Size Control of Nanoparticles in Semiconductor−Polymer Composites. 2. Control via Sizes of Spherical Ionic Microdomains in Styrene-Based Diblock Ionomers

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The size control of semiconductor nanoparticles via primary aggregate sizes in ionomers has been extended to include the precipitation of cadmium sulfide (CdS) within the spherical ionic cores of PS-*b*-PACd diblock ionomers of various ionic block lengths. This procedure yields clusters in the range of $2R = 29-50$ Å, using ionic block lengths of 4−32 repeat units. The sizes of CdS clusters formed in water-plasticized ionic cores, determined by UV−vis spectroscopy, were found to increase linearly with the size of the original core (correlation coefficient = 0.99) and scale with the ionic block length as $N_B^{3/5}$, in agreement with the Halperin model of "star micelles". Comparisons between CdS agglomeration numbers and the number of countercations in the original core were used to show that, except in the largest ionic cores, a single particle per core was obtained. The stability of the CdS-containing micelles in a selective solvent can be enhanced considerably by reneutralizing the poly(acrylic acid) layer surrounding the clusters within the core. These stabilized micelles can be dissolved in an organic solvent, precipitated into methanol, and redissolved several times, without significant changes in the UV−vis absorption spectrum. It was also found possible to process the CdS−polymer composites by casting from toluene or compression molding at 130 °C, without affecting the nanoparticle sizes. Cluster sizes can be increased by reneutralizing the CdS-containing micelle cores with cadmium acetate, followed by secondary treatment with H_2S. By this method, clusters of 37 Å in diameter were enlarged to 56 Å in two steps.

Introduction

The controlled precipitation of quantum-confined semiconductor clusters such as cadmium sulfide has been achieved in a wide range of media, including surfactant micelles,[1−4] vesicles,[5,6] zeolites,[7] random ionomers,[8−15] and ion-complexing block copolymers.[16−20] Several studies have been concerned with the control of cluster sizes by variations in the methods of preparation, though techniques of synthesizing monodisperse particles of predictable, thermodynamically controlled sizes are still quite rare. The aim of our work is to apply a priori knowledge of ionic aggregate sizes in a range of ionomers, in order to use these materials as hosts for the precipitation of semiconductor clusters of predictable sizes.

In the previous paper, CdS cluster sizes were controlled in the narrow range of 18−23 Å in diameter, using the relatively small aggregates of styrene-based random ionomers.[21] The sizes of these aggregates are controlled by the length of the spacers which separate the backbone from the ionic functional groups, with longer spacers resulting in larger aggregates.[22] In the present paper, the size control of CdS clusters will be demonstrated by precipitation within the spherical microdomains of cadmium-neutralized polystyrene-*b*-poly(acrylic acid) copolymers with variable ionic block lengths. As in the case of random ionomers, this size control should, in principle, be thermodynamic in origin,

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as the size of the growing particles is limited by the number of ions within the original aggregate. The ionic aggregates in block ionomers are very much larger than the aggregates in random ionomers, and these materials should therefore allow the size control of CdS clusters to be extended into a range of sizes not accessible with random ionomers. This paper will also demonstrate the solution stability of the CdS–diblock copolymer composites and will show that these materials can be dissolved, precipitated, and redissolved repeatedly, without significant changes in the CdS concentration or the size of the clusters. This solution stability is of interest in view of potential applications; for example, CdS particles have been used for the photochemical reduction of water both in colloidal solutions of reverse surfactant micelles[23] and in polymer films.[24,9] The present materials offer the unique possibility of photocatalytic semiconductor–polymer composites which can be used in both colloidal and solid-state media. To demonstrate the scope of their applicability, we will also show that these composite materials can be processed by casting from an organic solution onto surfaces or by compression molding, without affecting the size of the dispersed clusters.

A brief literature review of metal sulfide and metallic cluster precipitation in ion-containing polymers was presented in the previous paper and will not be repeated here in detail.[21] We will only remind the reader of some pertinent work in block copolymer systems, in which nanoscale particles have been synthesized within the metal-complexing microdomains of polystyrene-*b*-poly(2-vinylpyridine)[16] and within the metal-complexing microdomains of diblock copolymers formed by ring-opening metathesis polymerization.[17–20]

It is well-known that the morphology of microphase-separated regions in bulk-phase diblock copolymers (spherical, cylindrical, or lamellar) is determined by the relative volume fraction of the component blocks, while the size of these regions is determined by the absolute length of the microdomain-forming block.[25–27] For highly asymmetric AB diblock copolymers, the shorter block forms spherical microdomains within a matrix of the major component.[25,28]

Microphase separation into spherical domains in the bulk is analogous to the formation of diblock copolymer micelles in a selective solvent, in which the short insoluble blocks form a spherical core, surrounded by a corona of the soluble major component. Halperin's "star model" of diblock copolymer micelles,[29] among other theories, addresses the sizes of the spherical cores. The model states that the core radius scales as $N_B^{3/5}$, where N_B is the number of units in the short insoluble block. If no solvent enters the cores, the size of the micelle cores in solution will be identical to the size of the spherical microdomains for the same block copolymer in the bulk phase. This is the case for diblock ionomers, which form extremely stable micelles in various organic solvents (reverse micelles), due to the large differences in the solubilities of the two blocks. Small-angle X-ray scattering studies of a wide range of block ionomers with relatively short ionic blocks were found to agree well with the Halperin model, and a proportionality constant of 6.5 Å was determined by fitting the measured ionic core radii ($R_{core} = 6.5$ Å $N_B^{3/5}$).[30]

