

Spherical Assemblies of Semiconductor Nanoparticles in Water-Soluble Block Copolymer Aggregates

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Novel spherical assemblies of CdS-containing block copolymer reverse micelles in aqueous solution have been formed by the slow addition of water to mixtures of the reverse micelles and a polystyrene-*b*-poly(acrylic acid) stabilizer. The structures are large compound micelles (LCMs) with quantum-confined CdS nanoparticles dispersed throughout a spherical PS matrix, which is stabilized in water by a layer of solubilized hydrophilic chains. The size of the CdS particles ($2R_{\text{CdS}} \sim 3$ nm) is controlled by the ionic block length, N_B , of the block copolymer making up the reverse micelle. LCM formation is found to be dependent on the amount of added stabilizing copolymer. When the weight of stabilizer relative to the total polymer weight is 12% for the specific system under study, a single population of LCMs is formed ($D_{\text{ave}} = 64$ nm); each of these LCMs consists of an average of 58 reverse micelles and 87 stabilizing chains, with an average surface area per stabilizing chain of 148 nm². At 10% stabilizer, two LCM populations, $D_{\text{ave}} = 52$ nm and $D_{\text{ave}} = 152$ nm, are formed. When the concentration of stabilizing copolymer is increased to 21 and 35%, regular micelles with no internal structure coexist with LCMs. Without added stabilizing copolymer, most reverse micelles undergo macroscopic precipitation upon water addition, although some LCMs are observed in the remaining solution.

1. Introduction

The synthesis of metallic and semiconducting nanoparticles, or clusters, has become a topic of extreme interest in the field of material science, due in part to the wide range of optical and electronic properties that are accessible in the nanometer-size regime. The unique properties of such nanoparticles are attributed to quantum-confinement or surface effects, which become operative when the particle is too small to exhibit bulk behavior.^{1,2} Under certain conditions, nanoparticles of metals^{3,4} and semiconductors^{5,6} can be induced to undergo self-organization into three-dimensional superlattices. Such nanoparticle assemblies open the door to "tunable" materials, in which optical and electronic properties are dependent on both initial cluster sizes and the manner in which clusters organize to form larger structures.

Block copolymers have long been known to self-assemble in selective solvents, forming stable aggregates known as micelles or micelle-like aggregates.^{7–9} Quite recently, various types of block copolymers have been applied to the synthesis of metallic and semiconducting particles.^{10–15} In these systems, particle growth is restricted to ionic or highly polar microdomains, providing a mechanism for both size control and particle stabilization. In particular, we have synthesized CdS quantum dots of low polydispersity within the spherical ionic cores of polystyrene-*b*-poly(cadmium acrylate) (PS-*b*-PACd) reverse micelles.¹⁴ Excellent correlation was found between the micelle ionic core radii and the resultant sizes of the semiconducting particles. As well, the polymer–semiconductor composites were found to be extremely stable, and could be suspended indefinitely in organic solvents, or precipitated into polar solvents, without agglomeration or significant ripening of CdS

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particles within the polymer "host". In other work, relationships between ionic block length and core radius were determined for a wide range of polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA)-based reverse micelles, where the acid block was neutralized with several different counterions (Cs⁺, Ba²⁺, Ni²⁺, Co²⁺, Cd²⁺, Pb²⁺).¹⁶ This provides a versatile system of "tunable" inorganic microreactors, in which precursor ions can be converted to a variety of metallic and semiconducting particles of a specific size at the nanometer scale.

Another aspect of amphiphilic block copolymers that has been investigated extensively in this laboratory is their tendency to form interesting aggregate morphologies in aqueous solutions.^{17–23} Through variations in such parameters as relative block lengths, polymer concentration, solvent composition, and acid or electrolyte addition, a wealth of morphologies, including spheres, rods, vesicles, and several unprecedented bilayer structures, has been observed. Another new morphology found in these systems is the so-called large compound micelle (LCM).^{17–19} These are solid, micrometer-size spheres, generally with large polydispersities, consisting of assemblies of reverse micelles stabilized in water by a thin layer of hydrophilic chains. It has been observed that aqueous suspensions of LCMs do not coalesce, and can be easily resuspended when the larger particles settle to the bottom of their container. In typical LCM-forming systems (e.g., PS-*b*-PAA^{17,18} or polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO)¹⁹), the large compound micelles are formed from a single type of block copolymer amphiphile, with most of the hydrophilic chains making up the reverse micelle cores and the remainder stabilizing the assemblies in water.

In the present paper, we report on the synthesis of quantum-confined CdS nanoparticles within block ionomer reverse micelles, followed by the assembly of these reverse micelles to form aqueous suspensions of LCMs. LCM formation is initiated by the slow addition of water to solutions of CdS-containing reverse micelles and a stabilizing copolymer (PS-*b*-PAA). This is in contrast to previous examples of LCM-forming systems, in which aggregates were prepared from solutions containing only single chains; here, the primary "building blocks" are previously-formed reverse micelles. It should also be noted that the reverse micelles and the stabilizing chains are comprised of different block copolymers, another feature that distinguishes this system from past approaches to LCM formation. The present work can be divided into three distinct steps: (1) self-assembly of block ionomer single chains in organic solvent, (2) synthesis of CdS nanoparticles within the resultant reverse micelles, and (3) "secondary" self-assembly of reverse micelles in aqueous solution. The final structures consist of many hydrophilic regions, each containing a semiconducting nanoparticle, dispersed throughout a hydrophobic sphere which is solubilized by a hydrophilic outer shell. Another approach to the solu-

bilization of hydrophobic micelles in aqueous solutions is demonstrated in onion-type micelles, recently reported by Procházka et al.²⁴

Assemblies of quantum dots within a polymer matrix, spatially confined to spherical geometry at the nanometer to micrometer scale, may have interesting nonlinear or electrooptical applications. The aqueous nature of these suspensions is very appealing from the point of view of possible biological applications, or the conversion of water-soluble reagents; in such cases, CdS quantum dots could be replaced by catalytic metal particles. To our knowledge, this represents the first example of quantum-confined semiconductors assembled in a system of water-soluble block copolymers.

