Surface Modification of CdSe and CdSe/ZnS Semiconductor Nanocrystals with Poly(*N*,*N*-dimethylaminoethyl methacrylate)

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Received December 1, 2005; Revised Manuscript Received February 28, 2006

ABSTRACT: We report passivation of CdSe and CdSe/ZnS nanocrystals (NCs) with poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMA) through a ligand exchange process. We present the results from various techniques that were used to verify that ligand exchange occurred, including ^{1}H NMR, ^{31}P NMR, and changes in solubility/colloidal properties, hydrodynamic radius, and photoluminescence. We have examined the effect of polymer molecular weight on the surface passivation and quantum yields of the NCs. As additional evidence for the binding of the polymer to the surface of the NC, we were able to modify the polymer chemically to render the NC−polymer moiety water-soluble.

Introduction

Semiconductor nanocrystals (NCs) or quantum dots are of great interest due to their potential applications in light emitting diodes and lasers,[1] solar cells,[2] and biological labeling.[3] These applications are mainly based on their unique photoluminescence characteristics. NCs absorb light in the broad range of wavelengths from UV to near-IR with large extinction coefficients ($\sim 10^5$ M^{-1} cm^{-1}). Their emission spectra are narrow and dependent on material and size. For many applications envisioned for NCs, control of their surface chemistry is important. In particular, processing methods for nanocrystals will be reliant on the properties of surface groups that comprise the organic corona surrounding the NC, as well as the effectiveness of the binding of those molecules to the NC surface. Appropriate surface treatment of NCs prevents aggregation, facilitates NC dispersion in a large variety of solvents, and passivates the NC surface to improve their electronic properties and to increase their photoluminescence yield.

Colloidal CdSe NCs are generally synthesized in the presence of surface ligands such as trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO). Excess TOPO aids in the stabilization of the particles; when it is removed, the particles may begin to aggregate and finally precipitate. However, the hydrophobic phosphine layers are not stable or robust enough for many applications. TOPO-capped CdSe NCs are not soluble in water, nor are they soluble in protic solvents such as methanol and ethanol. Water solubility is highly desirable, for example, for biological labeling applications.[4]

Ligand exchange is a versatile way to modify the surface of NCs for end applications. It is believed that the phosphine ligands bound to the surface of NCs can be replaced with a species capable of more effectively binding to the NCs. Multidentate ligands are ideal for stabilizing the optical and electronic properties of quantum dots. Recent reports have demonstrated the use of organic dendrons,[5] amphiphilic poly(aminoamine) (PAMAM) dendrimers carrying different numbers of hydrophobic aliphatic chains,[6] polyelectrolytes,[7] and multidentate oligomeric phosphines as ligands.[8] More recently, our group synthesized poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMA) with $M_n = 4700$ g/mol and a relatively narrow molar mass distribution ($M_w/M_n = 1.3$) by atom transfer radical polymerization (ATRP). We demonstrated that a linear polymer with pendent tertiary amine groups could successfully passivate the surface of CdSe/ZnS NCs through a ligand exchange process.[9]

One of the challenges of any ligand exchange experiment is to find suitable tools that allow one to quantitatively characterize the extent of surface modification of NCs. Suitable quantification includes the amount of phosphine ligands released from the surface or the amount of the new species bound to the NCs. ^{1}H NMR has been widely used in ligand exchange experiments involving aromatic sulfur compounds. In such experiments, specific protons of the sulfur-containing ligands can be monitored to calculate the amount of the compound bound to the NC surface.[10] Unfortunately, this strategy is limited when the desired ligands have protons whose chemical shifts overlap with those of the ligand to be replaced, such as the TOPO proton signals at 0.5−2.0 ppm. ^{31}P NMR has been used to monitor ligand exchange, taking advantage of the fact that TOPO ligands bound to CdSe/ZnS give broad P signals. As PDMA replaces TOPO on NCs, free TOPO is released from the CdSe/ZnS NCs, resulting in sharp P signals at 30−50 ppm.[9] The use of thermal gravimetric analysis (TGA)[7] and FT-IR techniques[11] have also been reported.

