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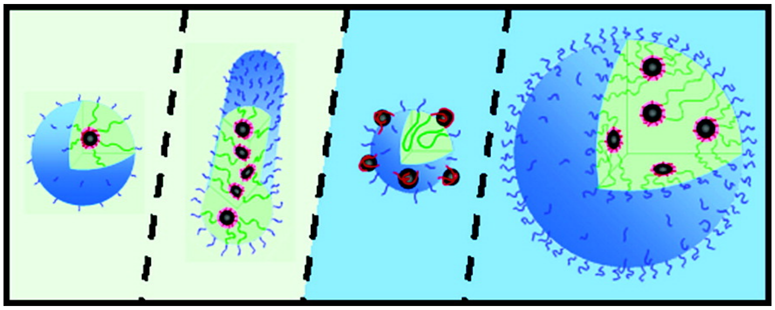

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Cadmium Sulphide Quantum Dots in Morphologically Tunable Triblock Copolymer Aggregates

Nicolas Duxin,[*,†] Futian Liu,[*,†] Hojatollah Vali,[*,‡] and Adi Eisenberg[*,†]

Contribution from the McGill University, Department of Chemistry, 801 Sherbrooke Street West, Montreal, Quebec, H3A 2K6, Canada, and McGill University, Facility for Electron Microscopy Research, 3640 University Street, Montreal, Quebec, H3A 2B2, Canada

Received January 25, 2005; E-mail: adi.eisenberg@mcgill.ca

Abstract: Cadmium sulfide (CdS) quantum dots (QDs) are formed within poly(ethylene oxide)-*block*-polystyrene-*block*-poly (acrylic acid) (PEO-*b*-PS-*b*-PAA) triblock copolymer aggregates of different architectures. These structures are obtained starting with the same ionically cross-linked primary micelles consisting of a cadmium acrylate core, a PS shell, and a PEO corona. One morphology is a worm-shaped micelle prepared in tetrahydrofuran (THF) in which the CdS QDs are surrounded by the PAA and aligned as a loose necklace in the PS matrix. The PEO serves as a corona around the PS rod. Another structure is a multicore spherical (ca. 50 nm) water soluble PS micelle, surrounded by PEO chains. The CdS particles within these two latter structures are formed by the reaction of cadmium ions present in the acrylate cores with hydrogen sulfide. In a third structure, the CdS QDs are located on the surface of PS micelles. A fourth spherical single-core micelle structure is postulated to exist in dilute THF solutions. The dimensions in all the aggregates can be controlled by the block length.

1. Introduction

Many studies have been performed on syntheses of semiconductor quantum dots (QDs) using various experimental approaches[1−9] not only for academic reasons but also for their potential use as biological labels,[10] catalysts,[11] nanoelectronic devices[12] and in many other areas of nanotechnology. In polymers, cadmium (Cd) ions can be incorporated into block copolymers, and the resulting QDs are then located either in the bulk or, if in solution, inside or on the surfaces of inverted micelles.[13−22] The preparation of solutions of cadmium sulfide (CdS) in block ionomer reverse micelles in an organic solvent was reported first by Moffitt et al.[15] In a follow-up study, aqueous solutions of polystyrene-*b*-poly (acrylic acid) (PS-*b*-PAA) compound micelles containing QDs were obtained.[16] Other preparations of CdS QDs in block copolymer assemblies involved also triblock copolymers such as hydroxylated poly(styrene-*b*-butadiene-*b*-styrene) micelles in toluene.[17]

Amphiphilic diblock copolymers in solution give a range of different morphologies,[23−36] and solvent controlled transitions have been observed.[27,32,37,38] In addition to diblock copolymers,

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† Department of Chemistry.

‡ Facility for Electron Microscopy Research.