2. Experimental Section

Synthesis of PS-*b*-PAA Diblock Copolymers. The synthesis of PS-*b*-PAA diblock copolymers used in the present study was performed by sequential anionic polymerization of styrene and *tert*-butyl acrylate; since this procedure is described in detail elsewhere,^{25–27} only a brief summary is presented here. Polymerization reactions were performed in tetrahydrofuran (THF), using *sec*-butyllithium initiator capped with a few units of α -methylstyrene. The molecular weights and polydispersity indexes (PI) of the PS blocks were determined using size-exclusion chromatography (SEC); a small amount of PS was therefore extracted from the reaction solution before addition of the *tert*-butyl acrylate monomer and injected into an SEC column. The molecular weights of the ester blocks were determined by quantitative FTIR of the diblock copolymer. The block copolymers in the ester form were hydrolyzed to PS-*b*-PAA by refluxing overnight in toluene with *p*-toluenesulfonic acid catalyst. The polymers were then recovered by precipitation into methanol, followed by drying under vacuum at 70 °C for 24 h. Two diblock copolymers were prepared in this manner: PS(240)-*b*-PAA(15) (i.e., 240 PS repeat units and 15 PAA repeat units; PI = 1.04) was used to prepare diblock ionomer micelles, in which CdS clusters were synthesized; PS(1100)-*b*-PAA(170) (i.e., 1100 PS repeat units and 170 PAA repeat units; PI = 1.06) was used as a stabilizing agent in the preparation of CdS-containing LCMs.

Preparation of PS-*b*-PACd Reverse Micelles. The copolymer PS(240)-*b*-PAA(15) was dissolved in benzene/methanol (10% methanol v/v) to obtain a 2% polymer solution (w/w). To initiate reverse micelle formation, the acid blocks were neutralized by the addition of excess cadmium acetate dihydrate in methanol (1.5 mol of CdAc₂·2H₂O:1 mol acrylic acid repeat units). A slight increase in turbidity indicated the presence of micelles, although a low aggregation number resulted in a relatively clear solution. The solution was stirred for 3–4 h, and then the solvent was removed by freeze-drying. The diblock ionomer (white powder) was dried at 70 °C overnight in a vacuum oven to remove residual solvent and acetic acid byproduct. Excess cadmium acetate was removed from the ionomer sample by repeated washings in methanol; the washed sample was dried under vacuum at 70 °C. A transparent film of the sample was cast on a KBr window, and FTIR was used to confirm that the acid block was completely neutralized; 100% neutralization was indicated by the disappearance of the carboxylic acid doublet at 1738 and 1710 cm⁻¹.

Preparation of CdS–Diblock Copolymer Composite. Diblock ionomer micelles of polystyrene-*b*-poly(cadmium acry-

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late) (PS(240)-*b*-PACd(15)) in the powder form were exposed to an atmosphere of 100% humidity for a period of 1 week. The powder was then placed in a closed container, into which "wet" H₂S (H₂S bubbled through water at 70 °C) was introduced. The ionomer powder was thus exposed to an H₂S environment for 8 h, during which time the sample turned yellow in color; excess H₂S was then removed from the powder by leaving the sample for 12 h under active vacuum.

In the process of CdS particle formation, the ionic blocks become protonated to PAA; it has been found that the stability of the CdS-containing micelles can be greatly improved by "fixing", i.e., reneutralization of the acid blocks.¹⁴ To this end, the reverse micelles were resuspended in THF and a stoichiometric quantity of NaOH was added. The solution was stirred for a least 4 h, then the yellow powder was recovered by precipitation into methanol. The CdS-block copolymer composite after "fixing" was designated CdS-MIC.

Quantum Dot Assemblies: LCM Formation. The composite material, CdS-MIC (yellow powder), was codissolved in *N,N*-dimethylformamide (DMF) with various quantities of the stabilizing copolymer, PS(1100)-*b*-PAA(170). Four solutions were prepared, in which the amount of stabilizing polymer relative to the total amount of polymer (stabilizing polymer + CdS-MIC) was 10, 12, 21, and 35% (w/w); in all cases, the concentration of CdS-MIC in DMF was 0.7% (w/w). Solutions prepared in this manner were comprised of CdS-containing reverse micelles suspended in a medium of DMF and PS-*b*-PAA single chains. A fifth solution of CdS-MIC without the stabilizing copolymer was also prepared.

The formation of micellar aggregates is generally induced by the addition of a precipitant for the PS blocks (water) to solutions of block copolymers in DMF. In the present case, deionized (Milli Q) water was slowly added to the clear yellow solutions (1 drop every 30 s) with rapid stirring; a dramatic increase in turbidity was observed at a water content of ca. 5% (v/v), indicating the onset LCM formation. In the solution without stabilizing polymer, a significant amount of yellow precipitate formed as water was added; all other solutions appeared to be stable. The addition of water was continued to ca. 40% water, and then the turbid solutions were dialyzed against distilled water to remove all DMF. Aqueous solutions prepared with 0, 10, 12, 21, and 35% stabilizing copolymer were designated LCM0, LCM10, LCM12, LCM21, and LCM35, respectively.

