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Letters

From Beads-on-a-String to Colloidal Aggregation: Novel Crystallization Phenomena in the PEO−SDS System

Epameinondas Leontidis,*,† Tasoula Kyprianidou-Leodidou,† Walter Caseri,‡ and Kyriacos C. Kyriacou§

Department of Natural Sciences, University of Cyprus, P.O. Box 20537, 1678 Nicosia, Cyprus, Institut für Polymere, ETH Zentrum, CH-8092 Zürich, Switzerland, and The Cyprus Institute of Neurology and Genetics, P.O. Box 3462, 1683 Nicosia, Cyprus

The anionic surfactant sodium dodecyl sulfate (SDS) interacts strongly with poly(ethylene oxide) (PEO) in aqueous solution, forming micellar aggregates attached to the polymer chains above the so-called critical association concentration (cac). By adding lead and sulfide ions to the PEO/SDS solution, we form lead-sulfide-containing crystallites directly on the polymer-bound micelles. We can then, through this indirect staining technique, visualize polymer chains with polymer-bound micelles using TEM. Subsequent aggregation of the particles adsorbed on the polymer chains through a bridging flocculation mechanism leads to the production of novel interesting organic/inorganic nanocomposites, in the form of long (0.5−5 μm) and thin (100 nm) rodlike colloidal aggregates. XRD analysis of these anisotropic aggregates reveals a well-defined layered structure with a spacing of 31 Å. Combination of elemental analysis, FTIR, XPS, and XRD measurements suggests that the aggregates consist of mixed dodecyl sulfate/acetate layers, which sandwich a layer of lead and sulfide ions. Similar colloidal aggregation phenomena have been observed with other cations as well, suggesting that polymer/surfactant complexes are useful novel templates for the preparation of organic/inorganic nanocomposite materials.

Introduction

The use of surfactants and polymers as templates for the crystallization of inorganic compounds has become an area of explosive research interest. Cylindrical[1] and reversed[2] micelles, vesicles,[3] cubic phases of surfactants,[4]

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* To whom all correspondence should be addressed.
† University of Cyprus.
‡ ETH Zentrum.
§ The Cyprus Institute of Neurology and Genetics.

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liquid crystalline phases,[5] surfactant monolayers and Langmuir–Blodgett films,[6] aqueous polymer solutions,[7] polymer gels, and block copolymers[8] have been used as templating media for metal, metal oxide, and semiconductor crystallization. The goal is the optimal control of the size, shape, morphology, and polydispersity of the crystals but also the production of novel organic/inorganic composite materials with interesting electrical, magnetic, and optical properties.

This study deals with aqueous solutions containing polymer/surfactant aggregates as templates for inorganic crystallization. This rather unconventional choice was made in the hope of producing semiconductor particles with new morphologies, since the results of a preliminary study[9] suggested that polymer/surfactant solutions offer significant flexibility in this respect. Water-soluble nonionic polymers, such as poly(ethylene oxide) (PEO) or poly(vinyl pyrrolidone) (PVP), are known to interact strongly with anionic surfactants in aqueous solutions.[10] The surfactants associate with the polymer chains forming micellar aggregates at a critical association concentration (cac), which is considerably lower than the critical micellar concentration (cmc) of the surfactant in pure water. The micelles formed in the system PEO/sodium dodecyl sulfate (SDS) have been particularly well characterized in the last 30 years[10,11] and have become a standard reference system. We are aware of only a few recent publications, which describe the formation of metal particles in polyelectrolyte/surfactant gels;[12] however, the systems used in those investigations and the results obtained are

completely different from those in the work described in this article.

Our choice of the present system as a crystallization template was based on the following considerations:

(a) Counterions are strongly adsorbed on micellar surfaces of the opposite charge; hence, crystallization will almost certainly occur at a much faster rate at the surface of the micelles than in the bulk of the solution. Heterogeneous nucleation should then be the main, if not the only, crystal formation process in such a system.

(b) Most significant, the spatial confinement of the micelles, effected through their adsorption on the polymer chains, should have a strong influence on the crystallization process, due to the high local concentration of crystallites growing directly on the polymer-bound micelles.

(c) The polymer acts as a stabilizer for the crystal dispersion, preventing the direct precipitation of the product.

