

Size Control of Nanoparticles in Semiconductor–Polymer Composites. 1. Control via Multiplet Aggregation Numbers in Styrene-Based Random Ionomers

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A priori knowledge of ionic aggregate sizes in random ionomers has been applied to the synthesis of semiconductor nanoparticles of predictable sizes. The size control of quantum-confined cadmium sulfide (CdS) and lead sulfide (PbS) clusters in the range of $2R = 18\text{--}23$ Å was accomplished within styrene-based random ionomers with ionic groups located at the ends of side-chains of variable lengths. CdS and PbS clusters were precipitated within the ionic aggregates (multiplets) of the ionomer, to form composites of semiconductor nanoparticles dispersed in a polymer matrix. The sizes of the semiconductor clusters increased with increasing side-chain length, and an approximate linear relationship was shown between the cluster sizes and the lengths of the side chains. These results are in agreement with the previous finding that the size of the ionic multiplet increases with the length of the side chain and show that a knowledge of ionic aggregate sizes can be used to form nanoparticles of predictable sizes. The semiconductor–polymer composites were characterized by UV–vis spectroscopy, small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM). This is the first of two papers in which the size control of semiconductor clusters through the primary ionic aggregate sizes of various ionomers is demonstrated. In the next paper, the use of PS-*b*-PACd diblock ionomers to precipitate CdS clusters of predictable sizes in the range $2R = 29\text{--}50$ Å will be described.

Introduction

The study of semiconductor clusters and their controlled precipitation in various media has received much attention in recent years. These clusters, which exhibit electronic and optical properties different from those of bulk semiconductors, may contain anywhere from several hundred to <10 units. In this regime of ultrasmall sizes, the particle diameter is comparable to or less than the diameter of the bulk semiconductor exciton, such that quantum confinement of electron–hole pairs increases the bandgap relative to that in the bulklike materials.

In the quantum-confined regime, the control of particle sizes allows the bandgap to be “tuned” to give the desired electronic and optical properties. For cadmium sulfide (CdS) particle diameters below ca. 60 Å, the absorption spectrum is “blue shifted” from the bulk, and correlations have been made between the absorption threshold and the size of the particles, using both theoretical calculations^{1–3} and experimental measurements.^{4,5} The control of semiconductor cluster sizes has been achieved in a wide range of colloidal and solid-state media, including reverse micelles,^{6–9} surfactant

vesicles,^{10,11} zeolites,¹² and several types of ion-containing polymers.^{13–26}

Ionomers have been recently defined as ion-containing copolymers “in which the bulk properties are governed by ionic interactions in discrete regions of the material (the ionic aggregates).”²⁷ Microphase separation of

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ionomers results in the formation of ionic aggregates within a matrix of the nonionic polymer component. For convenience, we can distinguish between two types of ionomers: random and block ionomers. In random ionomers, there is a statistical distribution of ionic units along the polymer chain. Block ionomers, on the other hand, consist of strands (or blocks) of ionic units and strands of nonionic units, linked in sequence through covalent bonds; a common case is the AB diblock ionomer, in which a block of nonionic A units is joined to a block of ionic B units. In both random and block ionomers, the relationship between morphological characteristics in the solid state and the structure or composition of the ionomer introduces a convenient method of controlling ionic aggregate sizes. As a detailed understanding of ionomer morphology has developed, it has become possible to form ionic aggregates of a specific size, simply by selecting an appropriate ionomer.

In the case of random ionomers, recent advances have greatly increased our understanding of the microstructure and physical properties of these systems. A model of random ionomers developed by this group (the EHM model)²⁸ is based on ionic aggregates (or multiplets) which are surrounded by regions of restricted mobility in the bulk polymer. At sufficiently high ion content, these regions overlap to form "clusters" of multiplets, resulting in phase-separated behavior. Such "clusters" must not be confused with the metal sulfide clusters which are the subject of the present paper.

A recent study has shown that it is possible to control aggregate sizes in random ionomers by varying the structure of the ionic unit.²⁹ For a series of styrene-based ionomers with variable-length side chains between the polymer backbone and the ionic groups, it was found that the ionomers with longer side chains formed larger multiplets; this trend was attributed to decreased steric hindrance to ionic aggregation when the ionic groups are further removed from the backbone. For example, small-angle X-ray scattering (SAXS) results showed that the multiplet aggregation numbers increased from ca. 28 to ca. 74, when the length of the side chain was increased by nine methylene groups.

