The Enzymatic Synthesis of Thiol-Containing Polymers to Prepare Polymer−CdS Nanocomposites

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Thiol-containing polyphenolics are enzymatically synthesized in the microstructured environment of reversed micelles. CdS semiconductor nanocrystallites, also synthesized in the water pools of reversed micelles, are then attached to these polymers through binding to the sulfhydryl groups. The polymer−CdS nanocomposite thus prepared exhibits luminescence characteristic of such quantum dot particles. Passivation of the CdS by the polymer suppresses low-energy emissions associated with surface recombinations, while slightly enhancing higher energy emissions resulting from the recombinations in the excitonic state of the crystallite interior. The polymer−CdS complex is stable in solution, and the solid form can be obtained in the morphology of microspheres.

Introduction

Nanometer-size semiconductor particles are of particular interest because of their size-dependent photophysical, photochemical, and nonlinear optical properties.,[1−3] In contrast to the bulk solid, such quantum dot particles exhibit quantum effects that arise from the spatial confinement of photogenerated charge carriers. Quantum dot particles exhibit structured absorption and emission with energies characteristic of particle size.[4−6] Typically, such semiconductor colloids also have a high density of surface defect sites.[7] The sites cover a broad range of energies and structures with many defect states existing at midbandgap energies. The surface defects are involved in trapping initially produced electron−hole pairs, as shown by the fact that emission is significantly red-shifted from the absorption edge. The existence of different trap states provides multiple pathways for radiative and nonradiative recombination.

Quantum state particles have a tendency to associate because of their large surface-to-volume ratio. To overcome the problem, various strategies of nanoparticle preparation and size control have been investigated. These include encapsulation in sol−gels[8] and in polymer matrixes[9] and the use of organic capping agents.[10] Among them, it is believed that chemical modification with organic reagents such as thiols is a useful preparation technique that inhibits particle aggregation, improves suspension stability, and results in new surface functionalities.[11] On capping with thiols, the weak sulfhydryl bond is replaced with a bond between sulfur and surface cadmium ions. The capping can lead to surface passivation by the annealing of surface defects.[12]

In this paper, we report the synthesis and properties of sulfhydryl group containing polymer that can be used to bind CdS thus resulting in a polymer−semiconductor nanocomposite. The monomer used is 4-hydroxythiophenol and we report the synthesis of copolymers of 4-hydroxythiophenol and an alkyl-substituted phenol, 4-ethylphenol. The polymer synthesis is carried out enzymatically using an oxidative enzyme, horseradish peroxidase. Enzyme-catalyzed phenol polymerizations have been previously shown to be feasible in monophasic organic solvents.[13,14] The novelty of the present work is the synthesis of thiol-substituted polyphenols and the synthesis medium which is the microstructured environment of water-in-oil microemulsions, or reversed micelles as they are often called. This micellar environment is ideally suited for the enzymatic synthesis of water-insoluble polymers. The organic phase helps sustain solubility of the monomer (and growing chain), while the microaqueous phase solubilizes the enzyme

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with full retention of catalytic activity. In this paper, we therefore report the feasibility of preparing polymers in reversed micelles, the morphology of such polymers, and the attachment of CdS nanoparticles to the polymer. The micellar environment can be used to synthesize both the polymer and the CdS nanoparticles. We report the steady-state luminescence characteristics of these interesting polymer−semiconductor nanocomposites.

Materials and Methods

The enzyme peroxidase (type II, from horseradish), the buffer HEPES [*N*-(2-hydroxyethyl)piperazine-*N*′-(2-ethanesulfonic acid)], and hydrogen peroxide, were purchased from Sigma Chemicals, St. Louis, MO. The monomers, 4-ethylphenol (EP), 4-hydroxythiophenol (HTP), the anionic surfactant bis(2-ethylhexyl)sodium sulfosuccinate (AOT), were all obtained from Aldrich Chemical Co. (Milwaukee, WI). The solvent isooctane (ACS reagent grade) was also obtained from Aldrich.