The predictability of core radii in microphase-separated diblock ionomers allows a wide range of desired ionic core sizes to be obtained, simply by selecting the length of the ionic block. Using anionic polymerization, polystyrene-*b*-poly(*tert*-butyl acrylate) diblock copolymers with specific poly(*tert*-butyl acrylate) block lengths can be synthesized routinely, and subsequent hydrolysis and neutralization allow the desired ion (or combination of ions) to be incorporated into the core. Block ionomers are therefore an ideal system for the formation of ionic aggregates of controlled sizes, which makes them well-suited for the size control of particles such as CdS clusters within the ionic cores. Cadmium-neutralized polystyrene-*b*-poly(acrylic acid) can be converted into the CdS-copolymer composite by treating the original polymer with H_2S; the resulting chemistry within the core will effect the precipitation of CdS crystallites and the reprotonation of the carboxylate groups.

In organic solvents, micelles of the CdS–copolymer composites will have cores consisting of one or more CdS clusters surrounded by the acrylic acid units of the polymer host. The polystyrene blocks will constitute the soluble corona, protecting the CdS particles from agglutination and precipitation. The presence of the acrylic acid layer within the micelle core offers the possibility of performing chemistry close to the surface of the semiconductor particle. For example, reneutralizing the acrylic acid units with sodium hydroxide should increase the stability of the composites in solution, as the solubility of poly(sodium acrylate) is much lower than that of poly(acrylic acid) in organic solvent. Along with stabilizing, or "fixing", the CdS-containing micelle, reneutralization should allow for the incorporation of a wide range of ions at the surface of the CdS clusters. The solution stability of the CdS–diblock copolymer composites with and without reneutralization will be explored, by repeated precipitation into methanol and redissolution in an organic solvent.

Isolated CdSe clusters, soluble in organic solvent, have previously been formed by functionalizing the surface of the particles with phenyl ligands.[31] As well, ion-containing polymers have been used to stabilize CdS clusters in aqueous solution and to isolate the clusters as redispersible powders.[32] The present study of semiconductor clusters within the cores of diblock ionomer reverse micelles demonstrates a novel combination of selected aspects of past work, in the form of polymer-stabilized clusters of a predictable size which are highly stable and soluble in a wide range of organic solvents.

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Table 1. CdS UV–Vis Absorption and Size Distribution Data in Block Ionomers

polymer	λ_e (±2 nm)	$2R_{CdS}(\lambda_e)$ (±1 Å)	$\lambda_{m,sh}$ (±2 nm)	$2R_{CdS}(\lambda_{m,sh})$ (± Å)	$d_{1/2}$ (Å)	RPI
PS(300)-*b*-PACd(4.0)	421	29	353	20	9	1.05
PS(470)-*b*-PACd(5.0)	421	29	353	20	9	1.05
PS(300)-*b*-PACd(10)	435	32	394	24	8	1.03
PS(320)-*b*-PACd(14)	457	38	421	29	9	1.02
PS(730)-*b*-PACd(22)	469	42	435	31	11	1.03
PS(300)-*b*-PACd(25)	479	47	438	32	15	1.05
PS(470)-*b*-PACd(32)	485	50	459	38	12	1.02
PS(300)-*b*-PACd(44)	485	50	459	38	12	1.02
PS(730)-*b*-PACd(84)	485	50	459	38	12	1.02

These micelles can be cast onto surfaces or compression molded above the T_g of polystyrene, without affecting the size of the CdS clusters.

Experimental Section

Synthesis of Diblock Copolymers. The synthesis of the block ionomers used in the present study was performed according to known procedures;[33-35] hence, only a brief summary is presented here. Series of polystyrene-*b*-poly(*tert*-butyl acrylate) with polystyrene blocks of constant length and poly(*tert*-butyl acrylate) blocks of variable length were synthesized by anionic polymerization. The initiator used in the synthesis was *sec*-butyllithium capped with a few units of α-methylstyrene. The block copolymers in the ester form were then hydrolyzed to polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) by refluxing overnight in toluene solution with *p*-toluenesulfonic acid as the catalyst. The polymers were recovered by precipitation into methanol and were then dried in a vacuum oven at 70 °C for 24 h. The molecular weight of the polystyrene blocks and the polydispersity indexes of all copolymers were determined by SEC. The polydispersity indexes of the block copolymers used in the present study varied between 1.04 and 1.10. The composition of the copolymers was determined by FTIR, using the copolymers in the ester form.

The copolymers PS-*b*-PAA were dissolved in benzene/methanol (5% methanol w/w) at a concentration of about 1% (w/w). The acid blocks were neutralized by addition of excess cadmium acetate dihydrate in methanol (1.5 mol of cadmium acetate dihydrate:1 mol of acrylic acid repeat units). The solutions were stirred for 3–4 h, and then the block ionomers were recovered by freeze drying. They were subsequently dried in a vacuum oven at 70 °C for 24 h to remove any remaining solvent and acetic acid byproduct. Excess cadmium acetate was removed by repeated washings of the block ionomers in methanol; the washed polymers were dried overnight under vacuum at 70 °C. FTIR was used to confirm that the polymers were 100% neutralized. The composition of each of the diblock ionomers used in this work is presented in Table 1, using the following nomenclature: PS(300)-*b*-PACd(4.0) indicates a diblock copolymer consisting of a polystyrene block of 300 repeat units covalently linked to a poly(cadmium acrylate) block of 4.0 repeat units.