In diblock copolymers, microphase separation results in a range of morphologies from lamellar to spherical, depending on the volume fractions of the component blocks.³⁰⁻³² A number of theories have been developed which allow the morphology of diblock copolymers to be predicted in terms of fundamental parameters;^{30,31,33-36} these are based on quantitative expressions for the free

energy, which is minimized to determine the equilibrium shape of the microdomains for various relative block lengths. When the volume fraction of one block is relatively low, it has been observed that the microdomains have a spherical morphology.^{30,37}

In diblock ionomers, spherical ionic aggregates are formed in a matrix of the nonionic component, even at extremely short ionic block lengths.³⁸ It is frequently found that Halperin's "star model" of diblock copolymers³⁹ is well-suited for describing the sizes of spherical ionic microdomains, both in the bulk^{40a} and in solution.^{40b} In solution, diblock copolymers form micelles, which consist of a core of the insoluble blocks, surrounded by a corona of the soluble blocks. Halperin's model states that the size of the micelle core (which becomes the spherical microdomain in the solid state), is determined exclusively by the length of the insoluble block (N_B), such that the core radius scales as $N_B^{3/5}$. Other models, such as those developed by Leibler, Orland, and Wheeler (the LOW theory)⁴¹ and Noolandi and Hong (the NH theory),⁴² have also been used to predict the core radii and critical micelle concentrations of block copolymers. Investigations of block ionomers have included detailed SAXS studies of polystyrene-*b*-poly(methacrylate) systems, which confirm that there is a relationship between the length of the ionic block and the size of the ion-containing core and demonstrate the control of ionic aggregate sizes through ionomer composition.⁴⁰

From this description of random and diblock ionomers, it is evident that size control of ionic aggregates can be achieved by selecting an ionomer of a particular structure and composition. When both groups of ionomers are considered, a wide range of aggregate sizes is accessible. In random ionomers, aggregation numbers in the neighborhood of 2-75 ion pairs are possible, with multiplet radii ranging from $<5-10 \text{ \AA}$.²⁹ In diblock ionomers with spherical microdomains, the radii of the ionic core can be varied conveniently from ca. 15-100 \AA , by selecting the appropriate ionic block length. In such cases, the aggregation numbers of the ionic cores vary from ca. 20-200 chains;^{40b} this means that the largest spherical cores in block ionomers are ionic aggregates of several thousand ion pairs.

The synthesis of metal sulfide and metallic clusters within ionomers and ion-containing polymers has been achieved by several groups.¹³⁻²⁶ Ion-containing homopolymers, random ionomers, and ion-complexing block copolymers have all been used to synthesize various metallic and semiconducting clusters, resulting in composite materials consisting of nanoparticles dispersed in a polymer matrix. Such composites have been shown to exhibit a wide range of interesting optical, electronic, and photocatalytic properties.^{13-18,26,43,44}

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In studies involving random ionomers, CdS clusters have been precipitated in perfluorosulfonate (Nafion) films,^{13–18} and PbS clusters have been synthesized in ethylene-based (Surlyn) polymers.^{19,20} The latter work demonstrated size control of PbS particles within the random ionomer, forming a range of particle sizes from monomolecular to bulk PbS. It should be noted that in refs 19 and 20, size control was achieved through control of the initial ion concentration and subsequent annealing conditions, and not through control of the primary ionomer aggregate sizes.

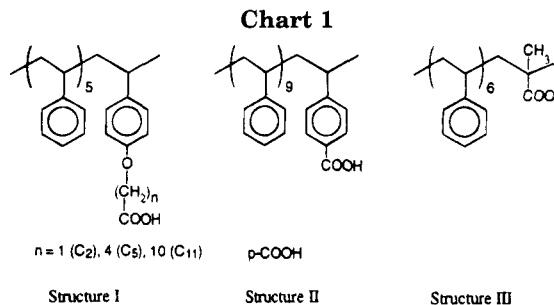
Synthesis of inorganic clusters within the metal-complexing microdomains of polystyrene-*b*-poly(2-vinylpyridine) has been reported by Moller.²¹ Subsequently, Schrock et al. demonstrated the synthesis of CdS and ZnS clusters within the microdomains of diblock copolymers formed by ring-opening metathesis polymerization.^{22,23} These workers have also used the norbornene-based metal-complexing blocks of such polymers to form metallic clusters of platinum, palladium, gold, and silver in the microseparated domains.^{24,25} Transmission electron microscopy (TEM) results showed that small clusters of narrow size distribution were formed preferentially within metal-complexing microdomains of lamellar and cylindrical morphology. Single clusters within microdomains of spherical morphology were also observed.²⁵