Polymer−CdS Synthesis. While both the polymer and CdS are synthesized in reversed micelles, the fact that Cd^{2+} deactivates horseradish peroxidase necessitates synthesis in separate micellar systems. The procedure used in polymer synthesis was a simple variation of our earlier procedure.[15] Essentially, the monomers were dissolved in a water-free reversed micellar solution containing 0.5 M of the anionic surfactant AOT (bis(2-ethylhexyl)sodium sulfosuccinate) in isooctane. The total monomer concentration was fixed at 0.15 M. To this solution, the required volume of enzyme-containing HEPES buffer was added to bring the water content to a w_0 value of 15 (w_0 is the water-to-surfactant molar ratio). The enzyme level in the buffer was adjusted so that the final enzyme concentration in the overall solution was 0.5 mg/mL.

Polymerization was initiated with the addition (in aliquots) of the stoichiometric amount of hydrogen peroxide required for complete monomer conversion (0.15 M). The initially clear solution becomes dark almost immediately and polymer begins to precipitate. Although most of the monomer conversion is completed within 10−15 min of reaction initiation, the solution was stirred for 24 h. The polymer was recovered, washed repeatedly with isooctane to remove adsorbed surfactant and air-dried.

CdS nanoparticles were synthesized in reversed micelles following standard procedures, using an 0.5 M AOT concentration level.[16] A 2:1 ratio of Cd^{2+} containing micelles (from $CdCl_2$ dissolved in the water pools) mixed with S^{2-} containing micelles (from Na_2S dissolved in the water pools) yields CdS with surface-enriched Cd^{2+}. The w_0 for synthesis was adjusted to 5 to yield CdS particles of diameter 2−3 nm.[17] The CdS containing reversed micellar solution was then dried to a residue containing CdS and AOT.

To prepare the composite, the polymer was dissolved in dimethyl sulfoxide (DMSO). The CdS + AOT was also dispersed into this solution resulting in CdS attachment to the polymer thiol groups. The solvent was then removed by evaporation in a vacuum oven at room temperature, and the residue washed with isooctane. The CdS that is not covalently linked to the isooctane-insoluble polymer becomes resuspended with AOT in the isooctane wash. After repeated washing with isooctane, much of the CdS not covalently attached to the polymer is removed. The isooctane wash also removes the AOT that is adsorbed to the polymer. The residue, which is now the polymer−CdS complex, with CdS covalently attached to the polymer, was recovered, dried, and stored for further characterization.

Characterization. The morphologies of the polymer and the polymer−CdS nanocomposite were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). For SEM analysis, a small amount of the solid polymer or the composite was dispersed in isooctane. A drop of this suspension was placed on an aluminum stub and allowed to dry at room temperature. The stub was then coated, first with 20 nm thickness carbon black and then with gold. The micrograph was taken at an accleration voltage of 15−30 kV in a JEOL JSM-820 scanning electron . For TEM analysis, a Philips 410 transmission electron microscope with a LaB_6 (lanthanum hexaboride) crystal electron source was used. The polymer containing CdS was dissolved in DMSO, and a drop of the solution was placed on a carbon coated copper grid and the grid was left to dry for a few minutes before transferring into the TEM sample chamber. Micrographs were taken at an acceleration voltage of 80 kV.

Molecular weight distributions of the polymers were measured using gel permeation chromatography (GPC). The setup consisted of a 25 cm Jordi Gel DVB mixed bed columnm a Perkin-Elmer biocompatible binary pump (Model 250) and a Perkin-Elmer diode array detector (model 235) interfaced with a personal computer. The eluent was THF, and the column operated under the eluent head pressure adjusted to maintain a flow rate of 0.75 mL/min. The dry polymer was dissolved in THF at a concentration of 0.1% (w/v) and 20 μL of this solution was used for the measurements. Polystyrene samples in the molecular weight range of 600−200 000 were used as calibration standards.