UV-Vis Absorption Spectroscopy. UV-vis absorption spectroscopy of the composite CdS-MIC was performed in toluene solution to characterize the sizes of quantum-confined CdS nanoparticles. Spectra were obtained on a Hewlett-Packard 8452 diode array spectrophotometer, by scanning between 250 and 550 nm. From the spectral absorption edge (λ_e), the CdS nanoparticle diameter was calculated using previous measurements correlating nanoparticle sizes with absorption onset data.^{28,29}

Transmission Electron Microscopy. Transmission electron microscopy (TEM) was performed on a Phillips EM410 instrument, and on a JEOL FX200 instrument with energy-diffusive X-ray diffraction (EDAX) capability. Both instruments were operated at an accelerating voltage of 80 kV.

For the determination of CdS nanoparticle sizes in the "unassembled" reverse micelles, a drop of CdS-MIC in dilute benzene solution (ca. 1 mg/mL) was placed on carbon-coated copper grids (J. B. EM Services Inc); excess solution was immediately removed with a piece of lens paper.

For the observation of LCM aggregates, aqueous solutions were diluted to ca. 1 mg/mL, and deposited onto carbon-coated EM grids; the grids had been precoated with a thin film of Formvar (J. B. EM Services) and then coated with carbon using an Edwards evaporator. A drop of solution was left on each grid for 20 min under ambient conditions, after which the remaining solution was blotted away with a piece of lens

tissue. To improve contrast for the observation of aggregate particle sizes and distributions, the samples were then shadowed with palladium/platinum alloy at a shadowing angle of 45°. Samples of each LCM solution were also prepared without shadowing, such that the internal structure of the aggregates could be observed. The beam was focused on one of the aggregates to obtain EDAX elemental analysis of the internal particles. The detection of LCM internal structure was optimized in the under-focus mode, with $\Delta f = 100\text{--}150$ nm. Features of both shadowed and unshadowed micrographs will be discussed.

3. Results and Discussion

The absorption spectrum of CdS-containing reverse micelles prior to LCM formation (CdS-MIC) is shown in Figure 1A. Since the block copolymer is not expected to show absorbance to the red of 300 nm, the spectrum can be attributed exclusively to the semiconductor particles. The clear appearance of an exciton shoulder and blue-shift of the absorption onset indicate that the CdS clusters are quantum-confined, suggesting particle diameters less than 6 nm.² From the position of the absorption edge (λ_e), 457 nm (Figure 1A), we calculate an actual CdS particle diameter of 3.8 nm.

An electron micrograph of CdS-MIC (Figure 1B) shows an even dispersion of dark semiconductor particles on the gray background of the polymer matrix. The average diameter of the particles is ~ 3 nm, in approximate agreement with the value calculated from λ_e on the UV-vis spectrum. It should be noted that CdS particle sizes calculated from the onset of the absorption spectrum generally represent the larger end of the size distribution, which explains the slightly smaller particle size determined from TEM. If we calculate the average particle sizes from the maximum of the absorption curve ($\lambda_m = \text{ca. } 425$ nm), we obtain a particle diameter of 2.9 nm, which agrees almost exactly with TEM results.

The difference between particle sizes calculated from λ_e and λ_m (i.e., $3.8 \text{ nm} - 2.9 \text{ nm} = 0.9 \text{ nm}$) gives the quantity $d_{1/2}$, which can be related to the width of the particle size distribution.¹⁴ Assuming a Gaussian distribution, $d_{1/2}$ can be converted into a radius polydispersity index (RPI) of 1.02 (where RPI = 1 defines a monodisperse sample). This suggests a low polydispersity of nanoparticle sizes in the present sample.

In previous work,¹⁴ we demonstrated size control of CdS particles in block ionomers by determining a relationship between ionic block lengths and the radii of nanoparticles synthesized in the micelle core (calculated from λ_m)

$$R_{\text{CdS}} = (0.19 \text{ nm})N_{\text{B}}^{3/5} + 0.94 \text{ nm} \quad (1)$$

where N_{B} is the number of repeat units in the ionic block. Applying eq 1 to the block ionomer "host" used in this study ($N_{\text{B}} = 15$), we calculate a CdS particle radius of 1.9 nm ($2R_{\text{CdS}} = 3.8 \text{ nm}$), which agrees exactly with our UV-vis results. This suggests that the mechanism of size control described previously, involving complete conversion of ions in the micelle core to a single semiconductor particle, is operative in the present case.

When water is slowly added to mixtures of CdS-containing micelles and stabilizing copolymer in DMF, the turbidity of the clear yellow solutions increased markedly at a water concentration of ca. 5% (v/v). The solutions remained turbid, though stable, as the water

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(29) The data in ref 28 has been digitized to obtain the equation: $2R_{\text{CdS}} = 0.1/(0.1338 - 0.0002345\lambda_e)$ nm.