In this paper, we describe our experiments to modify the surface of CdSe and CdSe/ZnS NCs with PDMA through ligand exchange. We examined ligand exchange of TOPO on the NCs with PDMA in detail using NMR techniques. For comparison, we examined ligand exchange with *p*-(dimethylamino)pyridine (DMAP) as a monodentate ligand. Polymeric samples of PDMA were synthesized by conventional solution polymerization of dimethylaminoethyl methacrylate in toluene. These polymers have relatively broad molar mass distribution ($M_w/M_n \approx 2-3$). We show that a narrow molar mass distribution is not necessary to passivate NCs. A series of samples of different molar mass (M_{7K}−, M_{10K}−, M_{15K}−, M_{19K}−, and M_{29K}−PDMA) were prepared by solution polymerization. In our notation, M_{iK} refers to the M_n value of the polymer (in thousands) as determined by gel permeation chromatography in *N*-methylpyrrolidone (NMP)

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10.1021/ma0525740 CCC: $33.50

based upon polystyrene standards. A sample of M_{35K}−PDMA was prepared by atom transfer radical polymerization. We explored the effect of chain length of PDMA on the passivation of both CdSe and CdSe/ZnS nanocrystals.

Experimental Section

Materials and Characterization. All reagents were used as received. Dimethylaminoethyl methacrylate (DMA, 99%), 1-dodecanethiol (C_{12}−SH), iodomethane (99.5%), p-(dimethylamino)-pyridine (DMAP), *m*-methoxyphenol (MPOH), *p*-dimethoxybenzene (DMB), and triphenylphosphine (TPP) were purchased from Aldrich. 2,2-Azobis (2-methylbutyronitrile) (AMBN, V-59) was obtained from Wako Chemie Co.

^{1}H and ^{31}P NMR spectra were recorded at 400 MHz using a Varian XL400 spectrometer.^{1}H NMR measurements were performed in C_6D_6 or deuterated pyridine (Py-d_5). For quantitative calculations, an internal standard was used. For ^{1}H NMR we employed either 1,4-dimethoxybenzene (p-DMB) or *m*-methoxyphenol (MPOH), whereas triphenylphosphine (TPP) was used for ^{31}P NMR. UV−vis spectra were recorded on a Perkin-Elmer Lambda 25 UV−vis spectrophotometer. PL spectra were recorded on a SPEX Fluorolog-3-v.2.1 luminescence spectrophotometer.

Synthesis of PDMA. A series of samples of PDMA were synthesized by conventional solution polymerization of DMA in toluene at 95 °C, initiated with an azo-type free-radical initiator, AMBN. Details are provided as Supporting Information. Dodecanethiol (C_{12}−SH) was introduced as a chain transfer agent to control molar mass. The molar mass distribution was measured by gel permeation chromatography (GPC) using a Waters liquid chromatograph equipped with a Waters 480 R410 differential refractometer (RI) detector at a flow rate of 0.6 mL/min. Either *N*-methylpyrrolidone (NMP) or THF with triethylamine (Et_3N) (2.0 vol %) was used as the elution solvent, with polystyrene samples as molar mass standards. A sample of PDMA of higher molar mass was synthesized by ATRP. Solid polymer samples were obtained by drying in a vacuum oven at 50 °C. The characteristics of the polymer samples are presented in Table S2 in Supporting Information.

Synthesis of TOPO-Capped NCs. Samples of CdSe and CdSe/ZnS NCs were prepared as described in our previous publication[9] by the method of pyrolysis.[12,13] Briefly, TOPO/TOP-passivated CdSe was prepared by injection of $Cd(CH_3)_2$/TOPSe into TOPO at 320 °C. To synthesize TOPO/TOP-passivated CdSe/ZnS, the aliquots of CdSe NCs were first partially purified to remove excess phosphine ligands by precipitation in MeOH. The dried TOPO-coated CdSe particles were redispersed in toluene. To the resulting dispersion was then injected $(CH_3CH_2)_2Zn$/trimethyldisilathiane/TOP at 180 °C. A sample of the CdSe NC precursor (9.8 mg), showed sharp P signals at 30−70 ppm in the ^{31}P NMR (C_6D_6) due to a small amount of free TOP and TOPO ligands. This sample, in the ^{1}H NMR (C_6D_6, ppm) showed signals at 0.86−0.91 (t, 9H, CH_3), 1.21 (m, 30H, the rest of CH_2 protons), 1.32−1.45 (m, 6H, OP−CH_2*CH_2*−), 1.49−1.51 (m, 6H, OP−*CH_2*CH_2−). Similar results were obtained for a core/shell CdSe/ZnS sample. The NCs were purified by three successive precipitations with MeOH followed by redispersal in toluene.

