldisilathiane $[S[Si(CH_3)_3]_2$, $S(TMS)_2]$ was either purchased from Aldrich and distilled prior to use or was purchased from Strem and used as received. Poly(ethylene oxide) (PEO, $\bar{M}_W = 200\,000$) and bis(2-ethylhexyl) sodium sulfosuccinate (AOT) were purchased from Aldrich and were used as received. Lead bis(*p*-bromophenoxide) $[Pb(OPhBr)_2]$ was synthesized by reaction of anhydrous lead(II) acetylacetonate (Strem) with 2 equiv of *p*-bromophenol (Aldrich) in tetrahydrofuran. Octane was anhydrous grade purchased from Aldrich and stored over 4A molecular sieves under inert atmosphere. It was filtered with a 0.45 μm Teflon syringe filter prior to use. Nickel TEM grids were purchased from Electron Microscopy Supplies and were rinsed with methanol or anhydrous acetonitrile and dried prior to use. All synthetic reactions and manipulations, except as noted, were performed under an atmosphere of dry argon using either a Vacuum Atmospheres

---

(20) Addadi, L.; Berkovitch-Yellin, Z.; Weissbucch, I.; van Mil, J.; Shimon, L. J. W.; Lahav, M.; Leiserowitz, L. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 466.

(21) Berkovitch-Yellin, Z.; van Mil, J.; Addadi, L.; Idelson, M.; Lahav, M.; Leiserowitz, L. *J. Am. Chem. Soc.* **1985**, *107*, 3111.

(22) Weissbuch, I.; Addadi, L.; Lahav, M. Leiserowitz, L. *Science* **1991**, *253*, 637.

(23) Addadi, L.; Moradian, J.; Shay, E.; Maroudas, N. G.; Weiner, S. *Proc. Nat. Acad. Sci. USA* **1987**, *84*, 2732.

(24) Jacquemain, D.; Wolf, S. G.; Leveiller, F.; Deutsch, M.; Kjaer, K.; Als-Nielsen, J.; Lahav, M.; Leiserowitz, L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 130.

(25) Leveiller, F.; Jacquemain, D.; Lahav, M.; Leiserowitz, L.; Deutsch, M.; Kjaer, K.; Als-Nielsen, J. *Science* **1991**, *252*, 1532.

(26) Gavish, M.; Wang, J. L.; Eisenstein, M.; Lahav, M.; Leiserowitz, L. *Science* **1992**, *256*, 815.

(27) Landau, E. M.; Levanon, M.; Leiserowitz, L.; Lahav, M.; Sagiv, J. *Nature* **1985**, *318*, 353.

(28) Landau, E. M.; Popovitz-Biro, R.; Levanon, M.; Leiserowitz, L.; Lahav, M.; Sagiv, J. *Mol. Cryst. Liq. Cryst.* **1986**, *134*, 323.

(29) Mann, S.; Heywood, B. R.; Rajam, S.; Birchall, J. D. *Nature* **1988**, *334*, 692.

(30) Mann, S.; Heywood, B. R.; Rajam, S.; Birchall, J. D. *Proc. R. Soc. London A* **1989**, *423*, 457.

(31) Mann, S.; Heywood, B.; Rajam, S.; Walker, J.; Davey, R.; Birchall, *Adv. Mater.* **1990**, *2*, 257.

(32) Walker, J. B.; Heywood, B. R.; Mann, S. *Mater. Chem. Commun.* **1991**, *1*, 889.

(33) Heywood, B. R.; Mann, S. *J. Am. Chem. Soc.* **1992**, *114*, 4681.

(34) Heywood, B. R.; Mann, S. *Langmuir* **1992**, *8*, 1492.

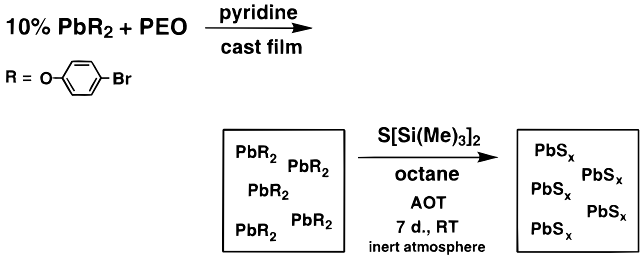
(35) Mann, S. *MRS Bull.* 1992, October, 32.