Experimental Section

In a typical experiment, the ratios of the two components in the PEO/SDS system were selected so that the system contains polymer-bound micelles only (no free micelles).[10] PEOs of molecular weights 2×10^5 and 5×10^6 Da and polymer concentrations 1.5–2 g/L were employed. At this concentration range, the solution is semidilute for the polymer with the higher molecular weight and dilute (but probably close to the semidilute regime) for the low-molecular-weight polymer. The amount of SDS is much higher than the amount used in a previous report,[9] in which PEO/PbS coprecipitation was observed. In the present case, the amount of SDS is in the range 4–8 mmol/L, intermediate between the known cac and cmc in the PEO/SDS system (as we also found by conductivity measurements), aiming to localize most of the surfactant in the form of polymer-bound micelles. To these solutions, Pb^{2+} salts were added (lead acetate or lead nitrate, to a final Pb^{2+} concentration of 3–4 mmol/L) and subsequently S^{2-} ions (sodium sulfide, to a final S^{2-} concentration of 3–4 mmol/L). After the initial addition of lead ions, the solution becomes cloudy, indicating an association of Pb^{2+} with SDS. Upon addition of S^{2-}, the solution acquires immediately a brown-black color. The particles formed remain in suspension at room temperature (20–25 °C) without stirring, being presumably stabilized by the polymer chains.

Results

We examined the obtained suspensions using TEM over a time period ranging from 1 day to several weeks. Figure 1a shows particles formed after 5 days in solution obtained with lead acetate and PEO of molecular weight 2×10^5. An uncommon aggregation phenomenon is observed: little crystallites aggregate and form cylindrical aggregates. The TEM picture shows also a large number of individual polymers and also clusters of chains, which have become visible because of the indirect staining achieved with the lead-containing crystals formed in the vicinity of the polymer-bound micelles. This is a clear, albeit indirect, optical observation of polymer/surfactant association and is in complete agreement with the prevailing ideas about this association phenomenon.[10,11] Related TEM work on a SDS/hydrophobically-modified poly(acrylamide) system, based for visualization on staining with an appropriate spin-probe, has revealed polymer micellization under the action of surfactants.[13] In addition, some recent fine cryo-TEM work on a polyelectrolyte/surfactant system[14] illustrated the binding of surfactant molecules on a polymer bearing the same charge, despite the electrostatic repul-

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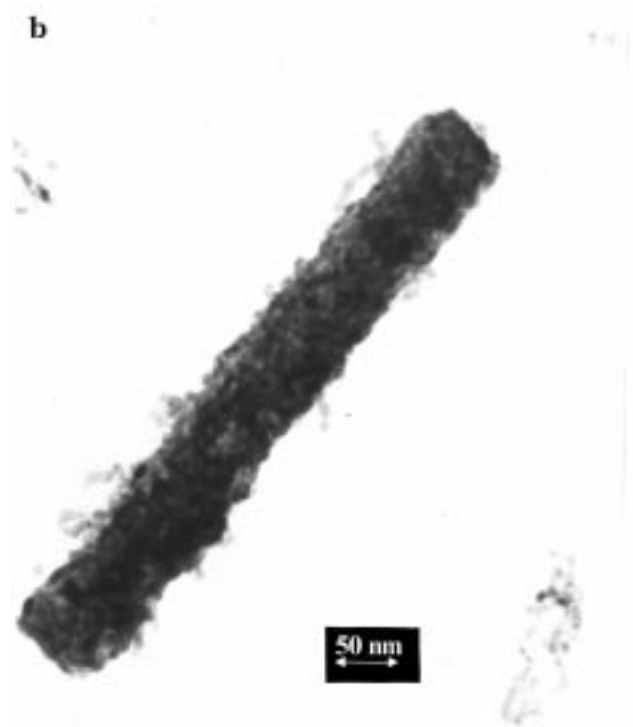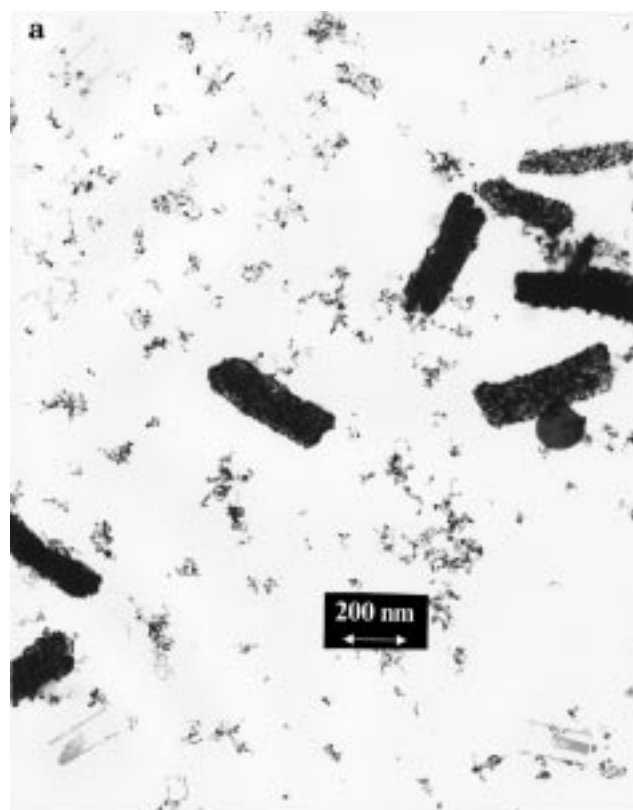(14) Zana, R.; Kaplun, A.; Talmon, Y. *Langmuir* **1993**, *9*, 1948.