An ATI-Mattson Galaxy 6021 FTIR spectrometer was used for FTIR measurements. A liquid sample cell (SpectraTech) with CaF_2 windows and path length 0.3 mm was used to measure liquid samples. KBr pellets made from a 1% (by weight) polymer/KBr mixture was used to record polymer spectra. The UV−vis spectra of the polymers and copolymers were recored using a Shimadzu UV-160 spectrophotometer. The fluorescence spectra were recorded using a Perkin-Elmer luminescence spectrophotometer (LB-50) equipped with a Xe lamp as the excitation source. The emission slit was kept at 10 nm resolution in all measurements.

A Perkin-Elmer atomic absorption spectrometer, fitted with a Cd lamp was used to determine cadmium loading in the polymer−CdS complex. the complex (0.01 g) was dissolved in 1 mL of DMSO. To this solution, 25 μL of concentrated HCl was added to ensure complete solubility of CdS. The above solution was diluted with water to a concentration of 0.1 mg composite/mL solution. The absorption of this solution at 322 nm was used to determine the Cd concentration from a standard calibration curve. The instrument absorbance was autozeroed using the DMSO/water blank.

Results and Discussion

General Characteristics of Polymerization. The monomers used and the structure of the anionic surfactant AOT are shown in Figure 1. Peroxidase-catalyzed polyphenol synthesis follows reaction mechanisms similar to those involved in biological lignin synthesis.[18] Phenoxy radical centers delocalize onto the ortho positions from which coupling occurs. The heme group of the enzyme (HRP) undergoes 2-electron redox reactions during monomer coupling.[19] The overall condensation reaction can be written as

$$(R1)H + (R2)H + H_2O_2 \rightarrow R1{-}R2 + 2H_2O$$

where (R1)H and (R2)H are the phenolic monomers or oligomers. The direct ring-to-ring attachment generates a conjugated polymer in contrast to the more conventional phenol−formaldehyde resins. Thus, enzymati-

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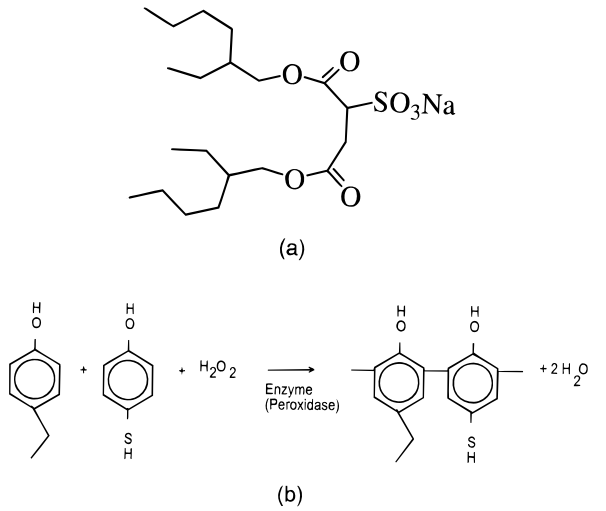

Figure 1. (a) Structure of the anionic surfactant AOT, bis-(2-ethylhexyl)sodium sulfosuccinate. (b) A simplified schematic of the coupling between 4-ethylphenol and 4-hydroxythiophenol.

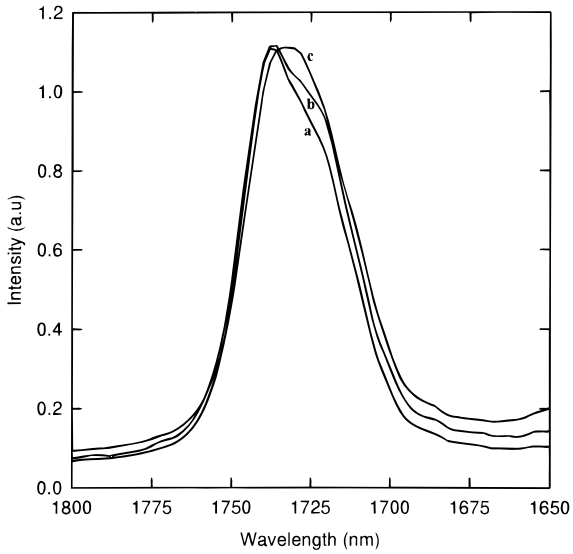

Figure 2. FTIR of AOT C═O vibrations in reversed micelles as perturbed by the monomers 4-ethylphenol and 4-hydroxythiophenol. (a) 0.5 M AOT/isooctane micelles with $w_0 = 5$. (b) Solution (a) with addition of 0.15 M 4-ethylphenol. (c) Solution (a) with addition of 0.15 M 4-hydroxythiophenol.