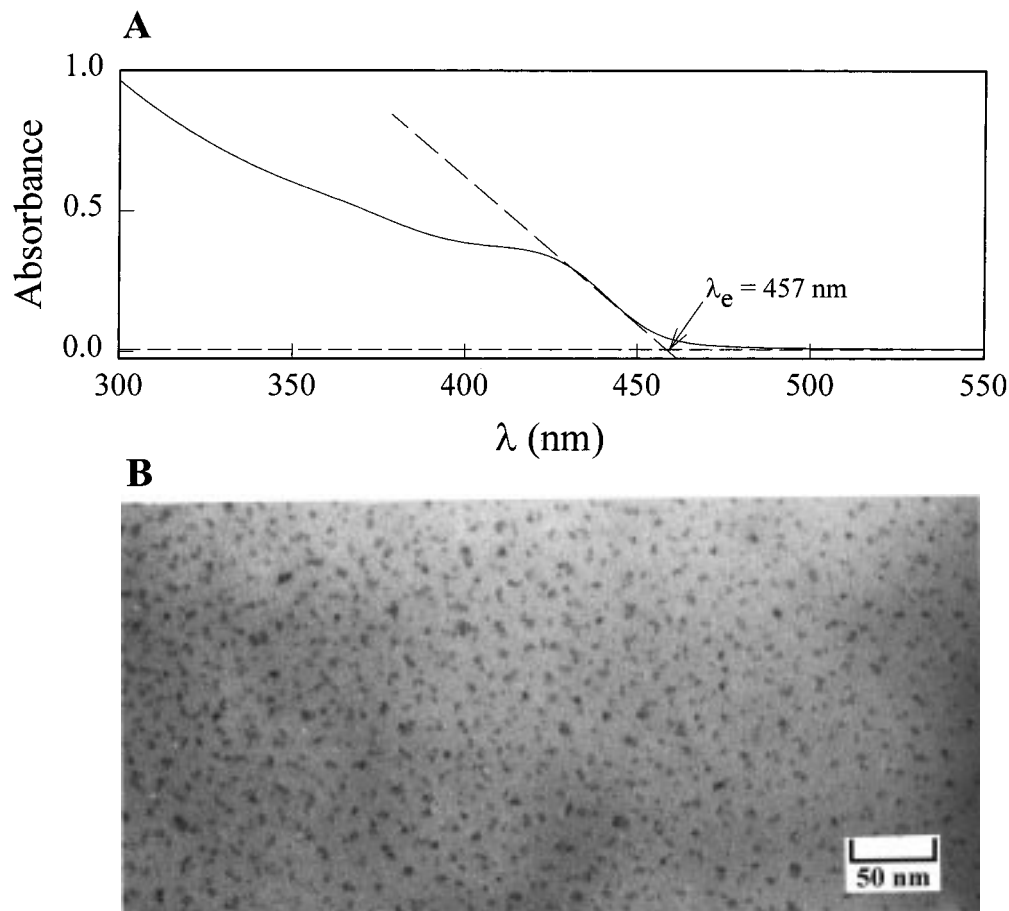


Figure 1. (A) UV-vis absorption spectrum of CdS-MIC, showing an absorption edge (λ_e) of 457 nm for the CdS nanoparticles. The semiconductor particle diameter calculated from λ_e is 3.8 nm. (B) Transmission electron micrograph of CdS-MIC. The dark particles are CdS, with an average diameter of ~ 3 nm.

concentration was increased further and the DMF was removed by dialysis. No macroscopic precipitation of the reverse micelles was observed, suggesting that they had been successfully solubilized in water. TEM of the aqueous solution revealed populations of spherical aggregates; the average size of the aggregates and the number of populations observed in the samples were dependent on the amount of stabilizing copolymer, with most solutions showing two distinct populations. We will discuss possible reasons for these dependencies later; for now, we turn our attention to one sample, LCM12 (12% stabilizing copolymer), in which a single population of spherical aggregates was observed.

Spherical aggregates in sample LCM12, with and without shadowing, are shown in the transmission electron micrographs of Figure 2. In the shadowed picture (Figure 2A), the Pd/Pt coating significantly increases the contrast of the aggregate relative to the background, and a single population of spheres is clearly visible. Distribution analysis of a larger number of aggregates than that shown in the figure reveals an average particle diameter, D_{ave} , of 64 nm, with a standard deviation of 8 nm. A micrograph of the same sample without shadowing (Figure 2B) reveals the internal structure of the aggregates, suggesting that they are large compound micelles (LCMs), rather than regular spherical micelles. The dark particles dispersed in the aggregates (unshadowed micrograph) are believed to be CdS nanoparticles in the cores of assembled reverse micelles; this is supported by (1) the yellow color

of the turbid solution, indicating that the CdS particles of CdS-MIC have been incorporated into the aqueous aggregates, (2) the size of the dark particles (~ 3 nm), which matches that of CdS particles in CdS-MIC (Figure 1B), and (3) EDAX results (Figure 3), which show both Cd and S bands when the electron beam is focused inside one of the aggregates. The prominent Cu and Si bands are due to the EM grid and small amounts of silicon grease in the sample, respectively. The LCMs in Figure 2A are relatively monodisperse, compared with those formed from single chains of PS-*b*-PAA or PS-*b*-PEO.¹⁷⁻¹⁹ The clustering of LCMs observed in the micrographs is an artifact related to TEM sample preparation and does not reflect the state of aggregates in solution. This is supported by the lack of macroscopic precipitation, which seems to indicate that the spheres are individually solubilized.