(1) Henglein, A.; Gutierrez, M. *Ber. Bunsen-Ges.* **1983**, *87*, 852−8.
(2) Rossetti, R.; Hull, R.; Gibson, J. M.; Brus, L. E. *J. Chem. Phys.* **1985**, *82*, 552−9.
(3) Tricot, Y. M.; Fendler, J. H. *J. Phys. Chem.* **1986**, *90*, 3369−74.
(4) Brus, L. *J. Phys. Chem.* **1986**, *90*, 2555−60.
(5) Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. *J. Am. Chem. Soc.* **1987**, *109*, 5649−55.
(6) Watzke, H. J.; Fendler, J. H. *J. Phys. Chem.* **1987**, *91*, 854−61.
(7) Murray, C. B.; Norris, D. J.; Bawendi, M. G. *J. Am. Chem. Soc.* **1993**, *115*, 8706−15.
(8) Braun, P. V.; Osenar, P.; Stupp, S. I. *Nature (London)* **1996**, *380*, 325−8.
(9) Alivisatos, A. P. *Science (Washington, DC)* **1996**, *271*, 933−7.
(10) Chan, W. C. W.; Nie, S. *Science (Washington, DC)* **1998**, *281*, 2016−18.
(11) Henglein, A.; Fojtik, A.; Weller, H. *Ber. Bunsen-Ges.* **1987**, *91*, 441−6.
(12) Klein, D. L.; Roth, R.; Lim, A. K. L.; Alivisatos, A. P.; McEuen, P. L. *Nature (London)* **1997**, *389*, 699−701.
(13) Cummins, C. C.; Schrock, R. R.; Cohen, R. E. *Chem. Mater.* **1992**, *4*, 27−30.
(14) Yue, J.; Cohen, R. E. *Supramol. Sci.* **1994**, *1*, 117−22.
(15) Moffitt, M.; McMahon, L.; Pessel, V.; Eisenberg, A. *Chem. Mater.* **1995**, *7*, 1185−92.
(16) Moffitt, M.; Vali, H.; Eisenberg, A. *Chem. Mater.* **1998**, *10*, 1021−1028.
(17) Wang, D.; Yaan, C.; Xintong, Z.; Zhiqiang, L.; Xinming, Q.; Xin, A.; Fengqi, L.; Dejun, W.; Yubai, B.; Tiejin, L.; Tang, X. *Chem. Mater.* **1999**, *11*, 392−398.
(18) Zhao, H.; Douglas, E. P.; Harrison, B. S.; Schanze, K. S. *Langmuir* **2001**, *17*, 8428−8433.
(19) Zhao, H.; Douglas, E. P. *Chem. Mater.* **2002**, *14*, 1418−1423.
(20) Liu, T.; Burger, C.; Chu, B. *Prog. Polym. Sci.* **2002**, *28*, 5−26.
(21) Ma, Y.; Qi, L.; Ma, J.; Cheng, H.; Shen, W. *Langmuir* **2003**, *19*, 9079−9085.
(22) Zhang, M.; Drechsler, M.; Mueller, A. H. E. *Chem. Mater.* **2004**, *16*, 537−543.
(23) Gao, Z.; Varshney, S. K.; Wong, S.; Eisenberg, A. *Macromolecules* **1994**, *27*, 7923−7.
(24) Honda, C.; Sakaki, K.; Nose, T. *Polymer* **1994**, *35*, 5309−18.
(25) Zhang, L.; Eisenberg, A. *Science (Washington, DC)* **1995**, *268*, 1728−31.
(26) Liu, G.; Qiao, L.; Guo, A. *Macromolecules* **1996**, *29*, 5508−5510.
(27) Yu, Y.; Zhang, L.; Eisenberg, A. *Macromolecules* **1998**, *31*, 1144−1154.
(28) Cameron, N. S.; Corbierre, M. K.; Eisenberg, A. *Can. J. Chem.* **1999**, *77*, 1311−1326.
(29) Harada, A.; Kataoka, K. *Science (Washington, DC)* **1999**, *283*, 65−67.
(30) Won, Y.-Y.; Davis, H. T.; Bates, F. S. *Science (Washington, DC)* **1999**, *283*, 960−963.
(31) Discher, D. E.; Eisenberg, A. *Science (Washington, DC)* **2002**, *297*, 967−973.
(32) Choucair, A.; Eisenberg, A. *Eur. Phys. J. E: Soft Matter* **2003**, *10*, 37−44.
(33) Hadjichristidis, N.; Pispas, S.; Floudas, G. *Block copolymers, synthetic strategies physical properties and applications*; Wiley-Interscience: New York, 2003.
(34) LaRue, I.; Adam, M.; da Silva, M.; Sheiko, S. S.; Rubinstein, M. *Macromolecules* **2004**, *37*, 5002−5005.
(35) Forster, S.; Plantenberg, T. *Angew. Chem., Int. Ed.* **2002**, *41*, 688−714.
(36) Bronich, T. K.; Ouyang, M.; Kabanov, V. A.; Eisenberg, A.; Szoka, F. C., Jr.; Kabanov, A. V. *J. Am. Chem. Soc.* **2002**, *124*, 11872−11873.
(37) Chen, L.; Shen, H.; Eisenberg, A. *J. Phys. Chem. B* **1999**, *103*, 9488−9497.
(38) Burke, S. E.; Eisenberg, A. *Langmuir* **2001**, *17*, 6705−6714.

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triblock copolymers are now also of interest.[39−41] Solvent controlled morphological transitions have also been seen in these systems.[42] Following Antonietti and Bronstein's early work on spheres,[43−45] assemblies of QDs in block copolymer solutions have been prepared in various polymeric systems, having various architectures. The QDs are present as chainlike structures[22,46,47] or compound micelles[16,18] or are located in the corona of micelles.[19,21]

In this study, we describe the templated synthesis of CdS QDs located in aggregates of poly(ethylene oxide)-*block*-polystyrene-*block*-poly (acrylic acid) triblock copolymers (PEO-(45)-*b*-PS(150)-*b*-PAA(108)), which display different morphologies, depending on the experimental and preparative conditions. These morphologies are obtained from the same spherical triblock copolymer inverse micelles in THF, which consist of a cadmium acrylate (CdAcr) core, surrounded by the PS chains, and further out, by PEO corona. One of these structures is a worm-shaped micelle containing the chainlike CdS QDs. Another is a water soluble spherical multicore micelle in which the QDs are located within the PS matrix. A fourth morphology consists of a PS core with the CdS QDs present on the surface. The use of solvents to manipulate the morphology of polymer aggregates containing CdS QDs, as well as the formation of the large spherical multicore triblock copolymer micelle structure, is novel.

2. Experimental Section

2.1. Synthesis of the Triblock Copolymer. The PEO-*b*-PS-*b*-PAA triblock copolymer was prepared by atom transfer radical polymerization (ATRP). The PEO macroinitiator was prepared through the reaction of PEO(45)−OH and 2-bromoisobutyryl bromide according to a method similar to that given in ref 48. The PEO(45)-*b*-PS macroinitiator was prepared by styrene polymerization, initiated by the PEO macroinitiator. As a typical example, a mixture of 1.5 g of PEO macroinitiator (PEO-(45)−Br) (0.6975 mmol), styrene (20.5 mL, 178.9 mmol), CuBr (11 mg, 0.6975 mmol), and 2,2′-bipyridine (326.8 mg, 2.0925 mmol) was freeze-dried before introducing N_2 and then kept in a bath at 100 °C. After 12 h, the viscous mixture was diluted with THF. The insoluble part was removed by filtration. A white polymer powder was obtained by precipitation of the filtrate into methanol. Gel permeation chromatography (GPC) was used to determine the molecular weight and the molecular weight distribution.