The present study demonstrates the control of semiconductor particle sizes by the control of the primary ionic aggregate sizes in several styrene-based ionomers. Ionomers are prepared by neutralizing the acid-form copolymer with cadmium or lead acetate, such that metal counterions are localized in aggregates of a size which is dependent on the nature of the polymer. These aggregates are the source of cations in metal sulfide formation and serve as microreactors for the synthesis of semiconducting particles. The size of the resulting particles will ultimately be limited by the number of cations in the aggregate, which is directly related to the ionic aggregation number. The first paper investigates random ionomers with variable-length side chains as a medium for metal sulfide cluster synthesis. The sizes of semiconducting particles synthesized in these materials were determined from the absorption edge of UV-vis spectra and compared with SAXS and TEM measurements. The subsequent paper deals with larger quantum-confined CdS particles ($2R_{\text{CdS}} = 29\text{--}50 \text{ \AA}$) in the ionic aggregates of diblock ionomers.

Experimental Section

Materials. The synthesis of styrene-based ionomers with variable length *p*-methyl alkanooate side chains was described in a previous publication.⁴⁵ Preparation of these materials involved direct attachment of the terminally carboxylated alkyl chains to the para position of the styrene rings through alkyl aryl ether linkages, to produce the following precursors: poly[styrene-*co*-4-[(carbomethoxymethyl)oxy]styrene], poly[styrene-*co*-4-[(carbomethoxybutyl)-1-oxy]styrene], and poly[styrene-*co*-4-[(carbomethoxydecyl)-1-oxy]styrene].

The precursors were hydrolyzed by refluxing (under nitrogen) with excess sulfuric acid in a 90:10 tetrahydrofuran/water



N.B. The numbers outside the brackets indicate styrene units per ionic unit, and represent average values.

solution for 3–5 days. Structure I (Chart 1) shows the resulting polymers in the acid form, with variable-length spacers ($n = 1$, termed C₂ ether; $n = 4$, termed C₅ ether; $n = 10$, termed C₁₁ ether). The carboxylic acid content was determined by titration of the hydrolyzed polymers with a standard 0.05 N methanolic NaOH solution. The acid content of the C₂–C₁₁ ether series was determined to be 18 mol %.

The synthesis of poly[styrene-*co*-4-(carboxy)styrene] (acid content 10%, structure II) was also described in a previous paper.⁴⁶ Poly[styrene-*co*-methacrylic acid] (acid content 14%, structure III) was prepared by standard free-radical polymerization techniques.

Preparation of Cd- and Pb-Neutralized Ionomer Films.

Transparent films of the Cd- and Pb-neutralized ionomers were required for UV-vis analysis of the subsequent CdS- and PbS-containing composites. Each polymer was cast in its acid form onto glass slides, from concentrated solutions in *N,N*-dimethylformamide. *N,N*-Dimethylformamide was evaporated under vacuum at 130 °C, and the films were left to dry overnight under the same conditions. The polymer films were neutralized by immersing them for 3 days in a 0.25 M solution of cadmium acetate dihydrate (Aldrich) in 70:30 methanol/toluene (v/v) or in a 0.12 M solution of lead acetate trihydrate (Analar) in 80:20 methanol/toluene (v/v), to obtain Cd- and Pb-neutralized films, respectively. The solutions were changed regularly over the 3-day period to remove acetic acid. Small amounts of the C₂, C₅, and C₁₁ samples were scraped from the glass slides and mixed with dried KBr. FTIR spectral analysis of these samples indicated between 82% and 91% neutralization by the present method. Following neutralization, the polymer films were soaked for 3 days in methanol/toluene solutions, to wash away excess metal acetate such that all cadmium and lead ions were bound to the ionic groups of the polymer. During neutralization and rinsing, the films were swollen with toluene, facilitating multiplet formation.

The films turned from transparent to cloudy during the rinsing step. After rinsing, the films were heated with a heat gun until transparency returned, then the neutralized polymer films were dried under vacuum at 130 °C for 3 days.