Determination of the Degree of "Bridged" Cadmium in Neutralized Diblock Copolymer Films. The percentage of bridged Cd^{2+} ions within neutralized and rinsed polymer films was calculated from the length of the ionic block and the total number of carbonyl moieties (both acetate and acrylate) in the polymer chain. The latter quantity was determined by FTIR, using the following calibration procedure. Known quantities of cadmium acetate dihydrate and polystyrene-*b*-poly(*tert*-butyl acrylate) (PS(50)-*b*-PtbA(330)) were dissolved in methanol, and films were cast from the mixed solutions onto KBr windows. For various mole percentages of cadmium acetate carbonyl moieties, the ratio of carbonyl absorbance (1550 nm^{-1}) to polystyrene absorbance (700 nm^{-1}) was calculated from the obtained spectrum. As cadmium acetate and cadmium acrylate carbonyl moieties are identical with respect to FTIR, the obtained calibration curve could be used to analyze spectra of Cd-neutralized block copolymers.

Preparation of Cadmium Sulfide–Diblock Copolymer Films. Thin, optically transparent films of polystyrene-*b*-poly(cadmium acrylate) (PS-*b*-PACd) with various ionic block lengths were cast onto glass slides by spin coating from toluene solution or by casting from tetrahydrofuran solution. The ionic core sizes in the polymer films are not affected by the solvent or method of casting. CdS–diblock copolymers composite films were then prepared by two methods, which shall be called "dry" and "wet" preparations. In the dry preparation method, the films were dried in a vacuum oven at 130 °C for 4 days to remove all traces of water. The dried films of PS-*b*-PACd were then treated with dry hydrogen sulfide (H_2S) for 5 h at 25 °C. After about 15 min, the transparent films turned from colorless to light yellow. The H_2S-treated films were stored overnight in a desiccator under vacuum, to remove excess H_2S. In the wet preparation method, the PS-*b*-PACd films after casting were dried in a vacuum oven at 130 °C overnight to remove any remaining solvent. They were subsequently exposed to an atmosphere of 100% humidity for several days, by storing over water in a closed container at ca. 70 °C. The "wet" ionomer films were then exposed to "wet" H_2S (bubbled through water at 70 °C) for periods of 4, 5, and 8 h. After 8 h exposure to H_2S, FTIR was used on the treated films to confirm 100% conversion of poly(cadmium acrylate) to poly(acrylic acid). The transparent yellow films of CdS-diblock copolymer composites were then stored overnight in a desiccator under vacuum to remove excess H_2S.

UV–Vis Absorption Spectroscopy. UV–vis absorption spectra of the CdS-diblock copolymer composites (yellow transparent films) were obtained on a Hewlett-Packard 8452 diode array spectrophotometer, by scanning between 250 and 550 nm. A clean glass slide was run as a blank, such that any absorbance from the glass was subtracted from each spectrum. The absorption edge (λ_e) was determined for each spectrum as described in the previous paper. For quantum-confined CdS clusters ($2R <$ ca. 60 Å), the absorption edge is known to be at lower wavelengths than that of the bulk material. Cluster sizes can be determined from the blue-shifted spectra, with smaller particles showing lower λ_e values. From values of λ_e, the CdS particle diameters ($2R_{CdS}(\lambda_e)$) in each of the composite films were calculated from Henglein's emperically determined correlation curve.[36] Along with a characteristic absorption edge, all spectra possessed either a distinct maximum (λ_m) or shoulder (λ_{sh}), and these features were also used to calculate CdS particle sizes ($2R_{CdS}(\lambda_{m,sh})$). Table 1 lists relevant spectral features and associated CdS particle sizes for several PS-*b*-PACd ionomers of varying poly(cadmium acrylate) block lengths.

Transmission Electron Microscopy. Electron microscopy was performed on a Phillips EM410 instrument. CdS–diblock copolymer composite films were prepared for electron microscopy by microtoming (microtomed film thickness = ca. 800 Å), and the microtomed sample was then mounted on a copper grid.

Stability of Cadmium Sulfide–Diblock Copolymer Micelles in Solution. CdS-containing micelles in toluene solution were prepared by a method analogous to the preparation of the CdS–diblock copolymer films. PS-*b*-PACd samples in the powder form were exposed to an atmosphere of 100%

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humidity for a period of 1 week. They were then treated with "wet" H_2S for 8 h; during exposure to H_2S, the powders turned from white to yellow, with samples of longer ionic block lengths becoming more intense yellow in color. To form micelles in solution, the yellow powder was dissolved in toluene; a clear yellow solution was obtained. Alternatively, to reneutralize the poly(acrylic acid) block, the yellow powder was dissolved in tetrahydrofuran, and a selected amount of sodium hydroxide (NaOH) or cadmium acetate dihydrate in methanol solution was added with stirring. The yellow composite was recovered by evaporation of the solvent. A solution of reneutralized CdS-containing micelles was then obtained by dissolving the solid in toluene.

The micelles with and without reneutralization were repeatedly precipitated from toluene into methanol, filtered, dried under vacuum at 70 °C for 4 h, and then redissolved in toluene. The solution stability of CdS–block copolymer composites was monitored, by preparing constant weight percent solutions of the yellow powders in toluene after each recovery, and comparing the absorbance and absorption edge of the obtained UV–vis spectra.

An attempt was also made to increase the size of the CdS clusters within the micelle cores by secondary exposure to H_2S. For this experiment, the CdS-containing micelles of PS(320)-*b*-PAA(14) were reneutralized by stirring with cadmium acetate (1 mol of cadmium acetate:1 mol of acrylic acid repeat units) in THF solution for a week. The reneutralized micelles were then recovered by precipitation into methanol, and the powder was dried at 70 °C for at least 4 h. The yellow powder was then exposed to "wet" H_2S for 8 h. The absorption edge of the micelles in toluene solution was determined. This process was repeated by neutralizing with cadmium acetate once again and then exposing the powder to "wet" H_2S for a third time.