(36) (a) Heywood, B. R.; Mann, S. *Adv. Mater.* **1992**, *4*, 278. (b) Reeves, N. J.; Mann, S. *J. Chem. Soc Faraday Trans.* **1991**, *87*, 3875. (c) Mann, S. *Adv. Mater.* **1991**, *3*, 316. (d) Heywood, B. R.; Rajam, S.; Mann, S. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 735. (e) Heywood, B. R.; Rajam, S.; Mann, S. *J. Phys. D: Appl. Phys.* **1991**, *24*, 154. (f) Mann, S.; Didymus, J. M.; Sanderson, N. P. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1873. (g) Mann, S. *Endeavor* **1991**, *15*, 120. (h) Meldrum, F. C.; Heywood, B. R.; Mann, S. *Science* **1992**, *257*, 522. (i) Mann, S.; Sparks, N. H. C.; Couling, S. B.; Larcombe, M. C.; Frankel, R. B. *J. Chem. Soc., Faraday Trans.* **1989**, *85*, 3033. (j) Mann, S.; Sparks, N. H. C.; Frankel, R. B.; Bazylinski, D. A.; Jannasch, H. W. *Nature* **1990**, *343*, 258.

(37) (a) Yang, J. P.; Fendler, J. H. *J. Phys. Chem.* **1995**, *99*, 5505. (b) Fendler, J. H.; Meldrum, F. C. *Adv. Mater.* **1995**, *7*, 607. (c) Yang, J. P.; Qadri, S. B.; Ratna, B. R *J. Phys. Chem.* **1996**, *100*, 17255. (d) Zhao, X. K.; Baral, S.; Rolandi, R.; Fendler, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 1012. (e) Yang, J.; Fendler, J. H.; Jao, T.-C.; Laurion, T. *Microsc. Res. Tech.* **1994**, *27*, 402. (f) Zhao, X. K.; Yang, J.; McCormick, L. D.; Fendler, J. H. *J. Phys. Chem.* **1992**, *96*, 9933. (g) Zhao, X. K.; McCormick, L. D. *Appl. Phys. Lett.* **1992**, *61*, 849. (h) Yuan, Y.; Cabasso, I.; Fendler, J. H. *Chem. Mater.* **1990**, *2*, 226.

(38) Dameron, C. T.; Winge, D. R. *Inorg. Chem.* **1990**, *29*, 1343.

Scheme 1



glovebox or standard inert atmosphere techniques. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were done at 120 kV on a JEOL 1200EXII, also equipped with an IMIX X-ray spectrum analysis system. For electron diffraction, camera length was determined experimentally using a thallium chloride standard. X-ray diffraction was performed on a Rigaku Geigerflex using a Cu Kα source, a graphite monochromator, and a DMAX-B controller. Selected area electron diffraction (SAED) and energy-dispersive X-ray spectroscopy (EDS) data were obtained at the W. M. Keck Electron Microscope Facility at the University of Massachusetts by using a JEOL 3010 high-resolution TEM configured with a PGT Imix Xe X-ray microanalysis system; a 100-s collection time was used for X-ray spectral analysis. Spectra were then quantified as weight percents for Pb and S using a galena PbS standard.

"Thick" films were cast from solutions composed of PEO and [Pb(OPhBr)$_2$] (9:1 ratio by weight to yield a total weight of 0.50 g) dissolved in 10 mL of anhydrous pyridine. "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 glass slide with a razor blade prior to reaction. The approximate thickness of these films was 0.2 mm as determined by micrometer measurements. "Thin" films were cast from solutions composed of PEO and Pb(OPhBr)$_2$ (9:1 ratio by weight to yield a total weight of 0.50 g) in 20 mL anhydrous pyridine (carried out in glovebox). "Thin" films were formed by dip-coating the TEM grids with the solution. Excess solution was wicked away with a clean-room wiper or a laboratory tissue to yield films that appeared mirrorlike upon drying. The approximate thickness of the thin films was <300 nm, as determined by TEM using the method of von Heimendahl on folded film edges.[39]

Syntheses of PbS$_x$ in the PEO matrix were carried out by immersion of the thick films or the film-coated grids in octane solutions of 0.027 M hexamethyldisilathiane [S(TMS)$_2$] and bis(2-ethylhexyl)sodium sulfosuccinate (AOT) (Scheme 1). The immersed grids were allowed to react under dry static argon at room temperature for 7−10 days, were then rinsed twice with dry octane, and were either air or vacuum-dried overnight. For each synthesis, three control reactions were also run simultaneously, so that each synthetic series contained four separate reactions: (A) Pb(OPhBr)$_2$/PEO, S(TMS)$_2$, AOT, octane; (B) Pb(OPhBr)$_2$/PEO, AOT, octane; (C) Pb(OPhBr)$_2$/PEO, S(TMS)$_2$, octane; and (D) Pb(OPhBr)$_2$/PEO, octane.