In theory, the ratio of doubly bound to singly bound Cd²⁺ and Pb²⁺ ions is determinable from FTIR analysis of the neutralized copolymer films. The quality of the obtained spectra, however, made such quantitative analysis impossible in the present case. This method was more successful with neutralized block ionomer films and will be discussed further in the next paper.

Ionomer films for small-angle X-ray scattering were prepared in an identical manner, except that generally thicker films were cast, and the transparency of the films was no longer critical. Ionomer films were prepared on Teflon sheets, and the subsequent composite films were then stacked to obtain thick films (ca. 1mm) for SAXS analysis.

Reaction of Ionomer Films with H₂S. After drying, the Cd- and Pb-neutralized films were reacted for 5 h in a closed flask with dry H₂S at atmospheric pressure and 25 °C. This was assumed to be sufficient time for all of the counterions in the ionic aggregates to be converted to CdS or PbS. Acrylate units were converted to acrylic acid in the course of the

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Table 1. CdS and PbS Cluster Diameters and Agglomeration Numbers in Styrene-Based Ionomers with Variable-Length Spacers and Comparison with Aggregation Numbers in Cs-Neutralized Ionomers

polymer	L_{sc} (Å)	λ_e (CdS) (nm)	λ_e (PbS) (nm)	$2R_{CdS}$ (Å)	$2R_{PbS}$ (Å)	n_{CdS}	n_{PbS}	n_{Cs}^a
methacrylate, 14%	1.5	340	459	18.5	19.8	66	77	
<i>p</i> -carboxystyrene, 10%	5.3	335	453	18.1	19.6	62	74	
C ₂ ether, 18%	8.0	344		18.8		70		28
C ₅ ether, 18%	11.5	374	506	21.7	21.9	107	104	44
C ₁₁ ether, 18%	18.7	388	535	23	23.3	130	125	74

^a Determined in 14% ether ionomers.

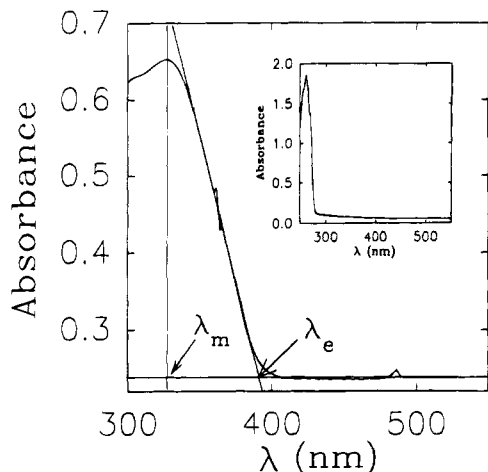


Figure 1. UV-vis absorbance spectrum of CdS formed in 18% C₁₁ ionomer. The polymer absorbance has been subtracted from the spectrum. The absorption edge is $\lambda_e = 390$ nm, and the maximum is $\lambda_m = 332$ nm. The absorbance of the untreated polymer is shown in the insert.

reaction. Within the first 10 min of the reaction, color changes indicated the formation of metal sulfide particles. CdS-containing films were pale yellow, while PbS-containing films ranged from dark orange to yellow, depending on the host ionomer. Following the reaction, the films were left under vacuum in a desiccator overnight, to remove excess H₂S.

Transmission Electron Microscopy. Electron microscopy was performed on a Phillips EM410 instrument. A film of the CdS-C₁₁ polymer composite was prepared for electron microscopy by microtoming (film thickness, ca. 800 Å), and the microtomed sample was then mounted on a copper grid.

UV-Vis Absorption Spectroscopy. UV-vis absorption spectra were obtained on a Hewlett-Packard 8452 diode array spectrophotometer. CdS- and PbS-containing films were scanned between 250 and 550 nm and between 200 and 800 nm, respectively. Absorption from the polymer and the glass slide was subtracted from each spectrum.

SAXS Instrumentation and Analysis. Small-angle X-ray scattering experiments were carried out at Laval University on a Rigaku rotating-anode instrument ($\lambda = 1.548$ Å). The CdS-containing polymer films were scanned from $2\theta = 0.3$ – 5.0 . The data were then plotted as scattering intensity vs q , where $q = (4\pi \sin \theta)/\lambda$. An air blank was also scanned, and this was subtracted from each scattering profile. Low scattering intensities relative to the blank resulted in very low signal-to-noise ratios. However, for the CdS-C₁₁ polymer composite, the obtained scattering peak was used to calculate Bragg spacings between scattering centers ($d_{Bragg} = 2\pi/q$, Å). The number of CdS units per particle, known as the agglomeration number (n_{CdS}), was then determined by space-filling calculations for a simple cubic lattice, using the appropriate assumptions.²⁹

Results and Discussion Section

UV-Vis Absorption Data for CdS Particles.