cally synthesized polyphenols are of interest for their electrooptical properties.[20]

An interesting characteristic of enzymatic polyphenol synthesis in reversed micelles is the observation of monomer−surfactant interactions and the possible partitioning of the monomer to the oil−water interface. Evidence of monomer access to the micellar interface is usually seen through IR evidence of perturbations to AOT headgroup vibrational frequencies as a result of AOT−phenol hydrogen bonding.[21] Figure 2 illustrates the shift of AOT C═O vibrations to lower frequency, upon the addition of the two monomers 4-ethylphenol and 4-hydroxythiophenol to AOT reversed micelles. We also note in this case, that the monomer, 4-ethylphenol

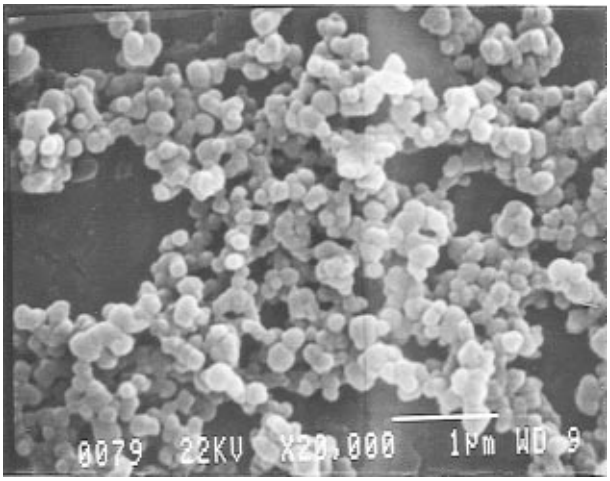

Figure 3. Scanning electron micrograph of copoly(4-ethylphenol/4-hydroxythiophenol) with a 1:1 monomer ratio. The spherical morphology is obtained with up to 60% 4-hydroxythiophenol monomer content. At higher levels of 4-hydroxythiophenol, the morphology is lost and the polymer becomes insoluble.

is virtually insoluble in water but highly soluble in isooctane. On the other hand 4-hydroxythiophenol is very sparingly soluble in isooctane, but its solubility is considerably increased by the addition of AOT and water. The micellar system therefore offers a method to bring mutually incompatible monomers together to the vicinity of the enzyme located in the microaqueous pools. The IR data also indicate that 4-hydroxythiophenol perturbs AOT C═O vibrations significantly more than 4-ethylphenol, perhaps implying stronger hydrogen bonding to AOT.

Polymerization is very rapid and within a few minutes, most of the conversion is complete. The polymer formed precipitates out of the solution and is collected, dried, and analyzed. As stated in the earlier section, the pure polymer from 4-hydroxythiophenol is an insoluble, intractable material and was not studied further. Copolymers from 4-ethylphenol and 4-hydroxythiophenol have been synthesized and characterized. Figure 3 illustrates the microspherical morphology obtained through synthesis in reversed micelles. The microsphere morphology is obtained reproduceably with a 3/1 AOT/monomer ratio in agreement with our earlier work with pure 4-ethylphenol polymers.[15] With the copolymers studied here, the microsphere morphology is obtained as long as the 4-hydroxythiophenol content is less than about 60% of the total monomer content. At these compositions, the copolymer and its composites with CdS are fully soluble in a variety of polar organic solvents. The implication here is that the incorporation of 4-ethylphenol into the system separates 4-hydroxythiophenol monomers during synthesis and thereby minimizes disulfide bridging.