The addition of the PAA block was accomplished as follows: 1.66 g of the PEO(45)-*b*-PS(145) diblock macromer, 14.3 mg of CuBr (0.1 mmol), 2.84 mL of *tert*-butyl acrylate (19.4 mmol), and 2.84 mL of acetone were charged into a round-bottom flask. This mixture was purged with nitrogen several times to remove the oxygen. Then 22.16 μL (0.1 mmol) of the ligand PMDETA (*N*,*N*,*N*′,*N*′,*N*′-pentamethyldiethylene triamine) was added. The mixture was put into a bath at 60 °C for 3 h. The final polymer was purified by precipitation into methanol and dried under vacuum for 3 days. The *tert*-butyl acrylate groups were hydrolyzed to acrylic acid by refluxing the mixture of triblock and an excess of trifluoroacetic acid overnight. The solvent was evaporated and the sample purified by precipitation into methanol.

At the end of each step, the products were characterized by ^{1}H NMR and IR spectroscopy; the polydispersity, determined by GPC, is equal to 1.12 for PEO(45)-*b*-PS(150)-*b*-PAA(108) and 1.21 for PEO(45)-*b*-PS(46)-*b*-PAA(30).

2.2. Preparation of the Polymer Solutions. The triblock copolymer was solubilized in THF (0.06 g polymer/2.97 g THF). A 60 μL aliquot of a 0.06 wt % cadmium acetate dihydrate ($Cd(Ac)_2$, $2H_2O$) aqueous solution was added dropwise to the 0.05 wt % polymer solution in THF, to neutralize and cross-link the acrylic acid, at a rate of 400 μL/h through a septum cap, with stirring, to different neutralization ratios $n_{Cd2+}/2n_{AA-}$.

2.3. Changing Solvent from THF to Water and Subsequent Dialysis. To change the solvent from THF to water, the THF solution was added dropwise to a large amount of water (10 times). Dialysis of the primary micelles solutions was performed by using wet Spectra/PorCE cellulose ester membranes (Spectrum Laboratories Inc, stored in 0.1% sodium azide), with a molecular weight cut off of 500 g/mol. The water in the beaker containing the dialysing samples was changed eight times during the run, with a minimum time separation of 2 h between changes. The unreacted Cd ions were eliminated in the process.

2.4. Characterization Techniques. Transmission Electron Microscopy. A JEOL 2000FX microscope was used for the TEM studies. The dilute water quenched samples were deposited on EM grids that had been precoated with carbon.

UV−visible spectroscopy was performed on an 8452A diode array spectrophotometer (Hewlett-Packard) using HP 89531A MS-DOS UV/VIS Operation Software. Spectra were recorded from 200 to 800 nm.

Dynamic Light Scattering. DLS experiments were performed on a Brookhaven Instruments photon correlation spectrophotometer equipped with a BI-9000AT digital correlator and compass 315M-150 laser (532 nm) from Coherent Technologies. All measurements were made in water at 20 °C. The dilute aqueous vesicle solutions were added to dust-free vials. The angle of detection was 90° for all measurements. The Contin algorithm was used to analyze the data.

3. Results

As described in the Experimental Section, a Cd acetate dihydrate ($Cd(Ac)_2$, $2H_2O$) aqueous solution was added to a dilute polymer solution in THF. Following this procedure, spherical micelles with a core containing CdAcr were obtained. We refer to these structures as "primary spherical inverse micelles" (PSIMs). The total amount of water added during the preparation was 2 wt %, which is five times smaller than the critical water concentration for the micellization of this polymer. The assembly of the individual triblocks (Figure 1a) into spherical micelles (Figure 1b1) is thus driven by physical cross-linking (ionic interaction between Cd^{2+} and PAA^-) and not by the insolubility of the PS in the aqueous solution containing some water. Transmission electron microscopy (TEM) is performed by vaporizing a drop of the solution on the TEM grid. As the THF evaporates, the water content increases, which makes the solvent unfavorable for styrene blocks, leading to the formation of rods, as reported previously for PS-*b*-PAA diblock copolymers.[25] These rods are seen on the TEM grids as discussed below. A model representing these two morphologies is shown in Figures 1b1 and 1b2, and the path and the process is symbolized by the light blue arrow between the figures.

TEM investigation of the aggregated PSIMs (Figure 2a) revealed the presence of contrast-rich regions corresponding to

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(39) Nardin, C.; Hirt, T.; Leukel, J.; Meier, W. *Langmuir* **2000**, *16*, 1035−1041.

(40) Liu, F.; Liu, G. *Macromolecules* **2001**, *34*, 1302−1307.

(41) Napoli, A.; Valentini, M.; Tirelli, N.; Mueller, M.; Hubbell, J. A. *Nat. Mater.* **2004**, *3*, 1476−1122.

(42) Lei, L.; Gohy, J.-F.; Willet, N.; Zhang, J.-X.; Varshney, S.; Jerome, R. *Macromolecules* **2004**, *37*, 1089−1094.

(43) Bronstein, L.; Mirzoeva, E. S.; Valetsky, P. M.; Solodovnikov, S. P.; Register, R. A. *J. Mater. Chem.* **1995**, *5*, 1197−201.

(44) Antonietti, M.; Wenz, E.; Bronstein, L.; Seregina, M. *Adv. Mater. (Weinheim, Germany)* **1995**, *7*, 1000−5.

(45) Antonietti, M.; Foerster, S.; Hartmann, J.; Oestreich, S. *Macromolecules* **1996**, *29*, 3800−6.

(46) Underhill, R. S.; Liu, G. *Chem. Mater.* **2000**, *12*, 3633−3641.

(47) Wyrwa, D.; Beyer, N.; Schmid, G. *Nano Lett.* **2002**, *2*, 419−421.

(48) Liu, S.; Weaver, J. V. M.; Tang, Y.; Billingham, N. C.; Armes, S. P.; Tribe, K. *Macromolecules* **2002**, *35*, 6121−6131.