Results and Discussion

The synthesis of oriented lead sulfide crystals was attempted in situ within a polymer film (Scheme 1), using the biomimetic synthetic method that had been shown to produce controlled crystallization in the CdS/PEO system.

Strong binding of metal ions by the polymer matrix has been shown to be crucial in controlling mineralization within polymer films.[18b] In the composite PEO/lead alkoxide films, there is no evidence of lead reagent phase segregation in the films prior to reaction, as determined by X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). By these analytical methods, the lead alkoxides appear to be homogeneously "solvated" in the PEO films, suggesting strong molecular interactions between the Pb^{2+} ions and the oxygens of the polymer chains. However, no low-angle peaks in the XRD spectra (at approximately 6° and 12° 2θ), similar to those seen in Hg^{2+} and Cd^{2+}/PEO films, are seen in any Pb^{2+}-containing film. These low-angle diffraction peaks are indicative of formation of crystalline metal/PEO complexes, and their absence in the XRD spectra of Pb^{2+}/PEO films suggests that binding of Pb^{2+} by PEO is not as optimum as that of Cd^{2+} or Hg^{2+}.[18b,40]

In syntheses of lead sulfides carried out in thick PEO films (~200 μm), no discrete mineralization was observed in the SEM, which was also the case with CdS. However, unlike CdS/PEO thick composite films, in which no crystalline material appeared, diffraction rings indicative of randomly oriented galena PbS were observed in XRD spectra of thick films. This difference in crystallization behavior is attributed to less strong binding of Pb^{2+} by PEO, which allows lead species more mobility within the film and therefore more opportunities to nucleate or aggregate.[40] As with the Cd^{2+}/PEO composites, the addition of surfactant to the reaction solutions produced no change in the properties of the mineralized product, indicating that surfactant control of these in-situ crystallizations is a surface-interface phenomenon and is therefore extremely dependent on film thickness.[18b]

In PbS$_x$/PEO thin films formed in the presence of AOT, large regularly shaped discrete particles are mineralized (Figures 1 and 2) that usually adopt cubic, hexagonal, or tetragonal shapes. These particles are single crystals, as evidenced by electron diffraction (insets, Figures 1 and 2), which display either hexagonal or cubic crystal symmetry. Analysis of the electron diffraction patterns indicates that these crystals are definitively not galena (Table 1), but are two previously unknown phases, one of PbS and the other of PbS$_2$. EDS analysis of the crystals demonstrates that those which show cubic symmetry contain 86.4% Pb and 13.6% S (calculated for PbS: Pb 86.6%, S 13.4%) and that the crystals of hexagonal symmetry contain 73.6% Pb and 25.5% S (calculated for PbS$_2$: Pb 76.4%, S 23.6%). The cubic diffraction pattern indicates a novel compressed PbS phase with a 4−5% contraction along the cubic axis compared to that of galena (Table 1). There are no reports of any PbS$_2$ phase that can be synthesized at atmospheric pressure, although α- and β- PbS$_2$ phases are formed at pressures >20 kbar and temperatures > 600 °C.[41] The diffraction pattern and calculated lattice constant (a = 5.39 Å) for the new hexagonal phase of PbS$_2$ reported here are consistent with those of α-PbS$_2$ with 38% a-axis expansion (Table 1). The a-axis length quoted here is calculated directly from the crystals' observed electron diffraction patterns in the TEM; the c-axis length of these crystals, which cannot be measured experimentally because of the crystals invariant

---

(39) Von Heimendahl, M. *Micron* **1973**, *4*, 111.

(40) Cates, E.; Pitcher, M. W.; Raboin, L.; Bianconi, P. A. Unpublished results.

(41) Silverman, M. S. *Inorg. Chem.* **1966**, *5*, 2067.