A schematic diagram of a large compound micelle such as those found in sample LCM12 (Figure 4) depicts a spherical assembly of reverse micelles, each with a hydrophilic core consisting of a single CdS particle and a thin layer of poly(sodium acrylate); PS chains radiate from these cores into the surrounding melt. The driving force for LCM formation is mainly enthalpic: the continuous addition of water to a solution of reverse micelles makes interactions between the solvent and the PS corona increasingly unfavorable; the reverse micelles eventually coprecipitate with the long PS blocks of the stabilizing copolymer. As shown in Figure 4, single chains of the stabilizing copolymer distribute themselves

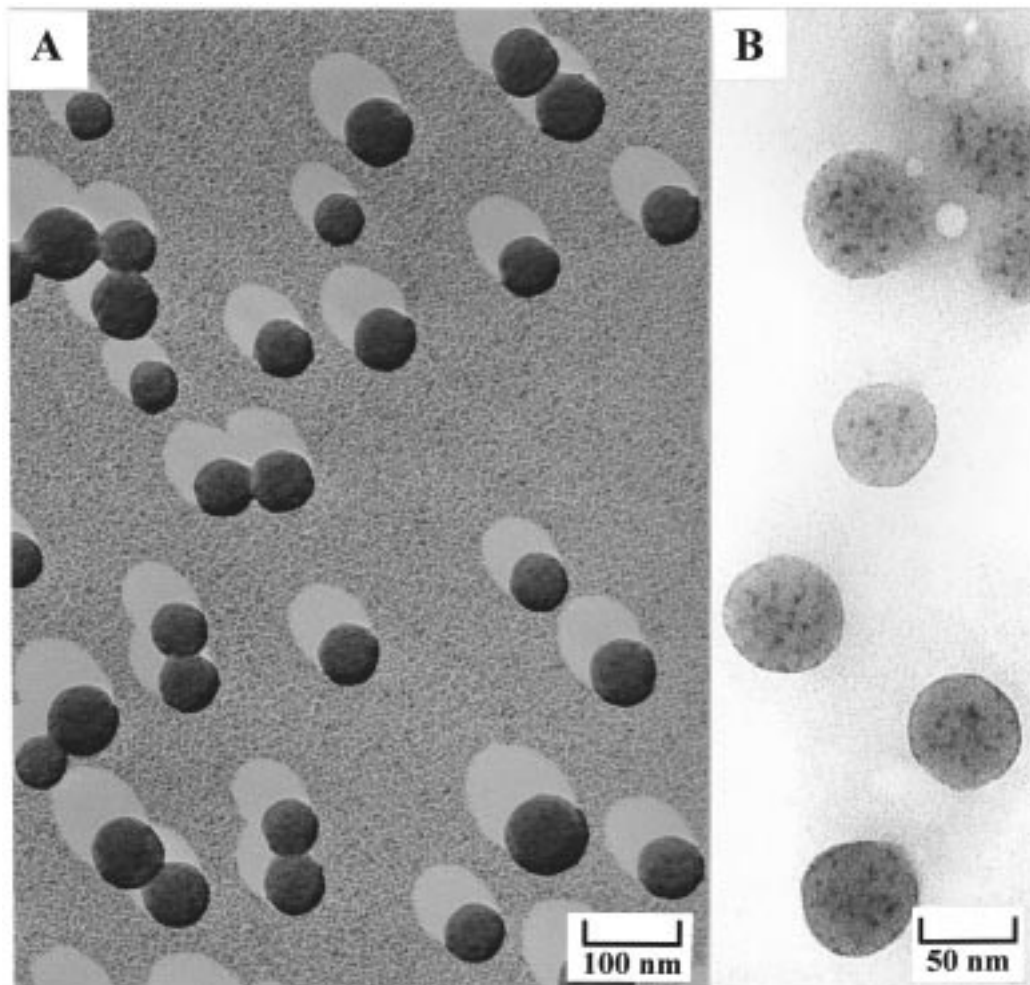


Figure 2. Transmission electron micrograph of spherical aggregates in LCM12, (A) with Pd/Pt shadowing and (B) without shadowing. The dark particles inside the spheres are CdS nanoparticles.

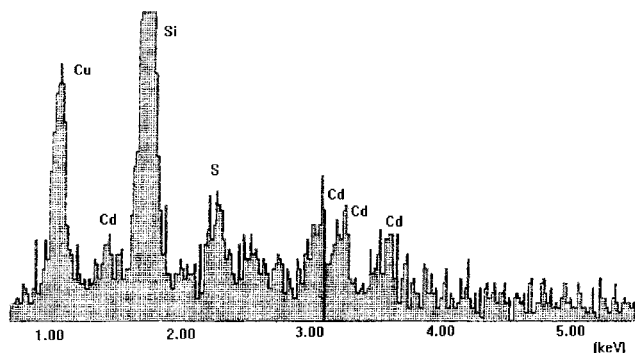


Figure 3. Energy-dispersive X-ray diffraction pattern of one of the aggregates containing dark particles, showing Cd and S bands.

at the surface of the LCM, minimizing interfacial tension through favorable interactions between water and the “free” PAA blocks; this, in effect, prevents flocculation of the aggregates and macroscopic precipitation of the reverse micelles. The copolymer chains which constitute the reverse micelles are essentially “locked” into the hydrophilic cores through strong ionic interactions, and are therefore unable to play a stabilizing role. The low polydispersity of the LCMs may be related to the restricted movement of these chains, which is governed by the movement of reverse micelles during secondary self-assembly.