Figure 1. (a) Particles formed during the precipitation reaction between lead acetate and sodium sulfide in the PEO/SDS system, 5 days after reaction onset. (b) Close-up of one of the particles, showing adsorbing polymer chains.

Figure 2. Evolution of the particles 4 weeks after reaction onset.

the aggregate with the trains, tails, and loops described in textbooks on polymer adsorption on surfaces.[15] Further, we observe a single chain or chain-cluster next to the aggregate. The formation of the aggregate itself appears to be mediated by the polymer chains. On one hand, these serve to bring particles together, initiating a bridging flocculation process, similar to those described in the computational work of Stoll and Buffle.[16]

On the other hand, the chains act as a glue, sticking to the developing surface and adding their crystal-stained micelles to the growing aggregate.

A similar aggregation picture was also obtained with lead acetate using PEO of higher molecular weight (5×10^6) and also changing the concentrations of PEO and SDS, taking care to stay in the regime of existence of polymer-bound micelles. If SDS is absent from the system, small PbS particles are formed, as evidenced by XRD analysis and observed in previous work.[9] If only SDS but no PEO is present, fewer, small cylindrical structures are evident, similar to those visible in Figure 1. However, those structures are not so well developed as those of Figure 1, probably because the absence of the polymer chains does not connect the micelles. Regarding the PEO/SDS system of Figure 1, some significant changes in the crystallizing solution appear over a time period of 2–3 weeks (Figure 2). The crystal aggregates become much longer and compact, through an unusual ripening effect. The solution appears to be depleted of polymer-bound micelles; hence, most of the inorganic material must have been deposited on the long rodlike aggregates. At the same

sion. We feel that Figure 1a of the present work provides an even clearer picture of polymer/surfactant association. A close-up of one of the particles (Figure 1b) reveals further interesting features of this unusual crystal aggregation. We can see polymer chains adsorbing on the surface of

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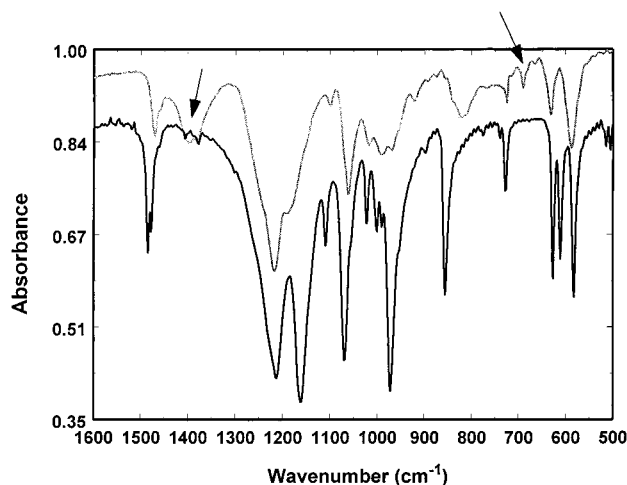
Figure 3. Powder FTIR spectra (in KBr) of the Pb/S/dodecyl sulfate/acetate composite material (upper line) and of lead dodecyl sulfate (lower line), with arrows indicating new absorption bands at 1400 and 680 cm^{-1}. The spectrum of the composite has been shifted upward for clarity.