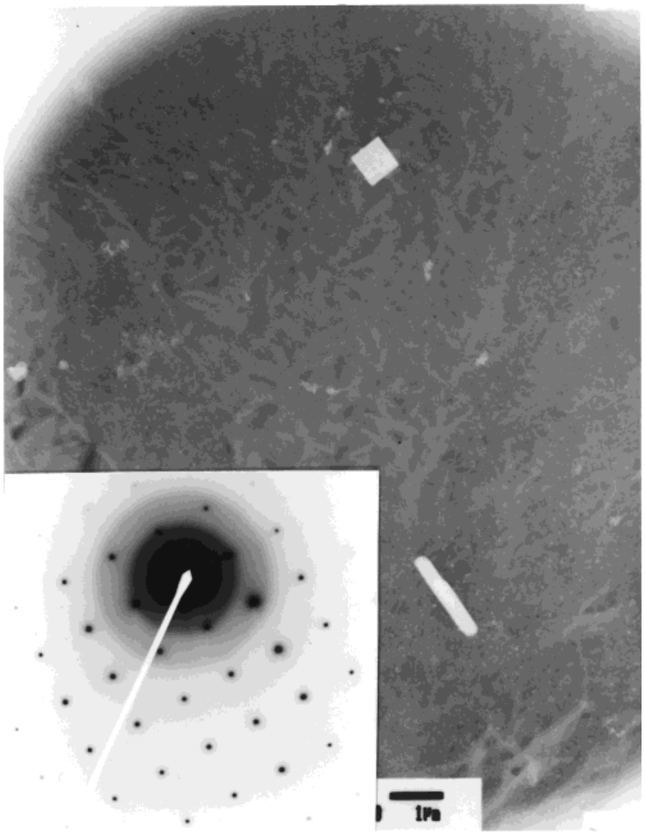


Figure 1. PbS/PEO composite thin film formed in the presence of AOT. Scale bar = 1 μm. Insert: electron diffraction pattern of “compressed” PbS single crystal.

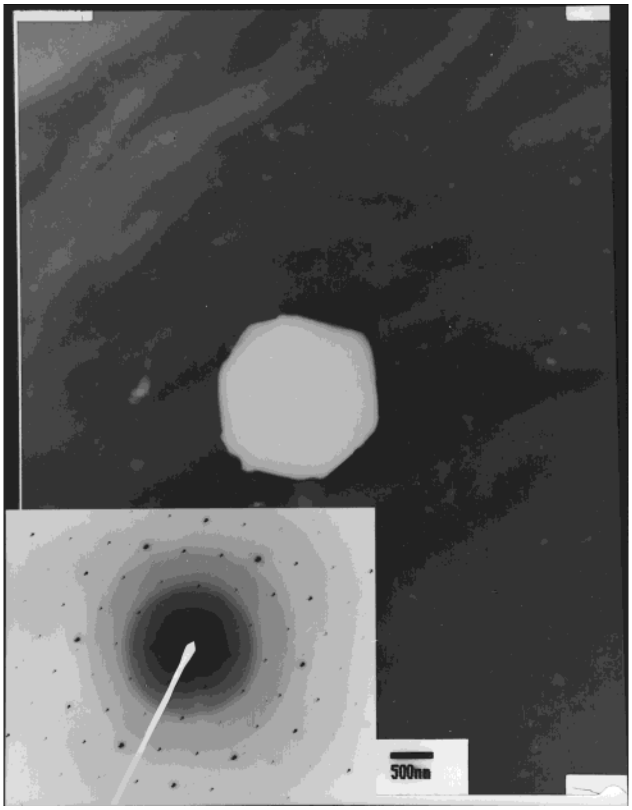


Figure 2. PbS_2/PEO composite thin film formed in the presence of AOT. Scale bar = 500 nm. Insert: electron diffraction pattern of PbS_2 single crystal.

