Nitroxide-Mediated Radical Polymerization from CdSe Nanoparticles

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We report the use of nitroxide-mediated controlled free radical polymerization directly from the surface of CdSe nanoparticles to prepare polymer−nanoparticle composite materials. While free radicals can quench the fluorescence of CdSe nanoparticles, nitroxide-mediated polymerization allows for the preparation of the desired polymer−nanoparticle composites while maintaining the inherent fluorescence of the nanoparticles. The low concentration of radicals inherent to this controlled free radical polymerization technique contributes to the success of this process. Nitroxide-containing ligand **2** was prepared for this study and used to functionalize 3−4-nm CdSe nanoparticles. By this method, polystyrene and poly(styrene-*r*-methyl methacrylate) copolymers were grown from the nanoparticle surface. Displacement of these polymers from the surface, and subsequent analysis by gel permeation chromatography (GPC), revealed the success of this method. The effect of the polymerization conditions on dispersion and fluorescence of the nanoparticles is described.

Introduction

Targets in nanotechnology include assemblies and structures in the nanometer size regime that cannot presently be accessed by top-down lithographic methods. Precise nanoscopic assemblies hold exceptional promise in a number of applications, including sensors, data storage, light-emitting diodes, single-molecule transistors, and substrates for biological tags and detection devices.[1−6] Semiconductor nanoparticles are candidate materials for all of these applications due to the unique electronic and optical properties that result from their nanometer size, and the low size distribution in which they can be produced. Cadmium selenide nanoparticles, or quantum dots, are especially promising as current synthetic methods give high-quality samples with low size distribution and narrow photoluminescence emission profiles that shift predictably with size.[7−9]

The processability, shelf life stability, and relevant applications of quantum dots depend on the nature of the ligand periphery. The extent to which this periphery can be tuned to meet the requirements of specific platforms will determine their ultimate applicability. We have previously reported the preparation of polyolefin[10] as well as PEGylated[11] CdSe nanoparticles, where graft-from and graft-to strategies, respectively, were used to attach the polymers to the nanoparticles. It would be very useful to expand the scope of polymeric ligand coverage on CdSe nanoparticles to conventional chain-growth polymers such as polystyrene (PS) and poly(methyl methacrylate) (PMMA). However, the typical methods used to prepare these polymers are not compatible with the nanoparticle itself. Anionic conditions are too severe to be used in the presence of the quantum dots, and radicals generated by conventional radical polymerization (e.g., azo-bisisobutyronitrile (AIBN) initiated) degrade the nanoparticle and quench its photoluminescence.

Advances in controlled radical polymerization are proving very useful for grafting-from particle surfaces. For example, Hawker and co-workers, as well as Beyou and co-workers, have demonstrated the use of nitroxide-mediated polymerization of styrenic and/or maleic anhydride monomers from the surface of SiO_2 particles,[12,13] while Sogah and co-workers have successfully polymerized styrene from nitroxides anchored to silicate sheets.[14] Recently, Takahara and co-workers have shown the utility of a phosphonic acid-functionalized nitroxide for growth of polystyrene from magnetite nanoparticles.[15] In the area of semiconductor nanoparticles,