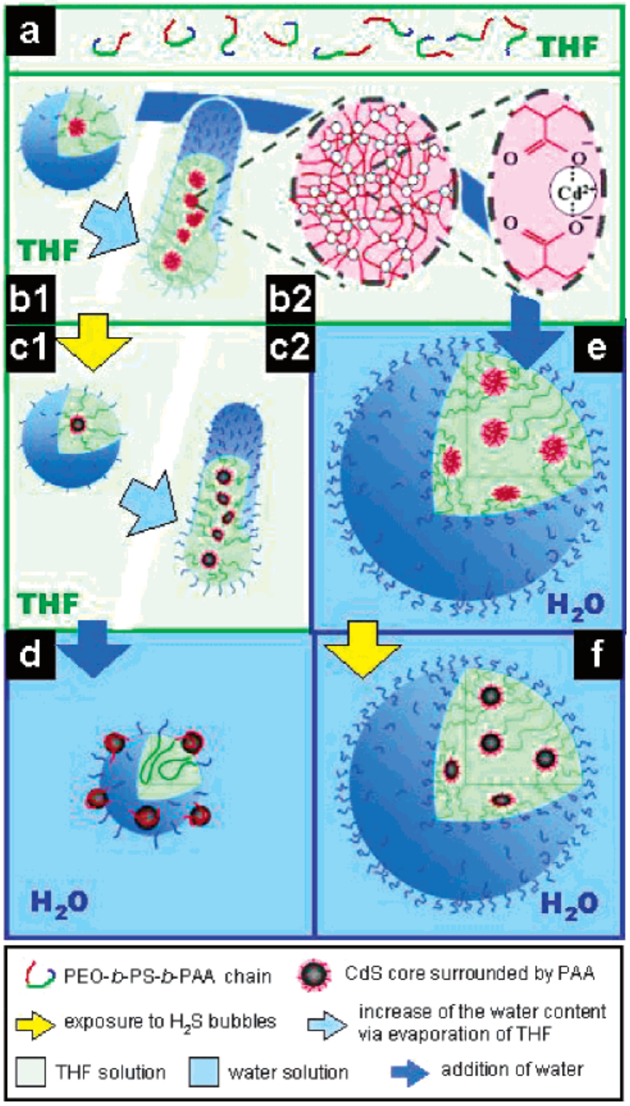

Figure 1. Schematic pictures of assemblies of PEO(45)-*b*-PS(150)-*b*-PAA-(108). (a) Single triblock copolymer molecules in THF. (b) Ionically cross-linked triblock micelles. (b1) primary spherical inverse micelles (PSIMs) in THF; (b2) wormlike micelles at higher water content. (c) Triblock copolymer structures with CdS quantum dots. (c1) spheres in THF; (c2) rods in water-rich solutions. (d) PS core micelles in water, surrounded by CdS nanoparticles. (e) Multicore cadmium acrylate supermicelle (SM) structures, following the change of the solvent to water of the PSIMs shown in part b. (f) Water soluble SM triblocks with CdS cores.

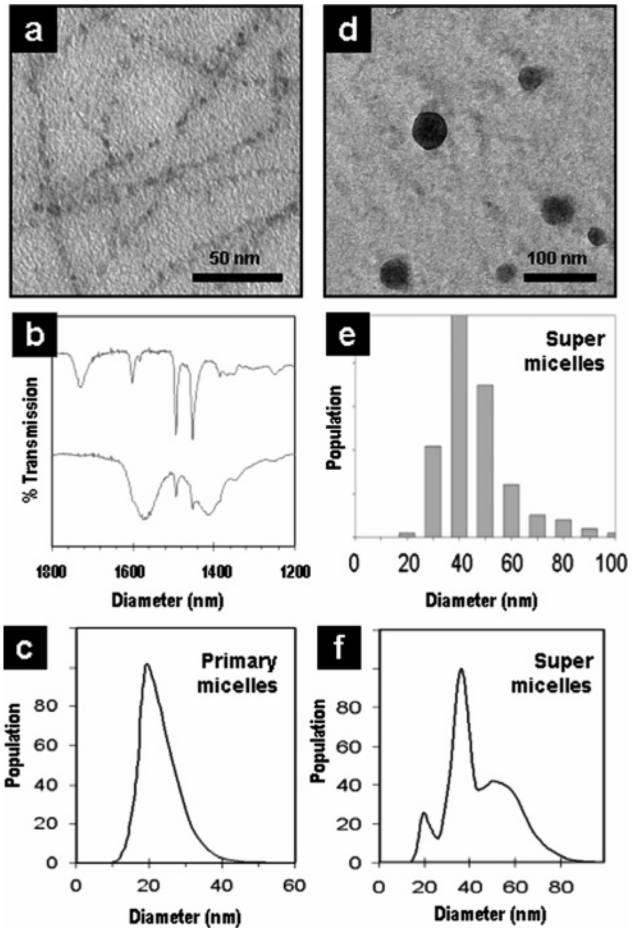

Figure 2. PEO(45)-*b*-PS(150)-*b*-PAA(108) triblock copolymer templates with Cd acrylate cores used for the syntheses of the CdS nanoparticles. Left column: preparations from tetrahydrofuran (THF). Right column: preparations from water. (a) Triblock copolymer rod micelles with cadmium acrylate (CdAcr) cores. (b) Infrared spectra of the triblock copolymer solutions. Top: single triblock copolymer molecules in THF. Bottom: micelles cross-linked by addition of cadmium ions. (c) Size distribution of the PSIMs from DLS. (d) Triblock copolymer multi-CdAcr-core micelles (supermicelles, SMs) in water. (e) Size distribution of the SMs. Average diameter: 40 nm. (f) Size distribution of the SMs, from DLS. Three populations are observed: single-core micelles, multicore micelles, and aggregated micelles. The average diameter is 40 nm.