While the microsphere morphology is observed with the synthesized copolymer, it is noted that the method of CdS attachment involves dissolving the copolymer in DMSO containing dispersed CdS, as described earlier. This procedure destroys the microsphere morphology of the nanocomposite. The microspheres can be regenerated by dissolving the nanocomposite in a polar solvent (e.g., acetone), followed by reprecipitation using an excess of an AOT−isooctane reversed micellar solution

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Table 1. Copolymer Molecular Weight and CdS Content as a Function of Monomer Composition[a]

monomer composition (% 4-hydroxythiophenol)	M_n	M_w	polydispersity (M_n/M_w)	CdS content in polymer (wt%)
0%	1650	2300	1.4	0
10%	1750	2550	1.5	3.2
30%	2500	3490	1.4	5.4
50%	4390	10775	2.2	7.2

[a] The copolymer molecular weights were measured prior to attachment of CdS.

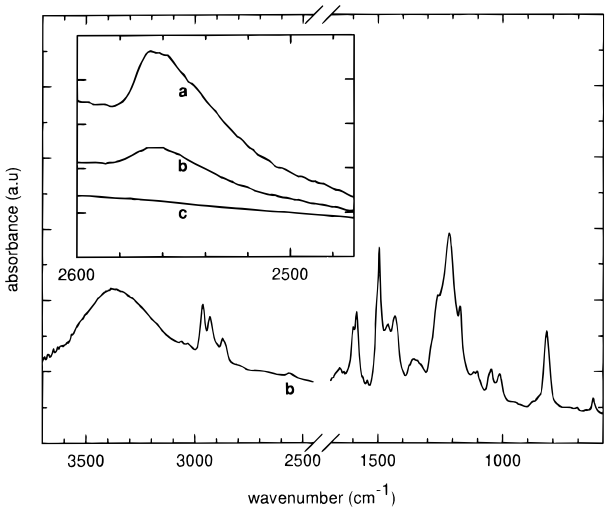

Figure 4. FTIR spectra of copoly(4-ethylphenol/4-hydroxythiophenol) prepared with an equimolar concentration of monomers. The S−H stretch is the small feature at 2560 cm^{-1}. The inset shows the expanded region. In the inset (a) illustrates the S−H stretch of the monomer 4-hydroxythiophenol, (b) the S−H stretch of the copolymer and (c) the lack of an S−H stretch when CdS is attached to the copolymer. These are solid-state IR samples prepared in a KBr pellet.

which is a nonsolvent for the composite.[22] It is also possible to attach CdS to the copolymer by reprecipitating the copolymer using CdS-containing micellar solutions. The use of the reversed micellar medium as a nonsolvent for presynthesized polyphenolics, the generation of microspheres, and the encapsulation of intramicellar solutes in the polymer matrix are described in detail in another paper.[22]

Table 1 lists the molecular weight data for the copolymers, and it is seen that the peak molecular weight shows a consistent increase with the 4-hydroxythiophenol monomer content. From oligomers with approximately 13 units (pure 4-ethylphenol monomer), the molecular weight increases to about 35 units when the 4-hydroxythiophenol content is increased to 50% total monomer. Additionally, the polydispersity index increases at 50% 4-hydroxythiophenol content. The table also lists saturation CdS contents of the composites synthesized from these copolymers indicating the increase in loading with an increase in the 4-hydroxythiophenol level. Evidence of CdS binding to the polymer is further shown by the inset to the FTIR spectra of Figure 4, where the weak band at 2560 cm^{-1} is attributed to the vibrations of the S−H bond. Curve (a) of the inset shows the S−H stretch for the monomer, 4-hydroxythiophenol, while curve (b) represents the