Results and Discussion

Control of CdS Particle Sizes in Diblock Copolymer Films. The absorption spectra of CdS clusters prepared by the "dry" method in the series of ionomers PS(300)-*b*-PACd(*x*) (x = 4.0, 10, 25, 44) revealed very similar absorption edges, corresponding to a particle size of $2R_{\mathrm{CdS}}$ = ca. 21 Å. The CdS absorbance was generally higher for longer ionic block lengths, although this trend was somewhat obscured by slight differences in film thickness. For the dry preparation, it appears that ionic core size does not influence the size of the CdS particles which precipitate within the core; restricted diffusion within the high-viscosity PACd core may contribute to the kinetic control of particle growth and a small particle size common to all copolymer compositions. Of course, materials with larger cores will have a greater number of ca. 21 Å CdS particles within each core, and therefore a higher concentration of CdS within the composite; this explains the higher absorbance values for CdS prepared in block copolymers with longer ionic blocks, despite marked similarity in the values of the absorption edge.

In contrast, absorption spectra of CdS particles prepared by the wet method showed spectral features with a clear dependence on the ionic block length of the host polymer. Figure 1 shows a series of spectra of wet-prepared CdS clusters in the diblock copolymers PS(300)-*b*-PAA(*x*) (x = 4.0, 10, 25, 44) and PS(320)-*b*-PAA(14), along with a spectrum of dry-prepared CdS in PS(300)-*b*-PAA(44). All samples in Figure 1 were treated with H_2S for a period of 5 h. Each spectrum exhibits a distinct exciton shoulder or maximum, which is an indication of relatively narrow-size distributions.[37] It is clear that the wet-prepared CdS particles are larger than the dry-prepared particles and that the wet-prepared particles show an increase in size with increasing acrylic acid block lengths. It is proposed that the addition of water to the poly(cadmium acrylate) core prior to treatment with H_2S plasticizes the ionic core, thus lowering its T_g and decreasing the viscosity of the medium in which CdS particles precipitate.

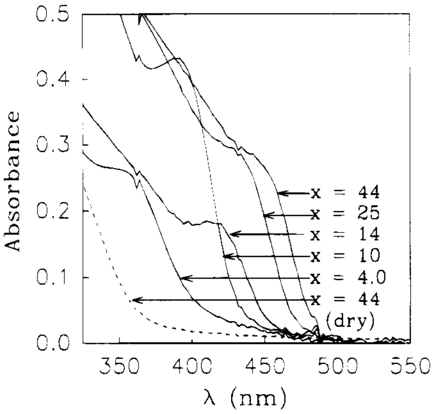

Figure 1. Absorbance spectra of CdS in PS-*b*-PAA copolymers with variable poly(acrylic acid) block lengths ($x = N_B$) for wet (solid lines) and dry (dotted line) preparations. All samples were treated with H_2S for 5 h. The baselines have been normalized, such that the vertical axis indicates absorbance above the baseline.

Two mechanisms of particle formation in the plasticized core can be imagined. In the first case, extremely small "seed" particles of cadmium sulfide form initially as H_2S diffuses into the ionic core; the mobility within the core then allows these particles to diffuse and associate. In the second case, the increased mobility in the plasticized core results in an increase in the rate of particle growth with respect to the rate of nucleation, restricting nucleation to a single site per core. In both cases, a single CdS cluster is formed within each water-plasticized core, such that the size of the cluster should be limited by the number of cadmium ions in the original ionic core.

The relationship between wet-prepared CdS particle sizes (after treatment with H_2S for 8 h) and original ionic core sizes in the host polymer (before H_2S treatment) is shown in Figure 2. Particle sizes were calculated from λ_e values using Henglein's correlation curve; ionic core diameters were calculated from ionic block lengths, using the scaling relation ($R_{\mathrm{core}} = 6.5N_B^{3/5}$ Å). The validity of this equation for cadmium-neutralized diblock ionomers has been confirmed for representative samples using SAXS.[38] Results for polymers with various polystyrene block lengths are plotted on the same figure, as the length of the nonionic block is known to have little influence on the size of the spherical core.[29] CdS cluster diameters were found to increase linearly with the ionic core diameters (slope = 0.31, correlation coefficient = 0.99), indicating that the particle sizes are indeed controlled by the sizes of the original ionic aggregates up to a core diameter of ca. 100 Å. CdS cluster sizes obtained in random ionomers are also included in the figure,[21] plotted versus multiplet radii which have been reported for cesium-neutralized iono-

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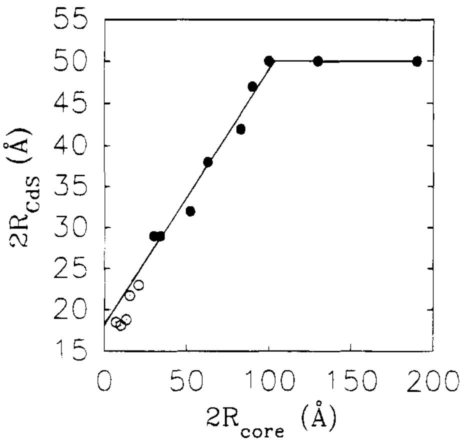

Figure 2. Plot of CdS cluster diameters ($2R_{CdS}$) versus the diameter of the original ionic core ($2R_{core}$) calculated from the scaling relation $2R_{core} = 6.5N_B^{3/5}$ Å. Dotted circles are cluster sizes obtained in random ionomers. The regression line is through the solid circles (excluding $R_{core} > 100$ Å) but has been extended manually to include the random ionomer data. The horizontal line is a guide for the eye.

mers of variable chain lengths;[22] the linear relationship is found to pass through these points, indicating that the control of cluster sizes by ionic aggregate sizes in diblock ionomers is an extension of the same type of size control observed in random ionomers. Though not shown in the figure, the smaller CdS cluster sizes, calculated from λ_m or λ_{sh}, were also plotted against R_{core}, and a linear correlation was found, with a correlation coefficient of 0.98.