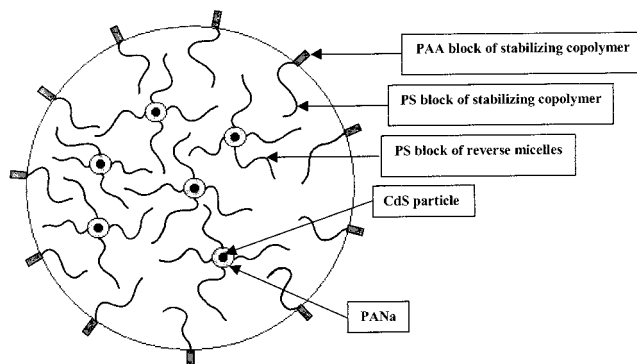


Figure 4. Schematic diagram of a large compound micelle containing CdS nanoparticles. The spherical aggregate is an assembly of reverse micelles, stabilized with added block copolymer.

From the average diameter of the aggregates, R_{LCM} , it is possible to calculate the average number of reverse micelles, N_{rm} , and stabilizing copolymer chains, N_{sc} , which make up the LCMs in Figure 2. The average volume of the aggregates is calculated from

$$V_{\text{LCM}} = \frac{4}{3}\pi R_{\text{LCM}}^3 \quad (2)$$

The LCM volume is the sum of the total volume of reverse micelles and stabilizing copolymer in the ag-

gregate, such that

$$V_{\text{LCM}} = N_{\text{rm}} V_{\text{rm}} + N_{\text{sc}} V_{\text{sc}} \quad (3)$$

where V_{rm} and V_{sc} are the volumes of reverse micelles and stabilizing copolymer chains, respectively; these values can be calculated from the composition of the block copolymers and the aggregation number of the reverse micelles, Z ,

$$V_{\text{rm}} = Z[240v_{\text{PS}} + 15v_{\text{PANa}}] + V_{\text{CdS}}$$

$$V_{\text{sc}} = 1100v_{\text{PS}} + 170v_{\text{PAA}} \quad (4)$$

where v_{PS} , v_{PANa} , and v_{PAA} are the bulk volumes of individual repeat units of polystyrene, poly(sodium acrylate), and poly(acrylic acid), respectively, and V_{CdS} is the average volume of a CdS nanoparticle within each reverse micelle. The aggregation number of the reverse micelles, Z , is determined from published scaling relations to be ~ 50 .¹⁶ Similarly, the masses of the reverse micelles and stabilizing copolymer chains can be calculated from

$$m_{\text{rm}} = Z[240m_{\text{PS}} + 15m_{\text{PANa}}] + m_{\text{CdS}}$$

$$m_{\text{sc}} = 1100m_{\text{PS}} + 170m_{\text{PAA}} \quad (5)$$

where m_{PS} , m_{PANa} , and m_{PAA} are the masses of polystyrene, poly(sodium acrylate), and poly(acrylic acid) repeat units and m_{CdS} is the average mass of CdS nanoparticles.

Assuming that all of the stabilizing copolymer in sample LCM12 is evenly distributed throughout the population of aggregates, N_{rm} and N_{sc} can also be expressed in terms of the following equation

$$\frac{N_{\text{sc}} m_{\text{sc}}}{N_{\text{rm}} m_{\text{rm}} + N_{\text{sc}} m_{\text{sc}}} = 0.12 \quad (6)$$

where 0.12 is the weight fraction of the stabilizing chains.

Combining eqs 2–6 for an LCM radius of $R_{\text{LCM}} = 32$ nm, we determine that an average aggregate in sample LCM12 is an assembly of 58 reverse micelles ($N_{\text{rm}} = 58$) and 87 chains of the stabilizing copolymer ($N_{\text{sc}} = 87$). This implies that an average of 58 quantum-confined CdS particles are evenly distributed throughout the mainly polystyrene spheres. From the volume of reverse micelles within the aggregates, V_{rm} , we have calculated an average spacing of 12 nm between CdS particles. The spacing between particles within the aggregates should be quite monodisperse, as it is mainly governed by the bulk volume of the reverse micelle coronal layers. As well, particle–particle spacing can be easily “tuned” by using reverse micelles with different PS block lengths.

A fundamental parameter in aggregate formation is the interfacial area per stabilizing copolymer chain, A_{sc} .¹⁸ For the single population of aggregates in sample LCM12, A_{sc} is calculated from N_{sc} and the average LCM surface area ($A = 4\pi R_{\text{LCM}}^2$) to be 148 nm² per chain. This value can be compared with A_{sc} calculated for regular spherical micelles formed from the stabilizing copolymer alone, i.e., without reverse micelles: 38 nm² per chain. In the early stages of LCM formation, when

Table 1. Spherical Aggregate Populations in Systems of CdS-MIC and PS-*b*-PAA Stabilizing Copolymer

sample	wt % PS- <i>b</i> -PAA ^a	observed aggregate populations ^b
LCM0	0	LCMs (CdS); $D_{\text{ave}} = 100$ nm ^c
LCM10	10	LCMs (CdS); $D_{\text{ave}} = 152$ nm LCMs (CdS); $D_{\text{ave}} = 52$ nm
LCM12	12	LCMs (CdS); $D_{\text{ave}} = 64$ nm
LCM21	21	1. LCMs (CdS); $D_{\text{ave}} = 63$ nm 2. PS- <i>b</i> -PAA micelles; $D_{\text{ave}} = 21$ nm
LCM35	35	1. LCMs (CdS); $D_{\text{ave}} = 50$ nm 2. PS- <i>b</i> -PAA micelles; $D_{\text{ave}} = 21$ nm

^aWt % is relative to total polymer in solution. ^b“CdS” in parentheses indicates that aggregates contain CdS particles. ^cExtensive macroscopic precipitation of CdS-MIC also observed in LCM0.

the PS regions are sufficiently swollen with the DMF solvent, a dynamic equilibrium is assumed to exist between the aggregates and their components (reverse micelles and stabilizing copolymer), such that the structures are an expression of a free energy minimum. As more DMF is forced out by the addition of water, however, the mobility of PS chains in the aggregates decreases, and the LCMs become essentially frozen. The final surface area per chain, A_{sc} , will therefore reflect a minimization of surface energy at a stage when both the polymer aggregates and the surrounding medium contain a considerable amount of organic solvent.