the CdAcr cores organized in chains. The size of the dark cores is approximately 4 nm. The presence of Cd was confirmed by energy dispersive spectrometry (EDS). Infrared (IR) spectra were recorded before and after $Cd(Ac)_2$ addition (Figure 2b). The upper spectrum represents the results from the micelle solution before Cd^{2+} addition. The broad doublet absorption band at 1738 and 1710 cm^{-1} is characteristic of carboxylic acid.[49] The bottom spectrum shows the total neutralization of the acrylic acid (AA) functions upon Cd^{2+} addition, characterized by the shift of the 1570 cm^{-1} band. Combined TEM and IR results suggest that each Cd^{2+} ion binds to two negatively charged acrylic acid (AA) residues leading to the formation of the CdAcr cores. Additional evidence for the presence of primary micelles was obtained from dynamic light scattering (DLS) (Figure 2c). This technique revealed that the apparent hydrodynamic diameters of the spherical aggregates range from 10 to 50 nm, with an average value of 22 nm. This value is much larger than the 2 nm radius of the CdAcr cores observed in TEM. This difference is due to the fact that the PS-*b*-PEO corona, which has a poor contrast, cannot be observed in TEM. This corona contains 195 units, corresponding to an estimated unperturbed length ($l\sqrt{n}$, where l is the contribution to the length per 2 backbone atoms, equal to 0.25 nm, and n is the number of units of the block copolymer) of ca. 4 nm and a fully stretched length of ca. 55 nm. It should be recalled that the PEO repeat unit consists of 3 backbone atoms.

Changing the solvent from THF to water resulted in the formation of a new micellar architecture (dark blue curved arrow from Figure 1b1 to Figure 1e). An aliquot (300 μL) of the primary micelles dispersion was added dropwise into 5 mL of stirred water at room temperature. The solution was then dialyzed against water (see Experimental Section). The TEM study of the resulting product revealed the presence of individual well-dispersed large micelles with an average diameter of 40

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[49] Zhong, X. F.; Varshney, S. K.; Eisenberg, A. *Macromolecules* **1992**, *25*, 7160−7.

nm (Figure 2d). The size of the majority of the micelles ranges from 30 to 60 nm (Figure 2e). The diameter of these micelles does not exceed the fully stretched length of the entire triblock copolymer, including the AA (~75 nm). The cumulative results of nine runs of DLS experiments on the SMs (Figure 2f) confirm the average size of 40 nm. In this experiment, three different populations of micelles were detected in the water solution, which are tentatively identified (with increasing size) as single-core micelles, multicore micelles, and aggregates of multicore micelles. The presence of the large multicore micelles (middle peak) suggests an extensive reorganization of the triblocks (see discussion below). For convenience, due to its large size, we refer to this structure as a "supermicelle" (SM).[50]

The CdAcr cores within the micelles dispersed in THF and the SMs dispersed in water were used as templates for the formation of CdS nanoparticles. In both cases, the bubbling of $\mathrm{H_2S}$ through the solutions was stopped at different time points. During the formation of CdS, the color of the solutions turned to yellow. The primary micelles, exposed to $\mathrm{H_2S}$ for 1 min (in THF), were selected for detailed study. As the reaction of the Cd^{2+} with $\mathrm{H_2S}$ was much slower in the SMs due to a slower diffusion rate through the glassy matrix of the PS (in water), the specimen collected after 30 min bubbling was selected for investigation.

Exposure of the THF solution to $\mathrm{H_2S}$ converted the CdAcr cores into CdS (Figure 1b1 to 1c1). For $n_{\mathrm{Cd2+}}/2n_{\mathrm{AA-}} = 2$, bubbling $\mathrm{H_2S}$ through the solutions for 60 s and vaporization of the resulting solution on the TEM grid led to the formation of an apparent network of wormlike micelles (Figure 1c1 to 1c2), as observed by TEM (Figure 3a). In this structure, the QDs are spherical and aligned nearly in single rows within the core of the wormlike micelles. In Figure 3b, a close-up displays the spatial distribution of QDs within the polymer aggregates. The mechanism of the formation of the worm-shaped micelles is similar to the situation seen in the micelles before $\mathrm{H_2S}$ treatment (Figure 1b1 to 1b2). A schematic picture of these QD containing micelles, both spherical and wormlike, is given in Figure 1c. EDS analysis showed the presence of both cadmium and sulfur. TEM images of a platinum−carbon replica of these micelles revealed their 3D structure (Figure 3c). From such pictures, the width of the triblock worms after deposition was estimated to be ~7 nm. The optical signature of the CdS QDs in the same structure is plotted in Figure 4a for different neutralization ratios, R_N, where R_N is equal to $n_{\mathrm{Cd2+}}/2n_{\mathrm{AA-}}$ ($n_{\mathrm{Cd2+}}$ and $n_{\mathrm{AA-}}$ are the total number of moles of Cd^{2+} ions and AA unit in the solution, respectively). The spectrum for $R_N = 2$ shows an absorption onset at 477 nm (from intersection of the straight line segment with the baseline, exemplified by the dotted line for the curve labeled 2) typical of CdS of an average QD size of 4.6 nm.[5] The effect of R_N on the sizes of the QDs and on the morphologies of the aggregates after THF evaporation has also been studied through UV−vis spectra (Figure 4a). For the largest value of R_N, e.g. 8, the absorption onset of 515 nm corresponds to the value for bulk CdS. It is well-known that the band gap of nanosized semiconductors increases as their size decreases, due to electron confinement;[9] the absorption onset of these QDs is directly linked to their sizes through Henglein's empirical formula.[5] As the amount of Cd^{2+} added in the solution decreases, the absorption onset shifts to lower wavelengths (blue-shift), corresponding to a decrease in particle size. The most highly elongated wormlike structures were observed for $R_N = 2$ to 4 (Figure 3a, b, c, and 4b). It should also be mentioned that the spectra were followed as a function of time. No time dependence was seen. This suggests that the QDs do not aggregate on storage.