For ionic core sizes $2R_{core} > 100$ Å, the size control described above is lost, and the CdS particle size levels off at ca. 50 Å. This "plateau" may be explained by the possibility that, for very large ionic cores, the diffusion of material over the large volume within the core results in a relatively slow rate of cluster growth. Thus, as the rate of cluster growth with respect to the rate of nucleation decreases in these large ionic cores, several particles per core are formed. This results in a kinetically controlled particle size, dependent on the viscosity of the plasticized core. It should be noted that the CdS spectra in the plateau region are still blue-shifted from the bulk material, which starts to absorb near 515 nm.[37] The two regions of Figure 2, therefore, indicate two kinds of size control over quantum-confined CdS particles: up to $2R_{core} = 100$ Å, the size of the particles is limited by the size of the ionic aggregates (thermodynamic control), while for $2R_{core} > 100$ Å, the viscosity within the core is the limiting factor (kinetic control), independent of the size of the aggregate.

The CdS particle radii (excluding the plateau region of Figure 2) were also plotted against the ionic block length, and these points were fitted to the Halperin scaling relation $R \propto N_B^{3/5}$ using the equation $R_{CdS} = aN_B^{3/5} + b$; a and b were found to be 1.9 and 9.4 Å, respectively. The fit is shown in Figure 3, along with a linear approximation, which does not deviate significantly from the scaling relation in the region of interest. Unlike the scaling relation for ionic core radii, the equation for R_{CdS} does not pass through the origin. It is noteworthy that the value of the y intercept, 9.4 Å, which represents a limiting case for block lengths tending to 0, corresponds very closely to our previously determined CdS particle diameter in the polystyrene–poly(cadmium methacrylate) random ionomer ($2R_{CdS} = 18.5$ Å).[21] This lends further credence to the claim that the size control of CdS particles in block ionomers is an extension of the same type of size control, based on the size of the original ionic aggregate, which has been demonstrated in random ionomers.

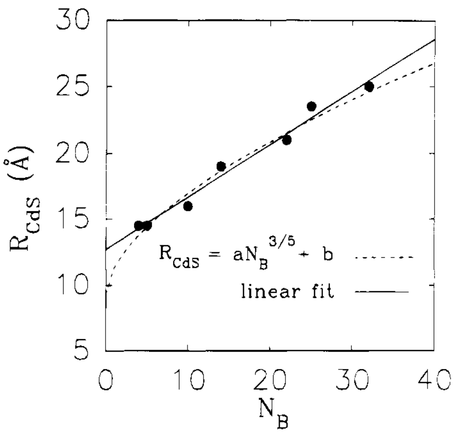

Figure 3. Plot of CdS cluster radii (R_{CdS}) versus the number of repeat units in the ionic block (N_B). The dotted line shows the best fit to the $N_B^{3/5}$ relation (equation shown in figure) with $a = 1.9$ and $b = 9.4$ Å. A linear regression through the data is also shown (solid line).

Within the region of apparent thermodynamic control ($R_{core} = 30-100$ Å), it has been assumed that all cadmium ions in the core become incorporated into a single cadmium sulfide particle. The validity of this assumption can be tested by determining the number of cadmium ions in the ionic core, and comparing this to the number of cadmium ions in the subsequent CdS particle. Assuming spherical clusters, these numbers were calculated using values of R_{core} and R_{CdS}, respectively, along with the unit volumes of the ionic core material and monomolecular CdS. The volume of a single unit of CdS was calculated from its density and molecular weight to be 50 Å^3. There are two possibilities for the unit volume of the ionic core, depending on the binding of countercations following neutralization with cadium acetate. In the first case, Cd^{2+} cations are each bound to two carboxylic anions, resulting in one counterion shared between two units of acrylate. In the second case, the singly bound $Cd(Ac)^+$ cation is invoked, such that there is a counterion for each acrylate unit. The core radius was assumed to be independent of the nature of cadmium binding, as implied by the equation $R_{core} = 6.5N_B^{3/5}$ Å. Quantitative FTIR analysis of the neutralized copolymers showed a combination of these possibilities, with various degrees of Cd^{2+} bridging ranging from 100% doubly bound Cd^{2+} in PS(300)-*b*-PACd(4.0), to 24% doubly bound Cd^{2+} in PS(730)-*b*-PACd(84). In Table 2, the two extreme cases have been considered independently, in order to calculate the number of cadmium ions within a core containing 100% doubly bound cadmium, $n_{Cd}(II)$, and the number of cadmium ions within a core containing 100% singly bound cadmium, $n_{Cd}(I)$. The unit volumes of the ionic core material for both cases were calculated approximately, starting from the experimentally determined density of poly(cesium acrylate) ($d = 2.0$ g/mL).[39]