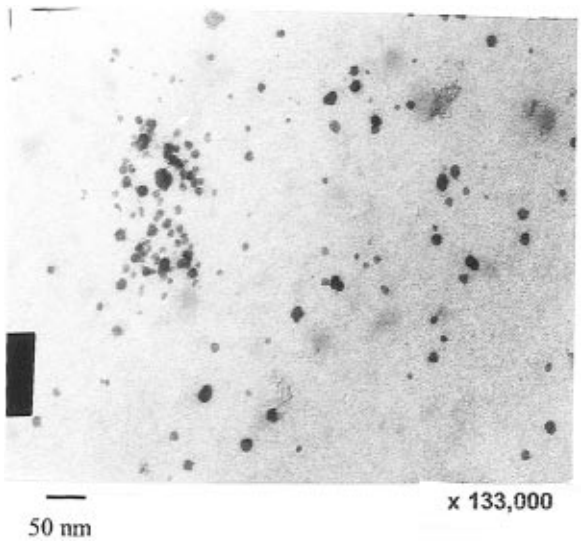

Figure 5. Transmission electron micrograph of CdS in polymer−CdS complex. The copolymer was prepared with a 1:1 concentration of 4-hydroxythiophenol and 4-ethylphenol.

copolymer prior to CdS attachment. The loss of this absorbance in curve (c) for the polymer−CdS complex is indirect evidence of CdS attachment at the copolymer thiol groups. The loss of the S−H stretch upon functionalization was first reported by Torimoto et al.[23] in their study of PbS attachment to 4-hydroxythiophenol. The present study implies that there is retention of thiol functionality upon enzymatic copolymer synthesis, and that CdS nanoparticles bind to these thiol groups. Figure 4 also illustrates the essential phenolic nature of the polymer through retention of the hydroxyl stretch band between 3100 and 3500 cm^{-1}. We also examined the ^{1}H NMR of the polymer−CdS complex, but the structural information is limited because of the broad and unresolved peaks in the aromatic region, typical of macromolecular species.

A transmission electron micrograph (TEM) of the polymer−CdS nanocomposite is shown in Figure 5 with the dark patches representing CdS particles (or particle agglomerates). The TEM shows sizes ranging from less than 5 nm to about 30 nm, with the vast majority of the particles below 20 nm. There appears to be a region with a high density of particles, but this region is not representative of CdS attached to a single polymer chain. Copolymer chains with 10−30 units represent end-to-end chain lengths of 5−12 nm. Thus, the CdS particle size is comparable to the length of the polymer chain. Let us consider a simple calculation with a copolymer chain 20 units long assuming a 1/1 distribution of the two monomers alternating on the chain. In a polar solvent, the chain adopts an open structure since segment−solvent interactions dominate over the intramolecular hydrogen bonding responsible for chain folding and curvature.[22] In such an open structure, a 20-unit copolymer chain has an extended length of 7.4 nm with the thiol groups separated by 0.74 nm (calculated using the HyperChem Molecular Modeling Software). Assuming a CdS particle size of 3 nm, the picture of the nanocomposite is one where there are just two or three CdS nanoparticles attached to a chain at

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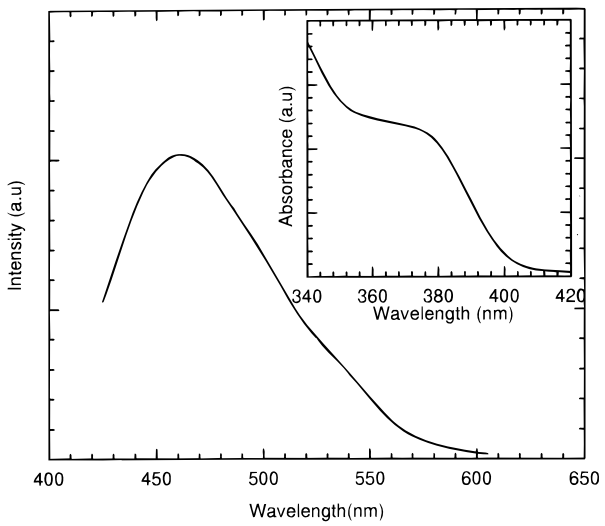

Figure 6. The emission spectra of copoly(50% 4-ethylphenol/50% 4-hydroxythiophenol)−CdS complex with excitation at 400 nm. The inset shows the corresponding absorbance spectra. The CdS particles here were first synthesized in w_0 5 micelles. Emission spectra obtained in chloroform.

most. It is also possible that chains could be bridged by being bound to the same CdS particle, and a multiplicity of such bridged chains and particles could lead to the particle clustering. GPC measurements of the polymer molecular weight after CdS attachment show a small (about 100 Da) but consistent increase in the peak molecular weight. This may simply be a result of changing GPC elution characteristics upon CdS attachment and is not necessarily indicative of chain bridging.