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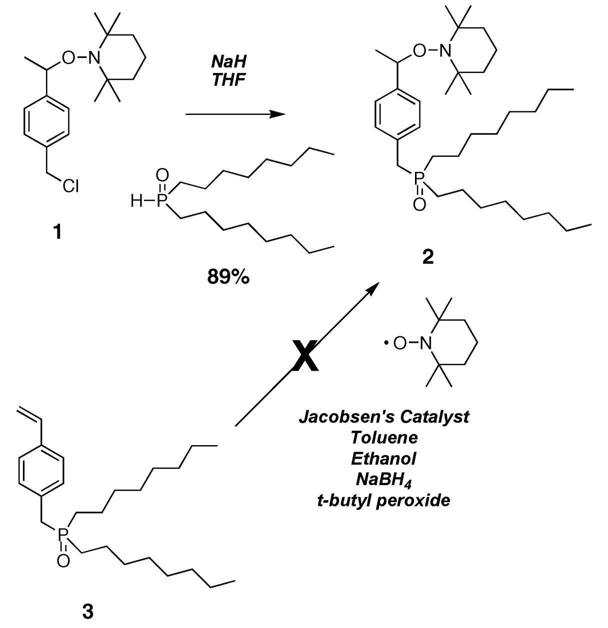
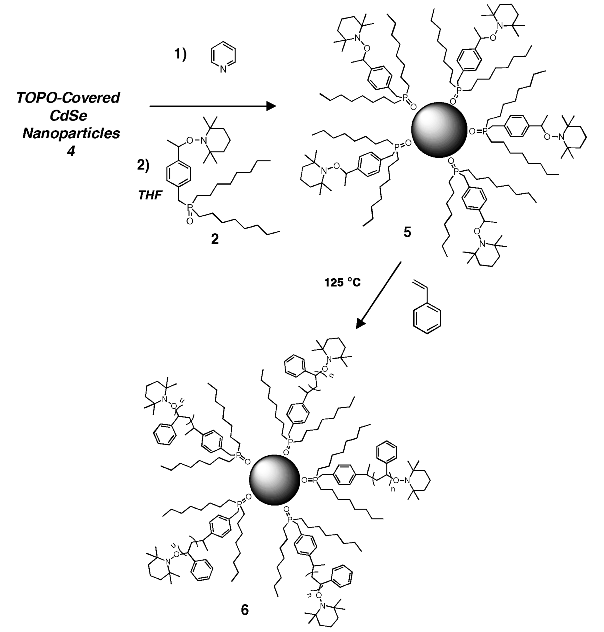
10.1021/cm035077b CCC: $27.50

Scheme 1. Synthesis of TEMPO-Functionalized Ligand 2



Scheme 2. Ligand Exchange and Polymerization from Nitroxide-Functionalized CdSe Nanoparticles 5



Patten and co-workers have shown that by encapsulating CdS quantum dots in a silica shell, atom transfer radical polymerization (ATRP) of methyl methacrylate is possible from the core–shell nanoparticle.[16,17] However, it would be useful to use "unprotected" quantum dots as substrates for this grafting polymerization, as this would eliminate the extra steps required for the core–shell synthesis and provide an intimate connection of the polymer to the nanoparticle core. As a first step in this process, we chose to investigate controlled nitroxide-mediated polymerization from CdSe nanoparticles, as the low concentration of free radicals inherent to this method suggests the potential compatibility of this method with quantum dots. In addition, the diverse chemistries and architectures recently reported for controlled nitroxide-mediated polymerization[18] make this an especially attractive target.

Results and Discussion

CdSe nanoparticles functionalized with phosphine oxide derivative **2** served as the key precursor in these graft-from polymerization studies. Ligand **2** was prepared as shown in Scheme 1. 2,2,6,6-Tetramethylpiperidinyloxy (TEMPO)-modified benzyl chloride **1**, originally reported by Hawker and co-workers,[19] was prepared and purified by column chromatography and then recrystallized from acetone:2-propanol:water mixtures to give a white powder. Reaction of **1** with di-*n*-octyl phosphine oxide and NaH in THF gave the target ligand **2** in 89% yield. This approach proved superior to our initial attempts to functionalize phosphine oxide **3**,[10] which led to an inseparable mixture of products and residual catalyst.

Tri-*n*-octylphosphine oxide (TOPO)-covered CdSe nanoparticles **4** were prepared according to reported procedures[20] and then functionalized with **2** by ligand exchange (Scheme 2) in THF, followed by removal of THF and addition of methanol. These nitroxide functionalized nanoparticles were stored as solutions under nitrogen atmosphere at −20 °C. These storage conditions prevented homolytic cleavage of the ligand that gives the nitroxide free radical and a benzyl radical. Free radicals lead to degradation of CdSe nanoparticles, as evidenced by blue shifts in the fluorescence spectrum. The ^{31}P NMR spectrum of **2**-functionalized nanoparticles showed one resonance at δ 48.1 ppm, corresponding to the phosphine oxide of the ligand; no TOPO phosphorus was observed. The ^{1}H NMR spectrum is in accord with the ligand structure, and no resonances for pyridine or TOPO were observed. The UV–vis and fluorescence spectra of **2**-functionalized CdSe nanoparticles were comparable to those of the original TOPO-covered batch, indicating an effective ligand exchange process.