Table 1. Comparison of Experimental and Reference Diffraction Data for Lead Sulfides

experimental		JCPDS					
PbS compressed	PbS_2 hexagonal	PbS galena		α-PbS_2 hexagonal		β-PbS_2 tetragonal	
d (Å)	d (Å)	d (Å)	(hkl)	d (Å)	(hkl)	d (Å)	(hkl)
	4.64	3.42	111	3.36	100	4.72	101
2.851	2.69	2.96	200	1.95	110	2.73	210
2.012	2.34	2.09	220	1.68	200	2.36	202
	1.77	1.79	311	1.27	210	1.79	104
	1.56	1.71	222	1.12	300	1.57	303
1.427	1.30	1.48	400	0.97	220	1.30	403
		1.36	331				
1.273		1.32	420				
		1.21	422				
		1.14	511				
0.953		1.05	440				
		1.00	531				
$a = 5.7$	$a = 5.4$	$a = 5.9$		$a = 3.8$		$a = 6.1$	

0001 orientation (see below), is estimated to be 8.08 Å, assuming a similar 38% expansion over the c-axis of α-PbS_2.

In PbS/PEO thin films in which mineralization occurred without exposure to any surfactant, particles with random morphologies are observed (Figure 3). None of the particles diffract as single crystals: electron diffraction of areas containing many particles shows the formation of poorly crystalline galena and poorly crystalline material of the new cubic PbS phase (inset, Figure 3). These results parallel those of the cadmium system: no single crystals of regular morphology are ever observed in the absence of surfactant.[18b]

The formation of a novel phase is seen in the cadmium system as well, although a surfactant is necessary to nucleate this material. In the biomimetic CdS synthesis a zinc blende-like phase that also exhibited a compressed lattice parameter was produced.[18b] Work by Brus and co-workers has shown that stabilization of high-pressure phases at STP should be more common in nanocrystals than in bulk crystals due, in part, to kinetic constraints imposed by surface passivation, in this case provided by strong binding of the crystals by the PEO matrix.[42] The formation of apparently compressed PbS in the absence of surfactant suggests that the ready formation of compressed phases in this biomimetic synthetic system is due to the greater density of the solid polymer matrix (“solid state” densification effect) relative to liquid, gel, or flux crystallization media, and not due to surfactant interactions or to any sort of templating or lattice matching effect. Apparently the density of molecular packing alone of this solid polymer crystallization matrix is great enough to alter the phase of the product mineral that is formed: there being no high-pressure phase of PbS (unlike CdS), compressed PbS is formed in the dense solid polymer environment. However, the novel PbS_2 phase is formed only in the presence of surfactant, suggesting that, like the nucleation of rock salt CdS,[18b] its nucleation is primarily due to polymer-bound metal ion/surfactant interactions. These data suggest that preferential nucleation of compressed or high-pressure phases in these solid solution syntheses is a general phenomenon. The hypothesized mechanism for the formation of high-pressure phases within these polymer

---

(42) (a) Brus, L. E.; Harkless, J. A. W.; Stillinger, F. H. *J. Am. Chem. Soc.* **1996**, *118*, 4834. (b) Nirnal, M.; Brus, L. E. *Mater. Res. Soc. Symp. Proc* **1997**, *452*, 17.

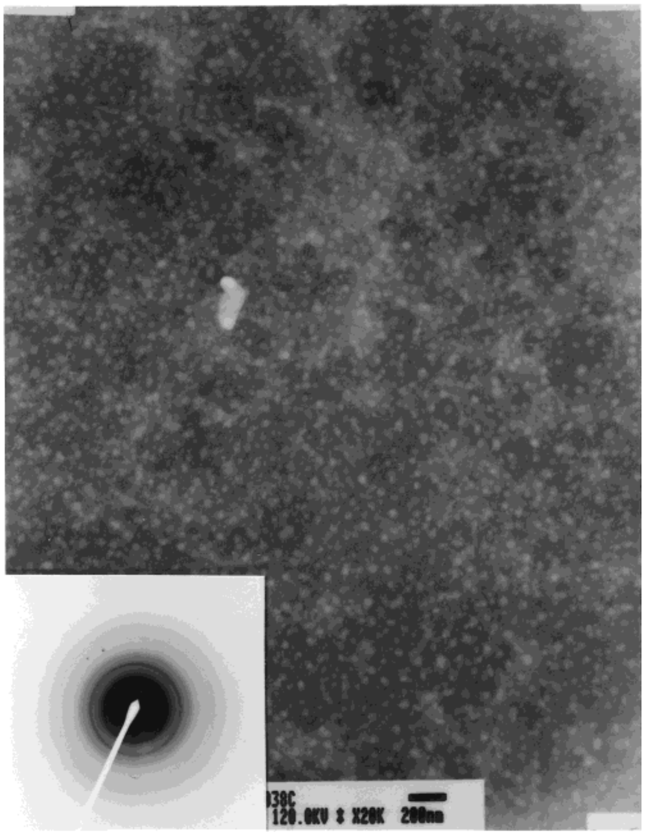


Figure 3. PbS/PEO composite thin film formed in the absence of surfactant. Scale bar = 200 nm. Insert: electron diffraction overview of a typical film.