As the amount of stabilizing copolymer is varied, TEM reveals distinct changes in the LCM populations; a summary of observed populations for different amounts of added PS-*b*-PAA is presented in Table 1. Micrographs of shadowed and unshadowed EM grids are shown in Figure 5 for samples prepared with 10, 21, and 35% of the copolymer PS(1100)-*b*-PAA(170). Whereas a single population ($D_{\text{ave}} = 64$ nm) was found with 12% stabilizing polymer, the sample prepared with 10% stabilizing polymer, LCM10 (Figure 5A), clearly contains two populations of spheres, with average diameters of 52 and 152 nm. Figure 5B shows a portion of the unshadowed grid, with several of the smaller spheres and a typical large sphere; the micrograph reveals that large and small aggregates both contain CdS particles, suggesting that both populations were formed by a mechanism of reverse micelle assembly. When the amount of stabilizing copolymer is increased to 21% (LCM21, Figure 5C), we find a population of spheres, $D_{\text{ave}} = 63$ nm, very similar to those formed at 12%, along with a second population of much smaller spheres ($D_{\text{ave}} = 21$ nm). Microscopy of the unshadowed grid of LCM21 (Figure 5D) shows the larger spheres to have internal structure, while the 21 nm particles appear as featureless “blotches” against the background, indicating that they do not contain any semiconductor particles. The situation is very similar when the amount of stabilizing copolymer is increased to 35% (Figure 5E), though the larger population has shifted to slightly smaller spheres ($D_{\text{ave}} = 50$ nm), compared with those in LCM21. The smaller population ($D_{\text{ave}} = 21$ nm) is identical to that found with 21% stabilizer and again does not show evidence of internal structure (Figure 5F). Qualitative comparison of LCM21 and LCM35 seems to indicate a greater number of smaller spheres on grids of the latter sample.

These results suggest that a single distribution of aggregates can only be obtained in a narrow window of