Table 2 also lists two sets of CdS cluster agglomeration numbers; $n_{CdS}(\lambda_e)$ corresponds to larger particles in a distribution of sizes, while $n_{CdS}(\lambda_{m,sh})$ corresponds

Table 2. Calculated Number of Cadmium Ions in the Ionic Core and in Subsequent CdS Particles

polymer	n_{Cd}(I)	n_{Cd}(II)	$n_{\mathrm{CdS}}(\lambda_e)$	$n_{\mathrm{CdS}}(\lambda_{\mathrm{m,sh}})$
PS(300)-*b*-PACd(4.0)	56	47	260	84
PS(470)-*b*-PACd(5.0)	82	68	260	84
PS(300)-*b*-PACd(10)	290	240	340	150
PS(320)-*b*-PACd(14)	520	430	580	260
PS(730)-*b*-PACd(22)	1200	990	780	310
PS(300)-*b*-PACd(25)	1500	1300	1100	340
PS(470)-*b*-PACd(32)	2100	1700	1300	580
PS(300)-*b*-PACd(44)	4600	3800	1300	580
PS(730)-*b*-PACd(84)	14000	12000	1300	580

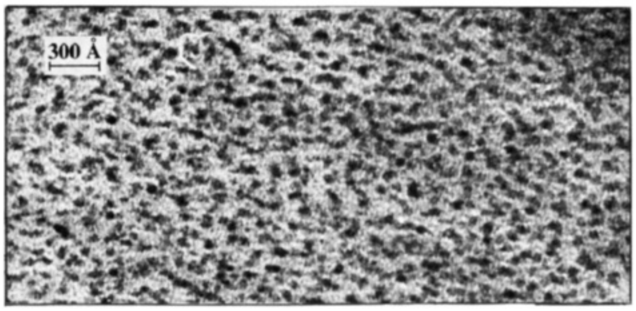

Figure 4. Transmission electron micrograph of CdS in PS-(470)-*b*-PAA(32). The dark regions are CdS particles dispersed in the polymer.

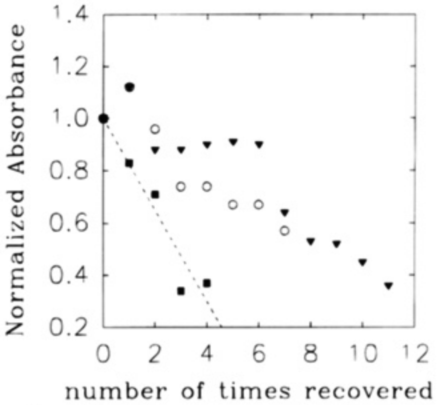

Figure 5. Normalized absorbance values for CdS-containing PS(1100)-*b*-PAA(23) micelles in toluene solution plotted versus number of recoveries by precipitation into methanol. Symbols indicate the preparation of the micelles prior to the first precipitation in MeOH: (■) no reneutralization, (○) reneutralization with excess NaOH and 15 min of stirring, (▼) reneutralization with excess NaOH and overnight stirring.

to particle sizes closer to the mean. For the two shortest block lengths, n_{Cd}(I) and n_{Cd}(II) are in good agreement with $n_{\mathrm{CdS}}(\lambda_{\mathrm{m,sh}})$; for longer block lengths, n_{Cd}(I) and n_{Cd}(II) show better agreement with $n_{\mathrm{CdS}}(\lambda_e)$. The copolymers PS(300)-*b*-PACd(44) and PS(730)-*b*-PACd(84) result in n_{CdS} values significantly lower than the number of cadmium ions in the original core. This is not a surprising result, if we assume that there are several CdS particles in ionic cores which are >100 Å in diameter, as is indicated by the plateau region observed in Figure 2.

A TEM micrograph of CdS-containing PS(470)-*b*-PAA(32) is shown in Figure 4. The dark regions are the CdS clusters, which appear evenly dispersed in the polymer matrix. The cluster size measured from the micrograph is ca. 50 Å, confirming the size determined from the UV–vis spectrum. The irregular shape of some of the dark regions is probably due to overlapping particles in different layers of the microtomed film. A total micelle diameter of 200 Å has been calculated for the solid state, which indicates that the microtomed film (thickness = ca. 800 Å) contains about four overlapping monolayers.

Polydispersity of CdS Particle Size Distributions. In UV–vis studies of quantum confined semiconductors, absorption spectra which exhibit distinct maxima and/or shoulders are generally associated with relatively monodisperse size distributions. A useful measure of the polydispersity of the sample is obtained by calculating $d_{1/2}$,[6] defined as

$$d_{1/2} = 2R_{\mathrm{CdS}}(\lambda_e) - 2R_{\mathrm{CdS}}(\lambda_{\mathrm{m,sh}}) \qquad (1)$$

If we assume a Gaussian distribution of particles, $d_{1/2}$ can be taken to be twice the standard deviation (σ_{2R}), and $2R_{\mathrm{CdS}}(\lambda_{\mathrm{m,sh}})$ will approximate the mean particle diameter. We can then define a radius polydispersity index (RPI) for each distribution:

$$\mathrm{RPI} = (\sigma_{2R}/\overline{2R}_{\mathrm{CdS}})^2 + 1 \qquad (2)$$

As shown in Table 1, RPI values for the CdS particles obtained in block ionomers are low, between 1.02 and 1.05. Very similar polydispersities have been found for the radii of ionic cores in block ionomers, as determined by SAXS.[30] It should be noted that the assumption of a Gaussian distribution may not be entirely realistic, and therefore the RPIs listed in Table 1 are only approximate values. In some cases, it is conceivable that the polydispersities of CdS particles are higher than the polydispersities of the original ionic cores. Such a situation would arise, for example, from slight nonuniformities in the degree of conversion throughout the composite; smaller particles in the distribution could therefore represent incomplete conversion from Cd^{2+} in the core to a single cluster of CdS. Incomplete conversion would explain some of the results in Table 2, which show that, in some cases, CdS agglomeration numbers for larger particles in the distribution ($n_{\mathrm{CdS}}(\lambda_e)$) show the best agreement with cadmium aggregation numbers.