films is not that high-pressure develops in the polymer, thereby converting galena PbS, for example, into compressed and high-pressure phases, but that there is selective nucleation of compressed or high-pressure phases within these polymer films, due to the (relative) density and rigidity of the solid polymer nucleation medium compared to more conventional crystallization media. Subsequent growth of the crystals by Ostwald ripening from the compressed or high-pressure phase nucleation sites then produces macroscopic crystals of these phases.[18b]

In addition to the formation of novel high-pressure phases, an invariant feature of the PbS_x/PEO/AOT thin film synthetic system is that all single crystals are oriented on the cubic 001 or the hexagonal 0001 zone axes (the electron diffraction patterns of different crystals are superimposable). These results again exactly parallel those seen in the cadmium system: the addition of an appropriate surfactant leads to the production of oriented single crystals of regular geometric morphology. As was seen in the cadmium system, the AOT appears to compete favorably with the polymer for Pb^{2+} binding, and so acts to nucleate discrete lead sulfide single crystals. However, unlike the cadmium system, the morphology of the crystals is not rigorously controlled. Whereas in the cadmium system all the crystals displayed a square morphology and were of uniform size, the lead sulfide crystals vary in geometric shape, size, and regularity. This is believed to be the result of weaker binding of Pb^{2+} than Cd^{2+} by PEO, as discussed above; because of this weaker binding, ion mobility of Pb^{2+} is higher in the film, and the morphology of the product lead sulfide particles is not as controlled. We saw similar effects in the CdS system; in films with higher ion mobility than the optimum, only highly dendritic aggregates, not single crystals, were formed, which is characteristic of very rapid crystal growth.[18b]

The action of surfactant in the biomimetic mineralization of lead sulfides in this system is consistent with that seen in the cadmium system, and the same trends and general effects are seen. The selective formation of the novel phases is primarily governed by the "solid-state" densification effect of the PEO matrix. It is significant that only single crystals of compressed PbS or PbS_2 are formed—no single crystals of galena are ever seen. In addition, all single crystals are oriented on the same zone axis. Thus, as in the CdS/PEO system, the surfactant appears to be responsible for the nucleation and orientation of single crystals.

The production of novel or high-pressure phases, seen in this biomimetic synthesis of organized crystals, is in many ways analogous to the biomineralization of metastable materials, such as the aragonite and vaterite phases of $CaCO_3$ in seashells, in which specific proteins determine which phase of calcium carbonate is produced.[43] From these data, it appears that this synthetic method for the production of oriented crystals within a PEO matrix is fairly general and, once reaction conditions are optimized, could be more generally useful in the formation and stabilization of high-pressure or completely novel crystalline phases.

Acknowledgment. We acknowledge the support of the Air Force Office of Scientific Research, Directorate of Chemistry and Materials Science, F49620-95-I-0225, and the Beckman Foundation, the Camille and Henry Dreyfus Foundation, the Alfred P. Sloan Foundation, and the E.I. DuPont de Nemours Corporation. We thank Rosemary Walsh and Wayne Kaboord of the Electron Microscope Facility for the Life Sciences in the Biotechnology Institute at the Pennsylvania State University for assistance in acquiring transmission electron micrographs.

CM990465S

---

(43) (a) Safinya, C. R.; Addadi, L. *Curr. Opin. Solid State Mater. Sci.* **1996**, *1* (3), 387. (b) Zaremba, C. M.; Belcher, A. M.; Fritz, M.; Li, Y.; Mann, S.; Hansma, P. K.; Morse, D. E.; Speck, J. S.; Stucky, G. D. *Chem. Mater.* **1996**, *8*, 679. (c) Belcher, A. M.; Hansma, P. K.; Stucky, G. D.; Morse, D. E. *Acta Mater.* **1998**, *46* (3), 733. (d) Addadi, L.; Berman, A.; Moradian-Oldak, J.; Weiner, S. *Croat. Chem. Acta* **1990**, *63*, 539.