Absorbance and Fluorescence Properties. The fluorescence spectrum for a copolymer−CdS complex is shown in Figure 6, with excitation at 400 nm. The corresponding absorbance spectrum is shown in the inset to the figure. The CdS nanoparticles were synthesized in reversed micelles of w_0 5 prior to capping with the copolymer. The CdS absorption edge of 400 nm is virtually unchanged upon capping. The particle size of the nanocrystals was calculated from the absorption edge to be 3 nm.[24] An interesting observation regarding the stability of CdS in the complex is the retention of the absorption spectrum upon extended storage in the absence of light. In contrast to uncapped CdS where Ostwald ripening effects are seen upon extended storage,[25] there is no red-shift in the absorption edge that would indicate particle growth. Such stabilization to agglomeration is a general phenomena of CdS and PbS capping by thiol-based compounds.[23]

The emission spectrum of Figure 6 is rather interesting as it exclusively shows a peak at 470 nm. CdS nanoparticles typically have two characteristic emissions, one at 540 and the other at 470 nm.[25,26] The emission at 540 nm is assigned to hole−electron recombinations at surface traps, while the higher energy emission at 470 nm near the band edge is attributed to recombination from the excitonic state in the crystallite interior.[27,28] To understand whether there is indeed a quenching of the low-energy fluorescence upon nanoparticle capping with the copolymer, the following experiment was carried out, the results of which are shown in Figure 7. Here, CdS nanoparticles were prepared in reversed micelles, following which the micellar system was completely dried leaving a CdS + AOT residue. This residue was then redispersed in chloroform and the fluorescence spectrum taken (spectrum a). The fluorescence shows typical CdS emission characteristics with a broad emission maximum extending from 470 to 540 nm. Copoly(4-ethylphenol, 50%/4-hydroxythiophenol, 50%) was then dissolved into the solution. An immediate quenching of the low-energy fluorescence is observed (spectrum b) with a small increase in the high-energy emission. The observed overall decrease in quantum yield is indicative of nonradiative pathways introduced through such surface passivation and capping. The selective quenching of the 540 nm emission has been observed by others upon addition of mercaptopyridines[26] and methylviologen.[29,30] These earlier studies attributed such selective quenching to the destruction of surface trap states through electron capture by the capping organic compound which acts as an electron acceptor.[26] Similar mechanisms may be operational here. Verification that the blue-shift is due to the 4-hydroxythiophenol content of the copolymer is obtained by adding pure poly(4-ethylphenol) rather than the copolymer (spectrum c). While there is some quenching of fluorescence, there is little change in the fluorescence maximum. The apparent quenching may be simply due to polymer self-absorbance at the excitation wavelength (400 nm).

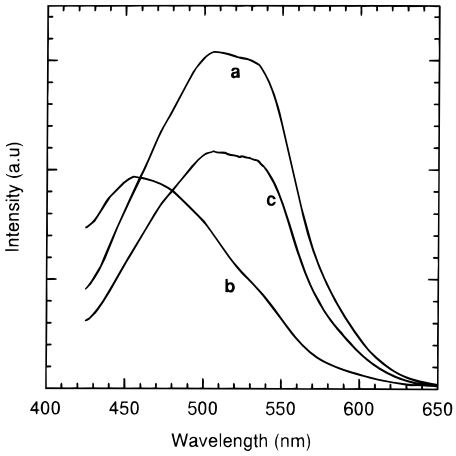

Figure 7. Emission spectra of (a) 2×10^{-4} M CdS ($Cd^{2+}/S^{2-} = 2$) prepared in reversed micelles dried, and redispersed in chloroform (b) sample (a) with addition of 0.012 mg/mL copoly-(50% 4-ethylphenol/50% 4-hydroxythiophenol) (c) sample (a) with addition of 0.012 mg/mL poly(4-ethylphenol). Excitation at 400 nm.