Figure 1 shows an absorption spectrum for CdS clusters synthesized in the 18 mol % C₁₁ ether ionomer. The glass slide was run as a blank, and the absorbance of

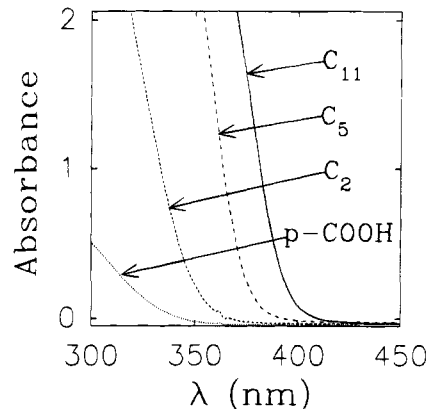


Figure 2. UV-vis spectra of CdS clusters formed in a series of styrene-based ionomers with variable-length spacers. The 10% *p*-carboxystyrene ionomer is denoted *p*-COOH. The baselines have been normalized, such that the vertical axis indicates absorbance above the baseline.

the polymer before reaction with H₂S was subtracted from the spectrum. The insert shows the absorption spectrum of a styrene-based ionomer before treatment with H₂S. Neither the glass slide nor the polymer shows significant absorbance above 300 nm, so the subtraction procedure does not interfere with the relevant spectral features. As shown in the figure, the absorption edge (λ_e) is obtained from the intersection of the sharply decreasing region of the spectrum with the baseline. The exciton maximum observed in Figure 1 (λ_m) is an example of spectral structure and indicates a relatively narrow distribution of cluster sizes.⁴⁷ For smaller CdS particles, λ_m could not be determined from the absorption spectra, as this feature was obscured by absorption from the polymer and/or glass.

The side-chain lengths (L_{sc}) of the host ionomers (Table 1) were calculated assuming an extended side chain.²⁹ Figure 2 shows the absorption spectra of CdS clusters in polymers with variable-length spacers. Comparison of these spectra shows that the wavelength of the absorption edge increases with the length of the side chain.

For all spectra obtained in this study, the absorption edge (λ_e) was converted into an associated CdS particle size, using Henglein's empirical curve which relates the wavelength of the absorption threshold to the diameter of the CdS clusters⁵ (the curve was digitized, and the best-fitting function was used to calculate cluster diameters⁴⁸). For the spectrum shown in Figure 1, it was also possible to calculate a particle size corresponding to λ_m . The difference between the particle size calculated from λ_e and that calculated from λ_m gives the

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(48) The equation used to calculate CdS cluster diameters was $2R = 1/(0.1338 - 0.0002345\lambda)$. The number of significant figures shown is that necessary to arrive at the reported results.

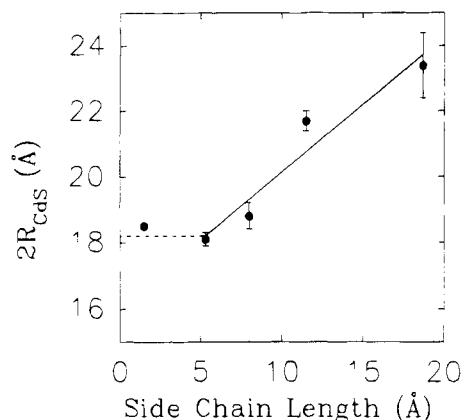


Figure 3. Plot of CdS cluster diameters ($2R_{\text{CdS}}$) versus ionomer side chain length (L_{SC}). A linear regression was performed (solid line), omitting the methacrylate ionomer ($L_{\text{SC}} = 1.5 \text{ \AA}$). The dotted horizontal line is a guide for the eye.

quantity $d_{1/2}$,¹¹ which indicates the width of the size distribution. Assuming a Gaussian distribution of particle sizes, $d_{1/2}$ can be used to calculate the radius polydispersity index (RPI), analogous to the polydispersity index (PI) of polymer molecular weights. From the spectrum shown in Figure 1, the CdS distribution has an RPI value of 1.03. This is a good indication that the particle sizes have a very narrow distribution.