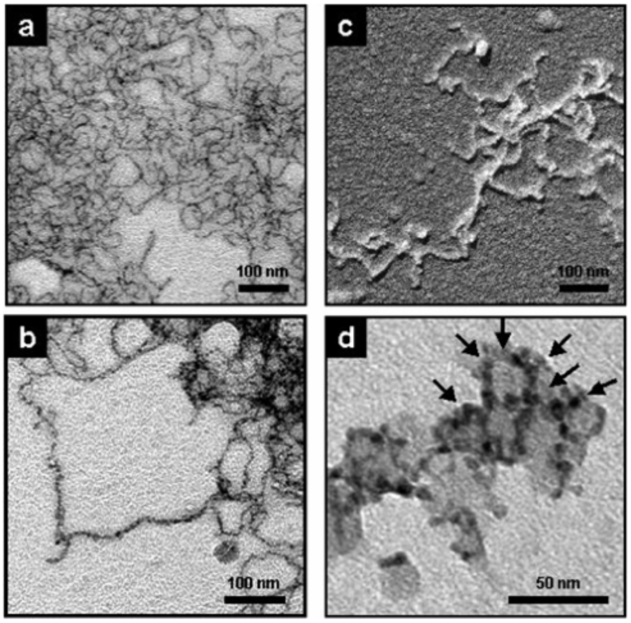

Figure 3. (a−c) Wormlike assemblies of PEO(45)-*b*-PS(150)-*b*-PAA(108) triblock copolymer, containing cadmium sulfide quantum dots in their core. The neutralization ratio, $n_{\mathrm{Cd2+}}/2n_{\mathrm{AA-}}$ is 2. (a, b) As prepared sample. (b) A close-up of (a), displaying the spatial distribution of QDs within the polymer aggregates. (c) Platinum−carbon replica at an angle of 45°. Negative picture (the shadow is dark). The average rod width is 7 nm. (d) PS core micelles in water, surrounded by CdS particles. The arrows are indicating the presence of some of the QDs.

The effect of the exposure time of $\mathrm{H_2S}$ on the size of the QDs was also investigated. After bubbling $\mathrm{H_2S}$ for 1−2 s, no change was observed between the original micelles and $\mathrm{H_2S}$ treated solutions. As shown previously, exposure to $\mathrm{H_2S}$ for 1 min yields CdS QDs within the chains. The size of the CdS QDs increases with increasing $\mathrm{H_2S}$ exposure with time, as detected by UV−vis spectroscopy. After 10 min exposure, flocculation of the CdS QDs is observed. This flocculation is most likely due to the total consumption of Cd^{2+} leading to the formation of CdS. Evidently the Cd^{2+}, which was responsible for the cross-linking of the PAA chains, is replaced by two hydrogen ions. This results in an increase in the mobilities of the now protonated PAA chains and leads to a decrease in the viscosity of the system and the flocculation of the QDs in the solution.

Another type of micelle was formed when the THF in the solution of the CdS-containing wormlike micelles was exchanged for water (Figure 1c1 to 1d). This was done by adding 300 μL of the wormlike micelles in THF to 5 mL of water at the rate of 2 μL/s under stirring at room temperature. The resulting suspension was dialyzed against water and transferred to a TEM grid. TEM revealed micelles of 20 nm in size, which were organized in irregular chains of micelles (Figure 3d). These micelles consist of a hydrophobic PS core and an outer region

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(50) *The SMs have some similarity to the previously described (ref 25) PS-b-*PAA large compound micelles (LCM) in that they are both multicore structures inside a hydrophobic matrix surrounded by a hydrophilic corona. However, in contrast to the LCMs, in which no mechanism exists which limits their size because they are composed of diblock, in the SMs, a size limitation mechanism does exist, as will be described in the text.

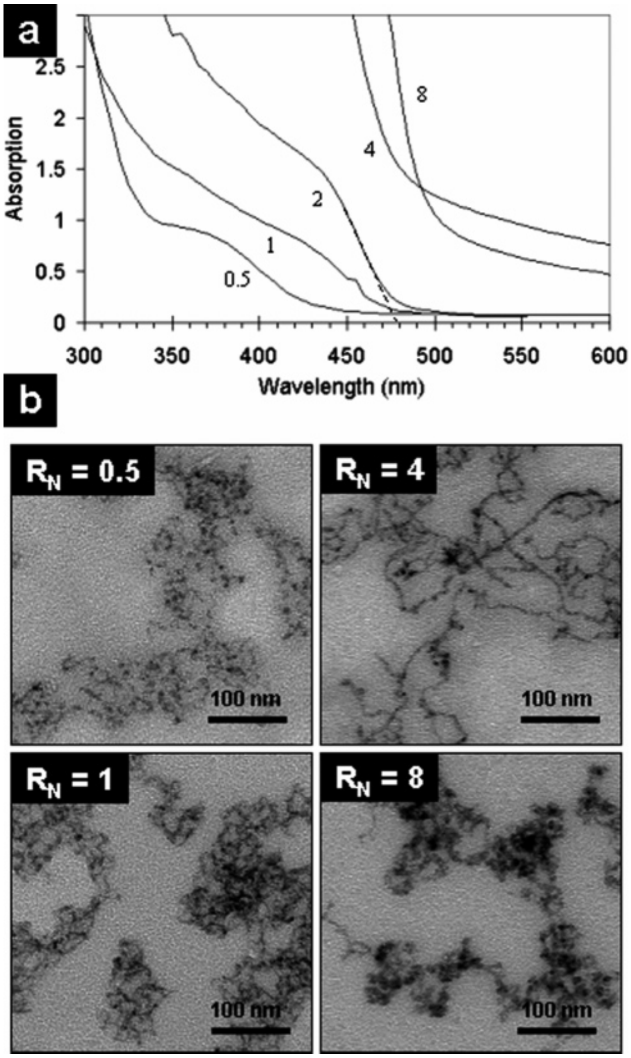

Figure 4. UV−vis spectra and morphologies obtained at different neutralization ratios. (a) Absorption spectra of individually dispersed QDs in the primary micelles for various $n_{\mathrm{Cd2+}}/2n_{\mathrm{AA-}}$ ratios. From the spectrum at $n_{\mathrm{Cd2+}}/2n_{\mathrm{AA-}} = 2$, the average size of the QDs is 4.6 nm. (b) TEM pictures of CdS nanoparticles in triblock copolymer obtained at various neutralization ratios.

composed of hydrophilic PEO chains with QDs located at the surface of the micelle core. The QDs probably are partly enveloped by PAA chains, possibly cross-linked with Cd^{2+}. Each PS core is surrounded by 10 to 20 QDs. A model is shown in Figure 1d. A similar morphology has also been observed in the group of Douglas.[19] UV−vis absorption of these structures displays an onset of 490 nm. This onset is larger than that for individual QDs in the triblock copolymer micelles, previously given (477 nm). The reason for this increase in the absorption onset can be either an increase of the diameter of the QDs from 4.6 to 5.3 nm or interactions between QDs, which is more likely. This latter explanation is confirmed in Figure 3d, which corresponds to the model shown in Figure 1d. This figure diplays aggregated QDs on the surface of polymer micelles.