Finally, Figure 8 illustrates the emission characteristics of copolymer−CdS complexes containing various levels of 4-hydroxythiophenol. As intuitively expected, the fluorescence intensity increases with the 4-hydroxythiophenol content of the copolymer. The data are

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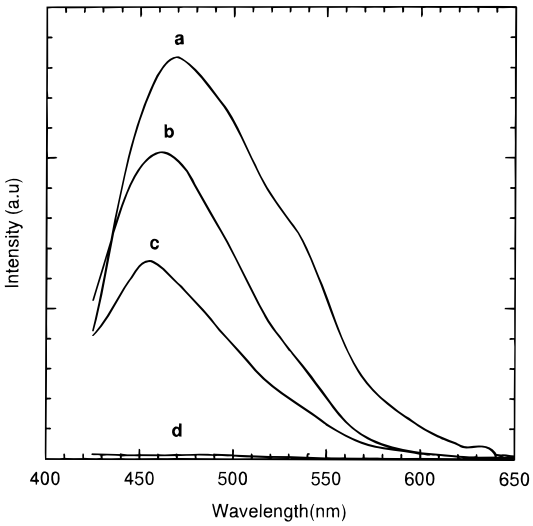

Figure 8. Fluorescence emission spectra of CdS from complexes containing (a) copoly (50% 4-ethylphenol/50% 4-hydroxythiophenol) (b) copoly(70% 4-ethylphenol/30% 4-hydroxythiophenol) (c) copoly (90% 4-ethylphenol/10% 4-hydroxythiophenol). (d) copoly(70% 4-ethylphenol/30% 4-hydroxythiophenol) but without CdS. Emission spectra obtained in chloroform with excitation at 400 nm. Saturation loadings of CdS used in all samples.

consistent with the observation that the saturation CdS loadings on the polymer increase with the 4-hydroxythiophenol content (Table 1). There is a small red-shift in the emission with increasing CdS loading and at the highest loading (spectrum a) a distinct shoulder is observed at 540 nm indicative of surface recombinations. Spectrum (d) is the polymer of spectrum (a) but without CdS, which verifies that the polymer has no intrinsic fluorescence when excited at 400 nm.

Conclusions

This work demonstrates a biocatalytic approach to synthesize polymers that can be formulated into photoluminescent composites by the attachment of semiconductor nanoparticles. We note that the micellar environment, while convenient for the synthesis of CdS nanoparticles, is not the best environment to synthesize monodispersed nanoclusters, and there are much superior synthetic routes to monodisperse II−VI semiconductor nanoparticles.[31] Regardless of how the semiconductor component is prepared, the task addressed here is the synthesis of the thiol-containing polymer, and this seems to be well-suited to the micellar environment. Once the polymer is synthesized, attachment of the semiconductor component is straightforward. The resulting nanocomposite is highly processible and can be fabricated into films, coatings, etc. An interesting aspect of polymer synthesis in reversed micelles is the observation that polymer microspheres can be generated implying an ease of dispersion in coatings applications. The complex displays the fluorescence characteristics of CdS but without the low-energy emissions associated with surface recombinations. The polymer thus caps and passivates the CdS nanoparticles. The complex is easily soluble in polar organic solvents. It is indefinitely stable in solution both in its solubility characteristics and in its luminescent properties.

Continuing studies seek to expand the application potential of these polymer−CdS nanocomposites. Due to conjugation in the polymer, these materials may be electroluminescent with consequent applications in sensor and display technologies. The conjugated polymer−CdS complex may also have applications in nonlinear optics as both components should have high third-order nonlinear susceptibilities. From another perspective, the hydroxyl groups present on the polymer imply ease in functionalization. For example, it is possible to attach affinity ligands to the polymer leading to further application in biosensor technologies. These materials may therefore represent a new class of polymer−inorganic composites with useful fluorescent properties.

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