UV-vis data and corresponding CdS particle diameters ($2R_{\text{CdS}}$) are listed in Table 1. To test the reproducibility of the results, each composite was prepared three times from the copolymer in the acid form. Average values of the repeat preparations are reported in the table. Only two preparations of the methacrylate composite were performed, as the same values of λ_e were obtained both times.

Figure 3 shows the CdS particle diameters plotted vs side chain length. The error bars indicate standard deviations of the repeat preparations. From the *p*-carboxystyrene ($L_{\text{SC}} = 5.3 \text{ \AA}$) to the C₁₁ ether ($L_{\text{SC}} = 18.7 \text{ \AA}$), the plot indicates that the CdS particle diameters increase linearly with the side chain length (slope = 0.41, correlation coefficient = 0.97). This is in agreement with the previous observation that multiplet sizes increase linearly with the length of the side chain. It is also interesting to note that the slope of the present line (0.41) is identical to that found previously for the plot of ionic aggregate radius of cesium-neutralized ionomers versus side chain length.²⁹ From the figure, it can be seen that the majority of points fall within 1 Å of the particle diameter on the regression line. It appears that the ionic multiplet size is the limiting factor in CdS cluster growth, and it seems reasonable to suggest that the particle sizes are controlled by the ionomer morphology. It should be noted that the methacrylate and *p*-carboxystyrene copolymers have lower ion percentages than the side-chain ether series, and this will lower their aggregation numbers slightly with respect to the other ionomers used in the study. However, since the effect of variable side-chain lengths has been shown to be more significant than the effect of ion percentage,²⁹ it was considered valid to plot the results of all five ionomers on the same graph.

The methacrylate point ($L_{\text{SC}} = 1.5 \text{ \AA}$) seems to fall within a plateau region, as the cluster diameters level off at ca. 18 Å. This lower limit may be due to a degree of association or ripening of extremely small CdS

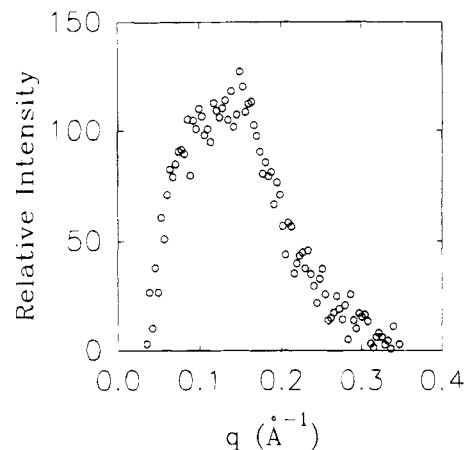


Figure 4. SAXS data for the CdS-C₁₁ polymer composite. An air background has been subtracted. The Bragg peak is found at $q = 0.12 \text{ \AA}^{-1}$.

clusters. It is also possible that the width of the size distribution increases as the particle sizes decrease, such that, in the plateau region (Figure 3), the particle sizes calculated from λ_e remain constant, while the average sizes continue to decrease. This possibility is supported by previous SAXS data on random ionomers with variable side chain lengths, which show that the size distribution of ionic aggregates is narrower in ionomers with longer side chains.²⁹

Table 1 also lists CdS cluster agglomeration numbers (n_{CdS}) calculated from particle sizes determined by UV-vis. For the calculation of n_{CdS} from the cluster diameter, spherical particles ($V = (4/3)\pi R^3$) were assumed, and the volume per CdS ion pair, 50 \AA^3 , was used.

SAXS Data. Figure 4 shows a typical air-subtracted SAXS profile for CdS-containing polymer films prepared by the present method. The scattering profile shows a definite peak, related to the Bragg spacing between the scattering centers (the CdS-containing multiplets) by $d_{\text{Bragg}} = 2\pi/q$. However, due to the low scattering intensities obtained, the subtraction procedure resulted in significant negative intensity values (not shown in the figure). As well, the number of counts obtained per scattering angle was relatively low. These factors contributed to a large margin of error in the peak positions and subsequent determination of n_{CdS} . For the CdS-C₁₁ polymer composite, which showed the most defined scattering peak, n_{CdS} was determined from the peak position shown in Figure 4 ($q = 0.12 \text{ \AA}^{-1}$), using space-filling calculations for a simple cubic arrangement of multiplets.²⁹ The use of this particular lattice model is discussed below.