time, some precipitation is observed, since the particles have grown to such an extent.

The chemical nature of the aggregates was examined by filtering the solution with 0.2−0.5 μm filters (so that the large particles observed in Figure 2 were retained) and analyzing the obtained powder using elemental analysis, FTIR, XPS, and XRD. Although the chemical composition of the precipitate depends somewhat on the conditions and concentrations employed, a typical elemental analysis gives a result of 30% C, 5.3% H, 40% Pb, and 9.2% S, the residual mass presumably being due to oxygen. Atomic absorption analysis and XPS revealed that no or only a negligible amount of Na is present (<0.1%). Analysis for free sulfur, that is, S atoms other than those present in the surfactant molecules, revealed that free S is 1.5% of the total material mass or roughly 15−20% of the total S in the composite. This analysis was performed by displacing free S using concentrated H$_2$SO$_4$ and trapping the evolving H$_2$S gas in a Pb(NO$_3$)$_2$ solution. This is in agreement with the sulfur signals in XPS measurements. The FTIR spectrum (Figure 3) is very similar to the spectrum of lead dodecyl sulfate, proving that the surfactant is an integer component of the composite material obtained. All previous analysis results indicate that the material obtained is an organic/inorganic nanocomposite.

The characteristic C−O−C IR frequency of the PEO (in the vicinity of 1100 cm^{-1}) is not visible. This band would overlap with large SDS bands; hence, the product could still contain small amounts of polymer. Two significant novel bands are observed in the FTIR spectrum at 1400 and 680 cm^{-1}. The new bands can be tentatively attributed to the acetate group, which was originally introduced as lead acetate, although the lead acetate band at 1550 cm^{-1} is not visible in the composite. Results of XRD analysis (Figure 4) reveal a very persistent lamellar spacing of roughly 30−31 Å, which is evident already for aggregates obtained after 4 days in suspension and much more clearly seen for samples that have remained in suspension for 2 weeks (Figure 4a). The peaks are narrow, intense, and visible up to very high angles. There is no evidence of free PbS in Figure 4a, although small PbS particles (in the nanometer range) with peaks of large width and low intensity would not be easily visible. Similar XRD spectra
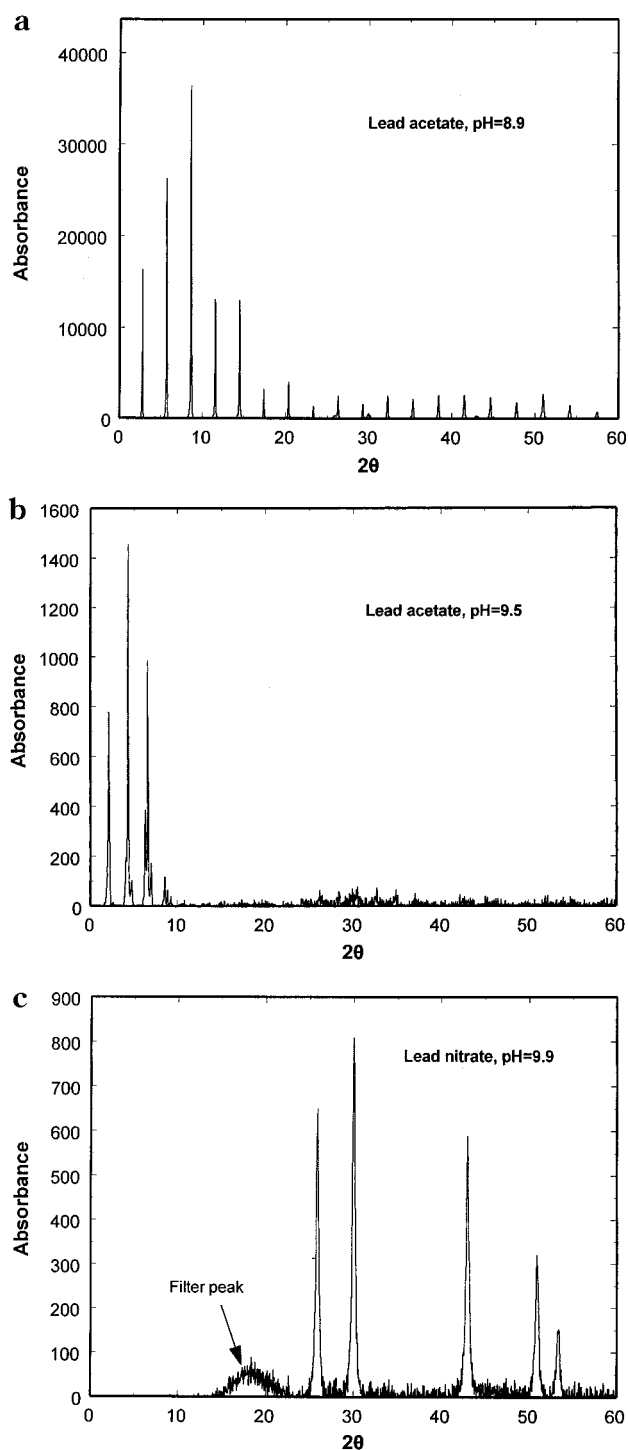