Both solution and bulk polymerization methods were utilized to grow polystyrene from **2**-functionalized nanoparticles. Solution polymerization was conducted in *o*-xylene at 125 °C for 48 h to give an 80% monomer conversion. Bulk polymerizations were performed in neat styrene solutions of nitroxide-covered nanoparticles (5−20 mg/mL) by heating to 125 °C for about 24 h; monomer conversions were greater than 90%. Random copolymers of styrene and methyl methacrylate were prepared in the bulk in similar fashion. The molecular weights and polydispersity indices (PDI) of the grafted polymers and copolymers grown from the nanoparticles were analyzed by GPC. This required a degradation of the nanoparticles prior to analysis, achieved by stirring

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Table 1. Molecular Weights and Compositions of Polymers Grafted from CdSe Nanoparticles[a]

		feed ratio		incorporation	
M_n	PDI	% styrene	% MMA	% styrene	% MMA
13400	1.29	100		100	
22600	1.35	100		100	
75500	1.34	100		100	
125900	1.76	100		100	
56800	1.46	80	20	78	22
27500	1.44	70	30	73	27
47400	1.40	60	40	60	40
108000	1.76	50	50	56	44
103000	2.00	40	60	45	55

[a] Molecular weight and distribution were determined by GPC. Monomer incorporation was determined by ^{1}H NMR. Styrene polymerizations were run for 24 h, while copolymers were polymerized for 18 h with a constant molar amount of monomer.

the composite material in a THF solution of *N*,*N*-dimethylaminopyridine (DMAP). Polymerizations performed in the bulk gave polystyrene molecular weights in the range of 20−130 K, while lower molecular weights were accessed by solution polymerization. Polydispersity indices for the polymers obtained ranged from 1.25 for lower molecular weight polymers to 1.8 for samples approaching 130000 g/mol (Table 1). Loss of control in the higher molecular weight regime is expected in nitroxide-mediated polymerization in the absence of added excess TEMPO and at high monomer conversion.[21] Random copolymers of styrene and methyl methacrylate (MMA) were prepared by bulk polymerization methods. Incorporation of MMA was varied between 10 and 60% over a range of molecular weights.

The graft-from method used here provides uniform dispersion of the nanoparticles in the polystyrene matrix, as shown by the TEM micrographs in Figure 1. This uniform dispersion was achieved for all PS graft molecular weights studied. Interestingly, the fluorescence spectra recorded on chloroform solutions of PS−CdSe composites showed an order of magnitude increase in intensity when compared to the nitroxide-functionalized nanoparticles (Figure 2). Quantum yields relative to Rhodamine 6G in ethanol ranged from 3% to 8% in $CHCl_3$, a substantial increase over the average value of 0.4% obtained for the nitroxide-covered particles **5**, though no trend in photoluminescence intensity with molecular weight was observed. In addition, no significant blue shift in the fluorescence maxima was observed in the PS−CdSe composites relative to the starting nitroxide-initiator functionalized CdSe. This illustrates the utility of the controlled free-radical method, as the use of AIBN or benzoyl peroxide to initiate polymerization of styrene in the presence of CdSe nanoparticles gave uncontrolled molecular weights and polydispersities and caused degradation of the nanoparticles within minutes. For example, in an experiment where 1 mg of AIBN or benzoyl peroxide was added to a solution of TOPO-covered CdSe nanoparticles in benzene, followed by stirring at 70 °C, the originally red nanoparticle solution became yellow, and then colorless, over a period of 15 min, suggesting complete nanoparticle degradation. Obviously, no fluorescence emission or UV-band edge absorption remained following this degradation.