In ref 40a, the sizes of ionic cores in block ionomers were calculated from SAXS structure factors, assuming several arrangements of cores within the polymer matrix. Simple cubic (sc), face-centered cubic (fcc), body-centered cubic (bcc), and hexagonal close-packed (hcp) were all applied in space-filling calculations. In general, the assumption of a sc lattice resulted in the best agreement with core sizes calculated directly from the shape factor. The simple cubic arrangement of cores (or multiplets) in ionomers is not necessarily the most accurate description; however, it should be noted that the assumptions involved in other lattice models are, most likely, equally unrealistic.

Along with the assumption of a simple cubic arrangement of multiplets, the space-filling calculation involved

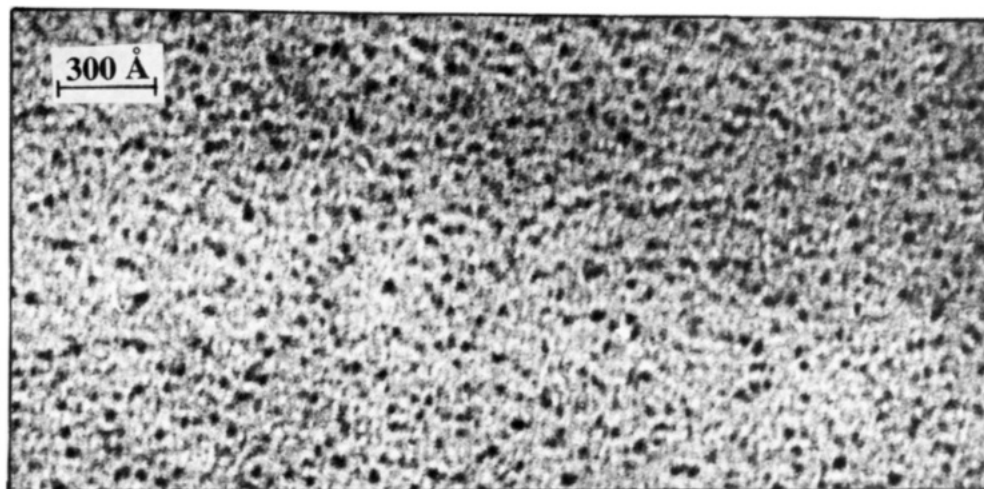


Figure 5. Transmission electron micrograph of the CdS-C₁₁ polymer composite. The dark regions indicate CdS particles dispersed in the polymer matrix.

Table 2. UV-Vis Absorption Data of CdS Clusters before and after 7 Months Storage under Ambient Conditions

polymer	λ_e (after 24 h) (nm)	$2R_{\text{CdS}}$ (after 24 h) (Å)	λ_e (after 7 months) (nm)	$2R_{\text{CdS}}$ (after 7 months) (Å)
methacrylate, 14%	340	18.5	349	19.3
<i>p</i> -carboxystyrene, 10%	332	17.9	353	19.6
C ₂ ether, 18%	344	18.8	354	19.7
C ₅ ether, 18%	376	21.9	381	22.5
C ₁₁ ether, 18%	390	23.6	411	26.7

the assumption of a single CdS unit per carboxylic acid group on the polymer chain. Although cadmium is a divalent counterion, this is not unreasonable, as the polymer films were neutralized with a large excess of cadmium acetate, which should favor the singly bound cadmium acetate counterion, Cd(Ac)⁺. The value of n_{CdS} calculated from SAXS data for the C₁₁ ionomer was 110, compared with $n_{\text{CdS}} = 134$, calculated from UV-vis data for the same ionomer (Table 1). This close agreement provides confirmation of particle sizes determined using UV-vis spectroscopy.

Electron Microscopy. Figure 5 shows a micrograph of CdS particles in the C₁₁ polymer. The small dark regions indicate well-defined CdS-containing multiplets, scattered throughout the (gray) polystyrene matrix. The dark regions indicate particle diameters of ca. 25 Å, confirming UV-vis results. It should be noted that the microtomed composite film (800 Å) does not constitute a monolayer, so a statistical assessment of the size distribution from the micrograph has not been attempted. The monolayer thickness was defined as the dimension of a cube consisting of a single CdS-containing aggregate and the surrounding styrene (simple cubic arrangement of multiplets) and was calculated to be ca. 60 Å. This value corresponds to an average of 13 monolayers in the microtomed film.