Figure 4. Powder XRD spectra of composites obtained with lead acetate (a) at pH = 8.9 and (b) pH = 9.5 and (c) with lead nitrate at pH = 9.9.

have been obtained with crystalline films of ammonium surfactants,[17] with lead stearate films deposited on glass substrates with the Langmuir−Blodgett method, after reaction with H$_2$S gas,[18] and with lead alkanoate films after reaction with H$_2$S.[19] For alkyl sulfate surfactants in particular, similar examples are provided in the work of Hirata and Iimura on complexes of sulfate surfactants

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with phenols and naphthols.[20] Strongly related to the present work is also the work of Tolbert et al. on the formation of composites between iron oxides and sulfate surfactants.[21] At this stage, it is difficult to give a precise picture of the structure of the composite materials obtained in this work, given the presence of dodecyl sulfate, acetate, lead, and sulfide ions in the structure and the impossibility of obtaining single crystals for diffraction work.

The results with lead acetate suggest that the pH is a critical parameter. Composite materials with well-developed lamellar structures are obtained at weakly acidic to weakly basic pHs, using acetic acid or NaOH to modify the pH, while at basic pHs (Figure 4b) the lamellar structures of the composites are slowly destroyed, presumably by the formation of lead oxides and hydroxides. Replacing lead acetate with lead nitrate revealed the significant role of the acetate in the formation of the layered structures. In the lead nitrate experiments, XRD analysis of the products did not reveal the typical diffractogram of the regular layered structure; the only visible pattern is that of PbS (Figure 4c). When lead acetate was replaced by the acetate salts of other metal cations in PEO/SDS solutions, it was found that Cu^{2+} forms aggregates that bear some similarity to those obtained with Pb^{2+} whereas Co^{2+} and Cd^{2+} do not form rodlike aggregates. These different behaviors must reflect both the specific interactions of the cations with the sulfate surfactants and their different interactions with the PEO chains, which have been studied to a certain extent in the literature.[22]

Conclusions

The crystallization of PbS in PEO/SDS solutions has offered a unique way to observe micelle-loaded polymer chains for the first time. The resulting crystallites aggregate with the help of the polymer chains through a bridging flocculation mechanism,[16] forming long rodlike aggregates, which eventually grow in length through a ripening mechanism and remain in suspension over a period of weeks. The final products of the experiment are novel organic/inorganic composite materials, characterized by a layered surfactant structure, which sandwiches a thin layer of lead and sulfide ions. Given the flexibility that the PEO/SDS system offers, in terms of precipitation reaction conditions, it appears to provide a promising new templating medium for the production of interesting organic/inorganic nanocomposite materials.

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