Based on TEM analysis, the size distributions of the water soluble SMs, before and after H_2S exposure, were similar (Figure 2d and 2e compared with Figure 5a and 5b, with models in Figure 1e and f). Each supermicelle contains up to 40 QDs of CdS (Figure 1f and 5a). The average size of the QDs is ca. 4 nm. Observation in TEM at various tilt angles revealed a change in the contrast of the QDs, indicating the presence of an ordered structure characteristic of a crystalline material, i.e., the CdS. Energy dispersive spectroscopy (EDS) analysis showed the presence of both Cd and sulfur, which confirms the presence of CdS. UV−vis absorption (Figure 5c) was used to determine the size of the QDs. The onset of absorption is seen at 482 nm, which corresponds to an average diameter of 4.8 nm according to Henglein's empirical formula.[5] The result from the UV−vis absorption experiment is in good agreement with the TEM results. To confirm the stability of this structure, the SMs were stored for three months and studied in TEM. Identical morphologies were observed, with the same degree of dispersion and size distribution.

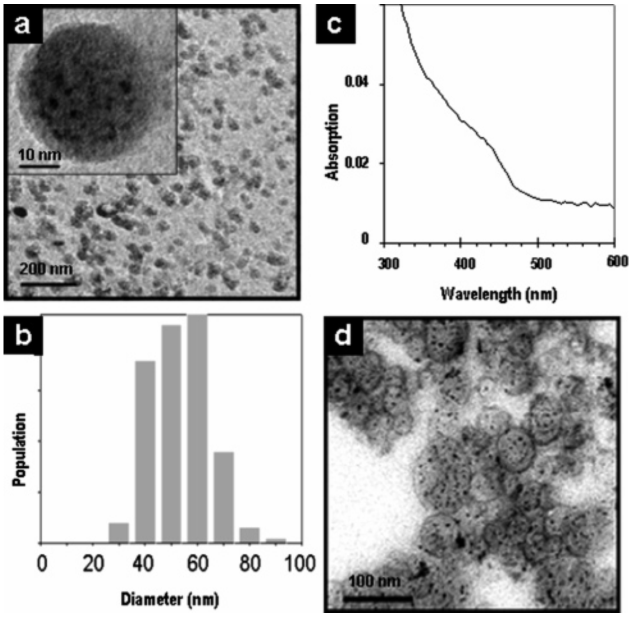

Figure 5. Water soluble multicore micelles containing cadmium sulfide quantum dots. (a) Supermicelles. Insert: close-up on one micelle. (b) Size distribution of the supermicelles. The average size of the micelles is 50 nm. (c) Absorption spectrum of CdS QDs in the supermicelles which corresponds to an average size of 4.8 nm. (d) Microtomed supermicelles stained with uranyl acetate. The dark corona reflects the presence of PEO chains.

It is worth mentioning that an experiment involving the same procedure leading to formation of SMs using a triblock copolymer with shorter PS and PAA blocks, such as PEO(45)-*b*-PS(46)-*b*-PAA(30), revealed the formation of smaller SMs with an average size of 30 nm.

To improve the contrast of the PEO polymer component in this SM and to improve the resolution of the QDs, the samples were embedded in epoxy resin, microtomed into ca. 100 nm slices, and stained with uranyl acetate. A dark ring is observed around the SMs (Figure 5d), which is associated with the PEO corona. This dark corona was not observable before the staining. The CdS QDs were much better resolved in the ultrathin sections compared to the whole SMs.

4. Discussion

A brief discussion of the detailed morphologies is given below. For the water soluble SMs, it is suggested that each of the styrene chains is linked at one end to the outer surface of the SM (via the PEO) and at the other end (via the PAA) to one of the QDs (Figure 1f). Such SMs were obtained by an accretion of the spherical micelles containg QDs, which is

Table 1. Summary of the Most Important Informations for the PEO(45)-*b*-Ps(150)-*b*-PAA(108) Supermicelles

average diameter of the nanocrystals	4.8 nm
average diameter of the supermicelles	50 nm
number of chains per supermicelle	1560
number of CdS ion pair per QD	1150
number of QD per SM	75
fully stretched length of the PS ($\overline{l*n}$)	37.5 nm
unperturbed length of the PS ($\overline{l\sqrt{n}}$)	3.06 nm

induced by the interactions of the PS, as the water content is increased. The PEO chains remain outside the SMs. It is of interest to inquire whether this arrangement is physically realistic in terms of the block lengths and the detailed aggregate morphologies.

It can be shown that the average distance from any point inside a sphere to the nearest point on the surface is $R/4$ (where R is the radius of the sphere). Therefore, since the average radius of the SMs is ca. 20 nm, the average distance from a QD in the SM to the nearest point on the surface is ca. 5 nm. On the other hand, the unperturbed (freely jointed) end-to-end distance ($d = 1\sqrt{n}$) of an average chain equal in length to the PS block ($n = 150$) is 3 nm, while the fully stretched length is 37 nm; therefore, the connection of any point within the micelle to the surface by a styrene chain seems realistic. The staining of the ultrathin section prepared from the microtomed SMs provided direct evidence for the presence of the PEO in the corona on the surface of the SMs (Figure 5d).