Solution Stability and "Fixing" of CdS-Containing Block Copolymer Micelles. Normalized absorbance values (A_{norm}) for CdS-containing micelles of PS(1100)-*b*-PAA(23) in toluene (identical weight percentages) after sequential recoveries are shown in Figure 5. The absorbance was determined at 400 nm, close to the shoulder of the absorption spectrum; the polymer host in toluene shows no absorbance at this wavelength, so that only the absorbance of the CdS clusters was monitored. Absorbance values were normalized by dividing the absorbance after each recovery by the value determined prior to the first precipitation of the micelles into methanol. Thus, a normalized absorbance value of 1 is obtained for "0 recoveries" on the horizontal axis. Since micelle solutions of identical weight percentages were prepared after each recovery, a drop in the absorbance of the solution may be interpreted as a drop in the CdS concentration of the composite. A normalized absorbance value of 0.5, for example, indicates (according to Beer's law) a 50% loss of CdS from the micelles.

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(39) Nguyen, D. Ph.D. Thesis, McGill University, Montreal, 1994.

Table 3. UV–Vis Absorption Spectral Features for CdS-Containing Micelles of PS(320)-*b*-PAA(14) after Sequential Recoveries from Toluene by Precipitation into Methanol

no. of recoveries	$\lambda_e{}^a$ (nm)	$A_{norm}{}^a$	$\lambda_e{}^b$ (nm)	$A_{norm}{}^b$	$\lambda_e{}^c$ (nm)	$A_{norm}{}^c$
0	449	1.00	452	1.00	456	1.00
1	456	1.10	452	0.99	456	0.98
2	456	1.26	454	0.91	457	0.96
3	453	1.01	454	1.01	457	0.97
4	455	0.97	453	0.92	457	1.09
5	455	0.66	453	0.87	456	0.97
6			454	0.83	458	0.78
7			454	0.85		
8			453	0.80		
9			455	0.77		
10			453	0.75		

[a] No reneutralization. [b] Reneutralized by stirring with excess cadmium acetate overnight. [c] Reneutralized by stirring with excess cadmium acetate for 1 week.

Three different methods of preparation were used prior to the first precipitation of the micelle solution into methanol. In the first case, the yellow powders were simply dissolved in toluene, without reneutralization of the poly(acrylic acid) block; this resulted in a nearly linear drop in the absorbance (Figure 5), with a 60% loss of CdS after four recoveries from toluene. It is possible that this loss is due to a micelle–single chain equilibrium of PS-*b*-PAA in toluene, which results in the partial dissociation of the micelles upon dissolution. The CdS micelles which were reneutralized by overnight stirring in excess NaOH, however, showed a much greater stability with respect to the normalized absorbance. After an initial rise to 1.1 and a subsequent drop to about 0.9, the normalized absorbance was found to plateau, indicating that no further CdS was lost until the sixth recovery. This enhanced stability of the UV–vis absorbance may be attributed to the enhanced solution stability of the composites following reneutralization; thus, reneutralization of the poly(acrylic acid) block can be said to “fix” the micelles. Since poly(sodium acrylate) has a much lower solubility in toluene than poly(acrylic acid), it is likely that single chains of PS-*b*-PANa have a much lower critical micelle concentration (or cmc) than single chains of PS-*b*-PAA. Considering the kinetics of the system, it is also reasonable to say that “fixing” results in an effective freezing of the core, such that the characteristics of the micelle approach those of a stable, non-equilibrium aggregate. Following the plateau (Figure 5), there was a clear drop in the normalized absorbance. This can be explained by reactions such as the following, which may partially convert the poly(sodium acrylate) back to poly(acrylic acid) after several precipitations in methanol:

$$H_2O + CO_2 \leftrightarrow H_2CO_3$$

$$RCOO^-Na^+ + H_2CO_3 \leftrightarrow RCOOH + HCOO^-Na^+ \quad (3)$$

For micelles reneutralized by 15 min stirring with NaOH, an intermediate degree of stability was found.

Table 3 shows the spectral features for CdS-containing micelles of another polymer, PS(320)-*b*-PAA(14), after sequential recoveries from toluene by the same method. In this case, the reneutralized micelles were prepared by stirring with cadmium acetate (1 mol of cadmium acetate:1 mol of acrylic acid repeat units), either overnight or for a period of 1 week. An interesting result is the greater stability of the normalized absorbance (determined at 400 nm) for unneutralized micelles of PS(320)-*b*-PAA(14), compared with unneutralized micelles of PS(1100)-*b*-PAA(23). Unlike the linear drop in absorbance which was observed for the PS(1100)-*b*-PAA(23) composite without reneutralization (Figure 5), Table 3 shows that the composite of PS(320)-*b*-PAA(14), prepared in an identical manner, suffered only a 3% drop in absorbance after four recoveries. This result points to a greater tendency for micelles of PS(1100)-*b*-PAA(23) to dissociate into single chains upon dissolution in toluene. This can be explained in terms of the different soluble and insoluble block lengths in the two copolymers. Despite the greater length in the insoluble block of PS(1100)-*b*-PAA(23), which would tend to lower the cmc of the single chains compared with single chains of PS(320)-*b*-PAA(14), its extremely long soluble block (1100 styrene units) may result in a cmc which is higher than that of PS(320)-*b*-PAA(14). In effect, the huge difference in the lengths of the PS blocks may dominate over the much smaller difference in the acid block lengths. A lower cmc value for the single chains implies greater stability for the PS(320)-*b*-PAA(14) composites in organic solvents. For both reneutralized micelle preparations of PS(320)-*b*-PAA(14), impressive solution stability is shown by the normalized absorbance values; up to 10 precipitations into methanol were achieved with only a 25% drop in the absorbance.