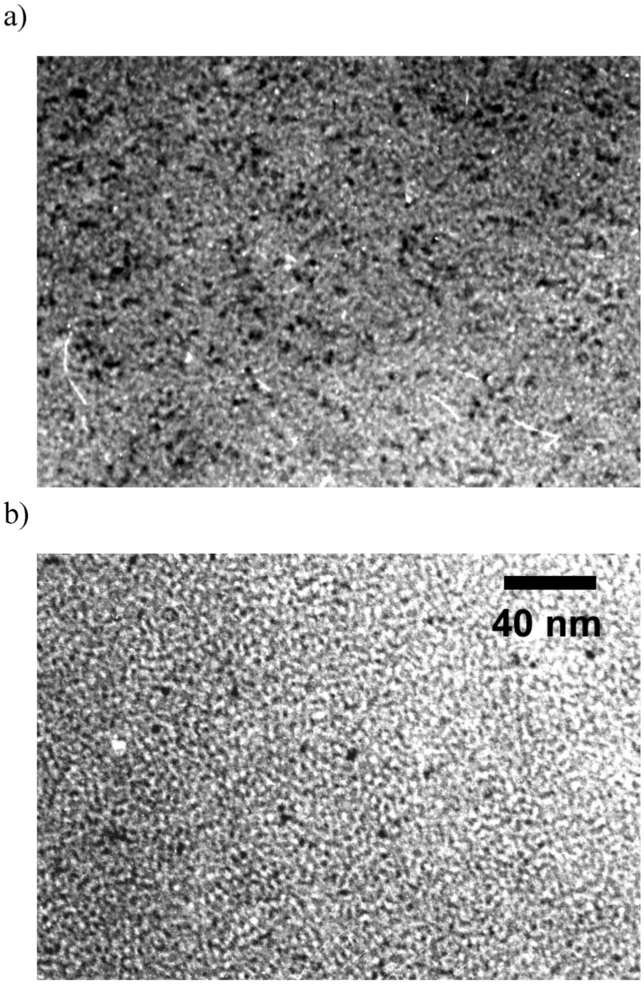

Figure 1. TEM micrographs showing (a) polystyrene-covered CdSe nanoparticles **6** and (b) polystyrene-covered CdSe nanoparticles **6** in a polystyrene matrix.

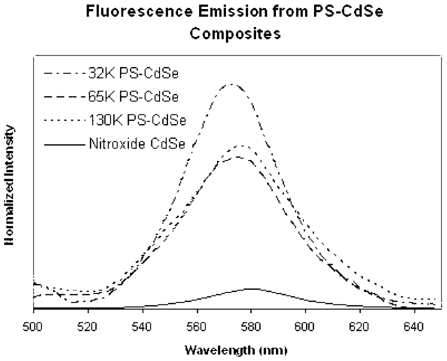

Figure 2. Fluorescence emission curves taken on chloroform solutions of polystyrene−CdSe nanoparticle composites and nitroxide-covered CdSe nanoparticles.

The observed increase in fluorescence intensity is likely a cooperative phenomenon that includes the effect of thermal treatment, and the resulting polymeric ligand coverage and structure.[22] CdSe nanoparticles are known to anneal at temperatures in the range used in our polymerization studies.[23] This annealing process

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reduces the number of crystal structure and surface defects, resulting in increased fluorescence intensity. To test the effect of heating at polymerization temperatures in the absence of monomer, control experiments were performed on TOPO- and nitroxide-functionalized CdSe nanoparticles. The fluorescence intensity of TOPO-covered nanoparticles was found to increase by about 100% as a result of heating in toluene at reflux (110 °C) for 8 h. However, heating nitroxide-covered nanoparticles in the absence of monomer is not practical, as particle degradation occurs at temperatures as low as 40 °C. While thermal annealing accounts for a measurable increase in fluorescence intensity, it does not account for the much larger increases that were observed for the prepared nanoparticle−polymer composites. The chain entanglement of the polymer ligands relative to small molecule ligands (e.g., TOPO) effectively anchors the ligand headgroup (phosphine oxide) on the nanoparticle surface. The corresponding reduction in vacant surface sites brings about the observed increase in fluorescence intensity. Thus, not only is fluorescence maintained in this controlled free-radical polymerization process, but it is enhanced. This result is quite encouraging for future studies, as we look to extend these composite materials to applications where nanoparticles are confined to the interfacial boundaries of polymer materials and fluids, where the inherent fluorescent properties of the nanoparticles can be utilized.

Experimental Section

General Methods and Materials. Technical grade tri-*n*-octyl phosphine oxide and styrene were purchased from Alfa Aesar. All other reagents were purchased from Aldrich and used as supplied. THF was dried over sodium/benzophenone and distilled before use. All reactions were run under an inert atmosphere. Styrene was washed with 1 N NaOH, dried with $MgSO_4$, and then distilled over CaH_2 prior to use. Tri-*n*-octyl phosphine oxide-covered CdSe nanoparticles were synthesized according to previously reported methods.[20] NMR spectra were obtained on a Bruker DPX 300 MHz spectrometer. Chemical shifts are expressed in parts per million (δ) using residual solvent protons as the internal standard. $CHCl_3$ (δ 7.26 for ^{1}H, 77.23 for ^{13}C) was used as an internal standard for $CDCl_3$. Gel permeation chromatography (GPC) measurements were performed in tetrahydrofuran (THF) at 1.0 mL/min using a Knauer K-501 Pump with a K-2301 refractive index detector and K-2600 UV detector, and a column bank consisting of two Polymer Labs PLGel Mixed D columns and one PLGel 50 Å column (1.5 × 30 cm) at 35 °C. Molecular weights are reported relative to polystyrene standards. Fluorescence measurements were recorded on a Perkin-Elmer LS-55 fluorimeter and UV−vis measurements were made on a Hitachi U-3010 spectrophotometer. Fluorescence spectra were normalized to the optical density of **5** at the excitation wavelength (400 nm). Transmission electron microscopy was performed on a JEOL 100CX microscope at 66 K magnification.