If this model is valid, one can calculate the aggregation number of the SMs from the physical parameters of the triblock copolymer, e.g., bulk density, molecular weight, and block length. From this calculation (see Supporting Information), the number of QDs for an SM of 40 nm diameter is found to be $n_{\mathrm{aggSM}} = 38$. The insert of Figure 5a shows an SM with a diameter of 40 nm, which contains ca. 35 QDs. The ratio of the volume of the micelle to the volume of the QDs contained in the micelle is large enough to allow the visual separation of every individual QD in the planar projection of the TEM. Therefore, the validity of the model is confirmed by the very comparable experimental and calculated values of the number of QDs per micelle. The average size of the SMs found in this study is 50 nm; the number of QDs for such an SM would be 75. Table 1 summarizes the most important features relative to the supermicelles.

It is worth noting that the number of CdS ion pairs in a QD is controlled by the block length of the AA, as it has been demonstrated by Moffitt et al.[15] for the case of hydrophobic aggregates. On the other hand, the total diameter of the SMs is found to be a function of the PS block length. If the triblock copolymer contains 150 PS units, the diameter of the SMs is ca. 50 nm. If the PS block length decreases to 46, the size of the SMs decreases to ca. 30 nm. Note that the stretching ratio, $R_{\mathrm{S}} = (l\sqrt{n})/(R_{\mathrm{SM}}/4)$, where R_{SM} is the radius of the SM, is $\sim$0.5 for both triblocks. Also, for both triblocks, the average distance from any point inside the SM to the surface, $R_{\mathrm{SM}}/4$, as well as R_{SM} itself, is much shorter than the length of a fully stretched styrene segment of the triblock, $l*n$.

The wormlike micelles are formed during solvent evaporation from the sample on the TEM grid as a result of the preferential evaporation of the THF (Figure 1c1 to Figure 1c2). The resultant increase of the water content, a nonsolvent for the PS blocks, induces the formation of rods (see above). Multiangle DLS could not provide clear evidence of the presence of rods in the solution. The apparent branching in the TEM image (Figure 3a−c) is due to the aggregation of the rods during drying. In these wormlike micelles, the CdS QDs are located near the axis of the worm, surrounded first by the PAA and then by the PS, which, in turn, is covered by the PEO chains (Figure 1c2). According to a calculation similar to that given in the previous paragraph, the number of QDs per 100 nm of the "worm" is estimated to be 30.

Starting with a spherical single-core CdAcr micelle in THF−water mixtures, even before the H_2S bubbling (Figure 1b1), one can, by increasing the water content, obtain rodlike micelles, with the CdAcr aligned near the center of the cylinder (Figure 1b2). The CdAcr in the spherical micelles in THF−water mixture can be converted to CdS cores, retaining the spherical morphology (Figure 1c1). As before, the CdS core spherical micelles can be converted to rodlike micelles by preferential evaporation of the THF and consequently increase in water content (Figure 1c2). If the spherical micelles (Figure 1b1) are transferred to water, the styrene regions aggregate, leading to the formation of SMs with CdAcr cores (Figure 1e). Exposure to the H_2S leads to CdS QDs in SMs (Figure 1f). If the spherical micelles with CdS QD cores (Figure 1c1) are now exposed to water, some aggregation of the styrene regions still takes places, but there appears to be sufficient mobility for the CdS QDs to move to the surface (Figure 1d).

It is noteworthy that the response of the primary spherical inverse micelles (PSIMs) to the addition of water is very different depending on whether the cores are CdAcr (Figure 1b1) or CdS (Figure 1c1). If the cores are CdS, the AA is not cross-linked, and therefore a major reorganization can occur. The styrene coalesces and forms the interior of the micelle, with both the AA and the EO going on the outside. (Figure 1d). The CdS is preserved. By contrast, if the cores of the inverse micelles are CdAcr, that structure remains frozen upon addition of water. The micelles coalesce. The styrene can still reorganize during the coalescence with other micelles. The CdAcr cores remain intact with the AA forming an integral part of the cores (Figure 1e).

5. Conclusion

We have shown that the same triblock copolymer, PEO(45)-*b*-PS(150)-*b*-PAA(108), after cross-linking with Cd^{2+}, can assemble into several distinct morphologies, depending on the solvent used, THF or water, and the sequence of steps involved. These structures are obtained from the same primary spherical inverse micelles (PSIMs) (Figure 1b1), which consist of a CdAcr core, surrounded first by PS and then by PEO.

Starting with PSIMs (Figure 1b1), by exposure to H_2S, one can convert the CdAcr cores to CdS (Figure 1c1). These spherical inverse micelles, with the CdAcr or CdS core, can, by increasing the water content (and polymer concentration) through the evaporation of THF from the solution, be converted to rod micelles (Figure 1b2 and Figure 1c2). In Figure 1c2, the CdS nanoparticles are located within the AA shells of the triblock copolymer structure. These AA shells are surrounded, first, by an expanded and mobile PS block and then by the PEO block, which is in contact with the solvent. The polystyrene block, because of its hydrophobicity, induces the formation of the “worms”, as the water content increases in the preparation. If, prior to H_2S bubbling, the PSIMs in THF (Figure 1b1) are transferred into water, a new multicore spherical structure is observed (Figure 1e), in which multiple CdAcr cores are located in the PS matrix, surrounded by a PEO corona. In this transfer, the CdAcr cores are preserved because of the cross-linking of the PAA. These CdAcr cores of these can, by exposure to H_2S, be converted to CdS (Figure 1f), with no change in the aggregate architecture, leading to water soluble supermicelles. These supermicelles consist of CdS QDs in PAA cores, in a collapsed and glassy PS matrix, surrounded by a PEO corona. Another structure is observed when transferring the PSIMs with the CdS core (Figure 1c1) from the initial THF solvent to water. This structure consists of PS core micelles, in the corona of which are located the CdS QDs, which, in turn, are probably coated by the PAA and PEO blocks (Figure 1d).

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Supporting Information Available: The calculation of the number of QDs per SM. This material is available free of charge via the Internet at http://pubs.acs.org.

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