The slight increase in the absorption edge (λ_e) with the first recovery of the unneutralized composites may be attributed to a certain of degree of Ostwald ripening (Table 3). The reneutralized materials, on the other hand, show impressive stability in the absorption edge, indicating that the size of the clusters within the micelles do not change, even after repeated precipitation of the composite into methanol. Comparing λ_e values before the first recovery for different methods of micelle preparation, a slight increase in the absorption edge with stirring time in the reneutralizing solution is observed; from this information, it seems that some Ostwald ripening occurs as the micelles are reneutralized over an extended period of stirring in THF. However, it should be noted that the increase in λ_e from 449 to 456 nm after 1 week of stirring represents only a 2 Å increase in the CdS cluster diameter.

Composite Stability under Various Methods of Processing. To test the stability of cluster sizes under different methods of processing the composite powder, the absorption edge of CdS clusters in micelles of PS(300)-*b*-PAA(4.0) was obtained by three methods. In the first case, a spectrum was obtained in solution by dissolving the powder in toluene (without reneutralization). In the second case, the CdS-containing micelles were cast from a 10% toluene solution onto a glass slide, and a spectrum of the transparent film was obtained. Last, a transparent film of the composite was prepared by compression molding the powder at 130 °C (above the T_g of the polystyrene matrix) for 7 min. For all three preparations, essentially identical absorption edges were obtained.

Continued Controlled Particle Growth. After reneutralization and secondary H_2S treatment of CdS-containing PS(320)-*b*-PAA(14) micelles, the yellow color of the powders became noticeably more intense. From UV–vis absorption spectra of the micelles in toluene solution, it was found that secondary H_2S treatment resulted in a red-shift in the absorption edge from 456 to 488 nm; this corresponds to an increase in the particle diameter from $2R_{CdS} = 37-52$ Å, or an increase in the spherical particle volume from $V_{CdS} = 27\,000-74\,000$ Å^3. This increase in cluster size may be explained by counterions in the reneutralized poly(cadmium acrylate) being converted to CdS upon treatment with H_2S; this newly formed CdS then deposits on the surface of the original cluster. Since the volume of the cluster more than doubled, it seems that all of the counterions in the reneutralized PACd layer became incorporated into the cluster in the form of CdS; excess cadmium acetate in the core may also have been involved. The next reneutralization/H_2S treatment resulted in a further increase in the cluster size to $2R_{CdS} = 56$ Å (calculated from the absorption edge), corresponding to an increase in the particle volume of 18000 Å^3. This indicates that about two-thirds of the counterions from the poly(cadmium acrylate) layer became incorporated into the growing cluster. It is possible that the rest of the cadmium in the core was converted into small CdS crystallites surrounding the larger particle.

Conclusion

This work has demonstrated the size control of CdS clusters within the water-plasticized cores of diblock ionomers in the range of $2R_{CdS} = 29-50$ Å. For ionic cores up to 100 Å in diameter, the size of the CdS clusters increased linearly with the size of the original core, while for cores with diameters >100 Å, a cluster size of 50 Å was obtained, independent of the original core size. In completely dry ionic cores, CdS particles of ca. 21 Å were obtained for all ionic block lengths. This size control of CdS clusters through a priori knowledge of primary ionic aggregate sizes is an extension of our work in styrene-based random ionomers, in which size control in the range of $2R_{CdS} = 18-23$ Å was demonstrated.

The solution stability of CdS-containing diblock copolymer micelles has also been shown by repeated precipitation of the micelles into methanol and redissolution in organic solvent. By "fixing" the micelles (reneutralization of the acid block), the solution stability of the composites was significantly improved. For solutions of "fixed" micelles, several precipitations into methanol were performed without significant changes in the CdS cluster sizes or losses in UV–vis absorbance. By reneutralizing the CdS-containing micelles with cadmium acetate and subsequent reexposure to H_2S, it was found that the original cluster sizes could be increased. By this method, particles up to 56 Å in diameter were obtained, demonstrating the possibility of "secondary" size control for CdS clusters >50 Å.

This combination of precise size control, solution and melt stability, and controlled continued growth makes PS-*b*-PAA-based diblock ionomers unique polymer hosts for the formation of quantum-confined CdS–polymer composites, or similar materials containing other types of particles. This system combines the advantages of semiconductor particles evenly dispersed in a polymer matrix with those of particles stabilized in colloidal solution. As well, it should be noted that, unlike other work involving small particles in block copolymers,[16–20] the incorporation of metal ions into the core of PS-*b*-PAA involves simple carboxylate–counterion associations and does not rely on the coordination of metals to the core-forming blocks. Therefore, metal ions that do not undergo complex formation (e.g., group IA and IIA metals) can also be incorporated into the core by neutralizing the poly(acrylic acid) block with the appropriate reagents. Subsequent chemistry within the core could then be carried out to form a wide range of metallic clusters of predictable sizes and varying composition.

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