Preparation of Nitroxide Ligand 2. Di-*n*-octylphosphine oxide[24] (1.21 g, 4.40 mmol) and NaH (0.12 g, 4.84 mmol) were stirred in THF (18 mL) at room temperature. The solution was heated to reflux and benzyl chloride **1**[19] (1.50 g, 4.84 mmol) was added. The mixture was heated to reflux with stirring and aliquots were removed for evaluation by ^{31}P NMR until the reaction reached completion (ca. 16 h). The mixture was allowed to cool, quenched with water, and extracted with CH_2Cl_2 (3 × 50 mL). The organic layers were dried over magnesium sulfate, filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography (SiO_2, CH_2Cl_2 followed by 3% MeOH in CH_2Cl_2) to afford a clear oil (2.14 g, 3.91 mmol, 89%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.18 (d, $J_{HH} = 2.17$ Hz, 2 H, Ar−*H*), 7.15 (d, $J_{HH} = 1.79$ Hz, 2 H, Ar−*H*), 4.74 (quart, $J_{HH} = 6.53$ Hz, 1 H, Ar−C*H*), 3.11 (d, $J_{HH} = 14.54$, 2 H, Ar−CH_2−P═O), 1.46 (d, $J_{HH} = 6.70$ Hz, 3 H, CH−CH_3), 1.32 (s, 3 H, C−CH_3), 1.26 (m, 28 H, alkyl), 1.16 (s, 3 H, C−CH_3), 1.00 (s, 3 H, C−CH_3), 0.88 (t, $J_{HH} = 6.42$ Hz, 6 H, CH_2−CH_3), 0.58 (s, 3 H, C−CH_3). ^{13}C NMR (300 MHz, $CDCl_3$, δ): 144.77, 131.33, 129.45, 127.65 (Ar, 6 C); 82.92 (CH_3−*C*H, 1 C); 53.61 ($(CH_3)_2$−*C*, 2 C); 40.50 ($(CH_3)_2$−C−*C*H_2, 2 C); 36.25 (P(O)-*C*H_2, 1 C); 31.96, 31.39, 29.45, 27.94, 27.07, 23.39, 21.78 (alkyl *C*H_2, 14 C); 22.81 ((*C*$H_3)_2$−C, 4 C); 17.36 (TEMPO CH_2−*C*H_2−CH_2, 1 C); 14.28 (alkyl *C*H_3, 2 C).

Preparation of 2-Covered Nanoparticles (5). To approximately 25 mg of pyridine-functionalized CdSe nanoparticles in THF (3 mL) was added nitroxide **2** (250 mg). The solution was stirred at room temperature for 16 h, at which point the solution was optically clear. Anhydrous methanol (4 mL) was added, and then the solution was concentrated to ca. 3 mL. To this was added anhydrous methanol (4 mL). The solution was centrifuged for 5 min and then the supernate decanted. The nitroxide-functionalized nanoparticles were dispersed in styrene (2.5 mL) and stored at −20 °C.

Polymer Growth from Nitroxide-Covered Nanoparticle 5. A solution of **5** in styrene (0.4 mL) was added to a reaction tube, purged with N_2, and subjected to five freeze−pump−thaw cycles. The mixture was heated at 125 °C for 4−24 h, depending upon the molecular weight desired. The reaction was cooled and the solid product was dissolved in THF and precipitated into methanol. The product was recovered via filtration to afford a pale red powder.

General Procedure for Removal of Polymer from Nanoparticle Surface for Molecular Weight Analysis. Twenty-five milligrams of DMAP was added to 15 mg of CdSe-polymer product dissolved in THF (1 mL) and then stirred at 50 °C for 4 h. The solution was precipitated into methanol and then the milky solution centrifuged for 10 min. The supernate was decanted, and a white solid was collected and dried by purging with $N_{2(g)}$.

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