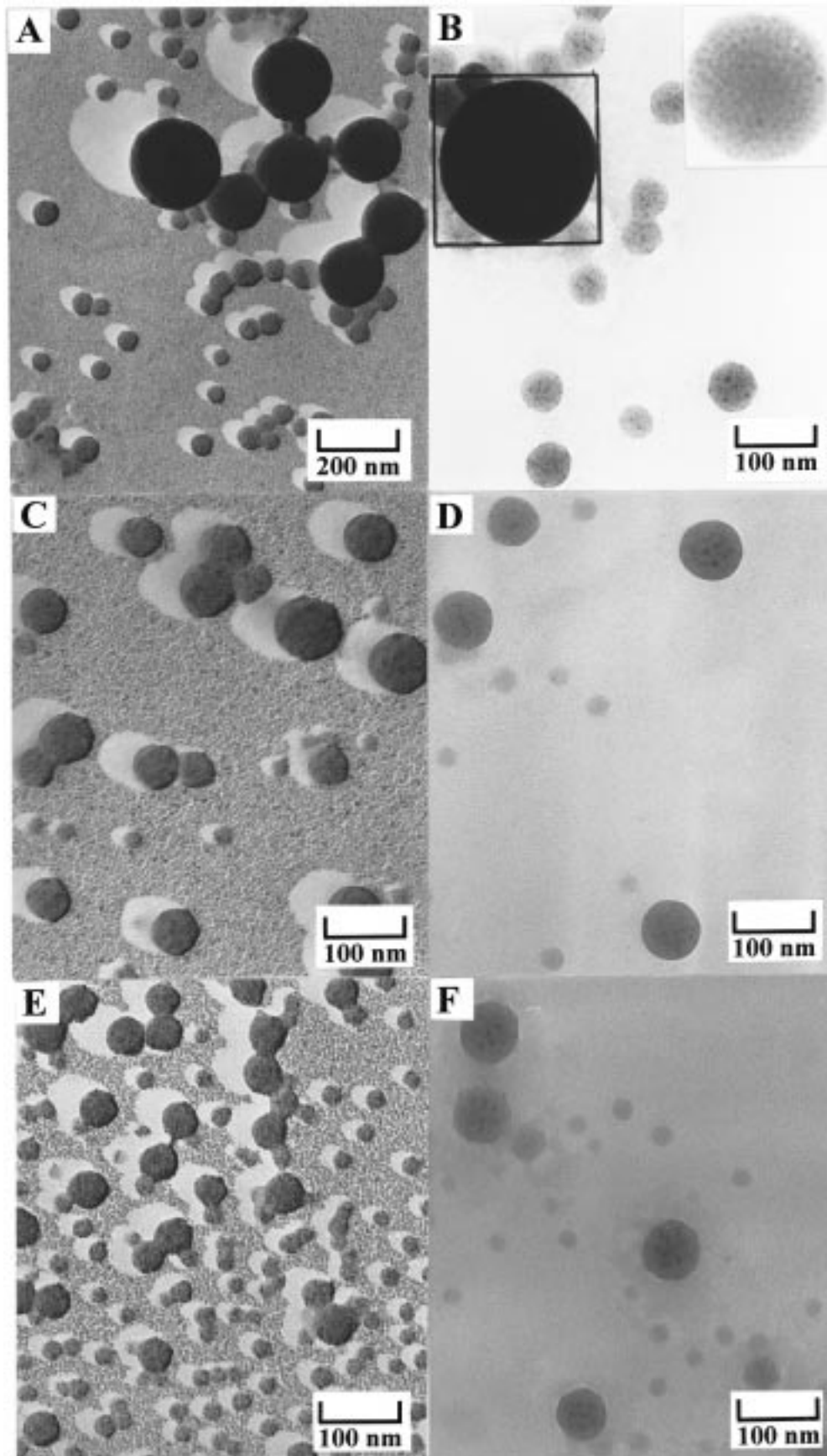


Figure 5. Transmission electron micrographs of spherical aggregates of LCM10, (A) with shadowing and (B) without shadowing; LCM21, (C) with shadowing and (D) without shadowing; LCM35, (E) with shadowing and (F) without shadowing. In part B, the inset shows the boxed region at a lower exposure time, revealing the internal structure of the large spherical aggregate.

conditions, i.e., $\sim 12\%$ of stabilizing copolymer for the concentration of reverse micelles used in this study. On

the other hand, we observe similar populations of spheres, with average diameters in the range 50–64

nm, in all four samples containing stabilizing copolymer. This is not surprising, since the size of the CdS-containing aggregates will depend on the number of nucleation sites and is therefore largely governed by the initial concentration of reverse micelles. The additional presence of larger LCMs in sample LCM10 (Figure 5A,B) suggests the crossing over of a phase boundary between 10 and 12% stabilizing copolymer. In the 10% sample, the initial formation of nucleation sites depends only on the concentration of reverse micelles, which accounts for the presence of the smaller spheres ($D_{\text{ave}} = 52$ nm); a lack of stabilizing copolymer, however, necessitates the clustering of some nucleation sites to decrease the total surface area of the system, resulting in a population of much larger spheres ($D_{\text{ave}} = 152$ nm). In the 21 and 35% samples, not all of the added block copolymer is required to stabilize the assemblies of reverse micelles; the "excess" copolymer, PS(1100)-*b*-PAA(170), therefore forms regular micelles with polystyrene cores and a poly(acrylic acid) corona. These are the small spheres ($D_{\text{ave}} = 21$ nm) in samples LCM21 and LCM35 that do not contain CdS particles. Since the amount of stabilizing copolymer is greater in LCM35 than in LCM21, a greater concentration of regular micelles is found in the former sample. It is also noteworthy that the average diameter of the LCM populations decreases between the 21 and 35% samples, which suggests that some of the "excess" stabilizer in LCM35 is actually incorporated into the large compound micelles, allowing a decrease in particle size via a lowering of the surface energy. It therefore appears likely that, below a certain concentration of added water, the equilibrium between single chains and regular micelles exists in tandem with the equilibrium between LCMs and their reverse micelle and single chain components.

In the absence of stabilizing copolymer (LCM0), most of the reverse micelles precipitated from solution as water was added. The yellow material settled to the bottom of the vial, though the remainder of the solution was found to be extremely turbid. Following dialysis, electron microscopy of the turbid solution revealed a number of CdS-containing LCMs, with an average diameter of ~ 100 nm. It has been found that a low concentration of single chains will exist in any solution of block ionomer reverse micelles, due to the small number of chains with ionic blocks too short to undergo self-assembly.²⁶ We believe that, without added copolymer, these single chains are able to act as stabilizers, allowing the reverse micelles that do not precipitate from solution to form spherical assemblies.

4. Conclusions

We have prepared novel spherical assemblies of quantum-confined semiconductors in aqueous solution by the slow addition of water to reverse micelles and a stabilizing block copolymer in organic solvent. The assemblies are best described as large compound micelles, consisting of CdS nanoparticles ($2R_{\text{CdS}} \sim 3$ nm) dispersed throughout a PS sphere which is stabilized in water by a layer of hydrophilic PAA chains. When the amount of stabilizing copolymer relative to the total amount of polymer was 12% (w/w), a single population of LCMs ($D_{\text{ave}} = 64$ nm) was observed; it was determined that these aggregates consist of an average of 58 reverse micelles and 87 stabilizing chains. At 10% stabilizing copolymer, two populations of LCMs were observed ($D_{\text{ave}} = 52$ nm and $D_{\text{ave}} = 152$ nm); the larger population is attributed to the agglomeration of nucleation sites due to a lack of stabilizer. When the concentration of stabilizing copolymer was sufficiently high (21 and 35%), regular micelles with no internal structure were found to coexist with LCMs. The amount of stabilizing copolymer required to obtain a given population is believed to be dependent on both the concentration and composition of the reverse micelles; this implies an inherent versatility in the system, through variations in several adjustable parameters. In the absence of stabilizing copolymer, most reverse micelles were found to precipitate upon water addition, although a number of LCMs were observed in the remaining solution; these are thought to be stabilized by single chains of low ionic content in the solution of reverse micelles.

Along with being a novel morphology, assemblies of semiconducting or metallic nanoparticles confined to polymer spheres of small dimensions may have numerous applications to nonlinear optics, electrooptical devices, or catalysis. For some applications, the PS matrix could be easily replaced by conducting or semiconducting organic polymers. Since the spheres are suspended in aqueous solution, they are also amenable to biological systems, in which catalytic or photocatalytic properties could be exploited.

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