UV-Vis Absorption Data for PbS Particles. Data for PbS clusters formed in the same series of ionomers are listed with the CdS data in Table 1. These values were obtained from a single preparation of each PbS-polymer composite. The correlation between absorption edge values and PbS particle diameters was made using a theoretical model developed by Wang et al.^{19,49} The PbS cluster agglomeration numbers (n_{PbS}) were calcu-

lated from the spherical particle volume and the volume of a single PbS unit, 53 Å³. Data for PbS clusters within the C₂ polymer are not reported, as a reliable absorption edge could not be determined from the spectrum of this composite. Comparison between n_{PbS} and n_{CdS} values for the same ionomers shows good agreement, which lends further support to the claim that particle sizes are controlled by the size of the ionic multiplet. It seems possible to use a selected polymer host to form nanoparticles of different materials with identical agglomeration numbers, assuming that the nature of the counterion does not significantly affect the size of the multiplet.

Comparison with Aggregation Numbers in Cs-Neutralized Ionomers. Table 1 also lists multiplet aggregation numbers for 14% Cs-neutralized ether ionomers (n_{Cs}), determined from SAXS data by Moore et al. using space-filling calculations.²⁹ Despite differences in ion content and method of preparation, it is still interesting to compare n_{CdS} and n_{PbS} with n_{Cs} , assuming that the CdS and PbS cluster agglomeration numbers correspond to the aggregation numbers of the Cd- and Pb-neutralized multiplets prior to reaction with H₂S. This assumption requires 100% conversion of the metal counterions into the semiconductor clusters. The results for the Cd- and Pb-neutralized C₂-C₁₁ ether series, determined by UV-vis spectroscopy of the semiconductor particles, are within a factor of 2 of SAXS-determined results for the Cs-neutralized samples. It is not surprising that aggregation numbers determined from UV-vis data are generally larger than those determined from SAXS, since, in a distribution of particle sizes, the UV-vis absorption edge corresponds to particles larger than the mean.⁴ SAXS results, on the other hand, are based on the average spacing between scattering centers and therefore reflect average particle sizes. The lower ion percentage in the Cs-

(49) The equation used to calculate PbS cluster diameters was $2R = \exp(0.9587 + 0.09468\lambda^{1/2})$. The number of significant figures shown is that necessary to arrive at the reported results.

neutralized samples will also contribute to lower aggregation numbers with respect to the Cd- and Pb-neutralized ionomers prepared in this study.

Long-Term Stability. To test for long-term stability, the CdS-polymer composites were stored under ambient conditions for a period of 7 months, after which UV-vis spectra were obtained. The absorption edges and associated particles sizes after 7 months are listed in Table 2, along with the original data for the same composites. In most cases, an increase in cluster diameter from 1 to 3 Å was observed, possibly due to long-term ripening under ambient conditions.

Conclusions

This investigation has shown that size control of semiconducting clusters can be achieved through a knowledge of primary multiplet aggregation numbers in the host ionomer. A linear relationship between the ionomer side-chain length and the resulting CdS particle diameter has been shown, along with excellent agreement between values of n_{CdS} and n_{PbS} determined independently for the same ionomers. Agreement between n_{CdS} values determined by UV-vis and SAXS data was found for the C₁₁ ionomer. TEM results show CdS particles evenly dispersed in the polymer matrix. We believe that CdS or PbS particle formation is restricted to the ionic multiplets of the polymer host, such that multiplet size is the limiting factor in cluster growth. In random ionomers, the multiplet sizes can

be controlled by varying the length of the ionomer side chain, with longer side chains resulting in larger multiplets and thus larger semiconducting particles. With an understanding of the relationship between ionomer structure and morphology, the use of predictable multiplet sizes to control the sizes of nanoparticles within ionomers may have the advantages of precision and convenience over other methods of size control, such as controlling the initial ion concentration and/or thermal annealing of particles following precipitation.^{19,20} This method of size control, of course, is not limited to semiconducting clusters, and other types of nanoparticles (e.g., magnetic, catalytic, etc.) within random ionomer aggregates are also conceivable.

The present paper has shown size control in the narrow range of 18–23 Å using random ionomers of various side chain lengths. The following publication will deal with larger semiconducting clusters in the larger aggregates of diblock ionomers.

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