Ligand Exchange. To synthesize PDMA-capped CdSe, an aliquot of dry polymer was added to a solution of the NCs in an organic solvent. As a typical example, M_{7K}−PDMA (45 mg) was added to a solution of purified TOPO-capped CdSe (7.9 mg) in C_6D_6 (1.5 g) and then stirred at room temperature overnight. The resulting solution was optically transparent and homogeneous.

To prepare DMAP-capped CdSe, DMAP (44 mg) was added to a similar sample of purified TOPO-capped CdSe (18.9 mg) dissolved in C_6D_6 (1.5 g). The optically transparent solution became turbid as it was stirred at 70 °C for 4 h. The dispersion was centrifuged at 13 000 rpm for 5 min at room temperature. The clear supernatant was decanted, and the precipitate was washed several times with toluene to remove free DMAP. Its presence in each wash was monitored by ^{1}H NMR. After the last wash, the precipitate was dried in a forced-air oven for 1 min at room temperature. The solid could be redispersed in Py-d_5 for NMR analysis.

Ligand Modification. A selection of PDMA-coated CdSe NCs were treated with known excess amounts of methyl tosylate (MTS) to quaternize the tertiary amino groups to promote dispersibility in water. The PDMA-coated CdSe sample was prepared by mixing 1.59×10^{-2} M PDMA (27K, PDI = 3.9) with 4.7×10^{-7} M CdSe−TOPO in toluene. The mixture was divided into three equal parts, and different amounts of MTS were added. The mole ratios of MTS to dimethylamino groups in the three samples were 1:1, 1:2, and 1:10, respectively. The samples were stirred overnight, and then an equal volume of distilled water was added to each sample. After the aqueous phase became colored and the toluene phase became clear, the aqueous phase was separated and analyzed by UV−vis and fluorescence spectroscopy.

Transmission Electron Microscopy (TEM). The TEM images were taken using a Hitachi 5200 STEM instrument with 200 kV electrons and 13 μA current. To prepare each specimen, a small drop of a solution of the CdSe NCs in an organic solvent (1 wt %) was placed onto a carbon-coated copper TEM grid (400 mesh, purchased from Electron Microscopy Science). Each grid was dried in air.

Particle Size Distribution. Hydrodynamic radii of samples of NCs were measured by dynamic light scattering with a Protein Solution Pro Particle Sizer at a fixed scattering angle of 90 ° at 25 °C equipped with a 10 mW He−Ne laser. A CONTIN plot of the corresponding data gives an indication of the hydrodynamic size distribution.

Photoluminescence (PL) Decay Measurements. PL decay profiles were measured using a single photon timing instrument from IBH.[14] The samples were excited with a pulsed diode at 370 nm. The emission was monitored through a monochromator at the wavelength of the PL maximum.

Results and Discussion

Quantum Dot and Polymer Synthesis and Characterization. After synthesis, the NCs were dissolved in toluene and purified to remove excess TOPO using the usual procedure of precipitation by addition of methanol followed by redispersion in toluene. It was necessary to repeat this procedure three times to ensure that free phosphine ligands were completely removed, at which point no sharp signals that correspond to free phosphine ligands appeared over the range −50 to +200 ppm in the ^{31}P NMR spectrum. Instead the spectra showed multiple features at 30−60 ppm, indicating a complex chemical environment associated with multiple binding sites and modes for surface-bound TOP and TOPO.[15,16] The corresponding ^{1}H NMR spectra of the purified NCs exhibit multiplets at 0.8−2.0 ppm arising from the aliphatic protons of the phosphine and phosphine oxide ligands. Using these signals, the ligand coverage can be quantified if spectra are taken for solutions that contain an internal standard. As an example, Figure 1a shows the ^{1}H NMR spectrum of purified TOPO-capped CdSe (12.8 mg, NC diameter $d = 3.2$ nm) in C_6D_6, which contains a known amount of 1,4-dimethoxybenzene. The spectrum also contains small peaks due to residual toluene and methanol from the NC purification steps. From analysis of the peak integration, we deduce that this NC sample contains 2.2 mg of TOPO. This value of 20 wt % TOPO corresponds to that reported by Bawendi et al.,[17] who used thermal gravimetric analysis (TGA) to obtain ca. 23 wt % TOPO coverage of similar sized CdSe particles.

PDMA samples were synthesized by solution polymerization and were characterized by GPC. Useful GPC profiles for the polymers were obtained both with Et_3N in THF (2 vol %) as the eluent solvent, as reported by Armes,[18] and with *N*-methyl pyrrolidone (NMP). The molar mass and molar mass distributions were determined using polystyrene (PS) standards. The

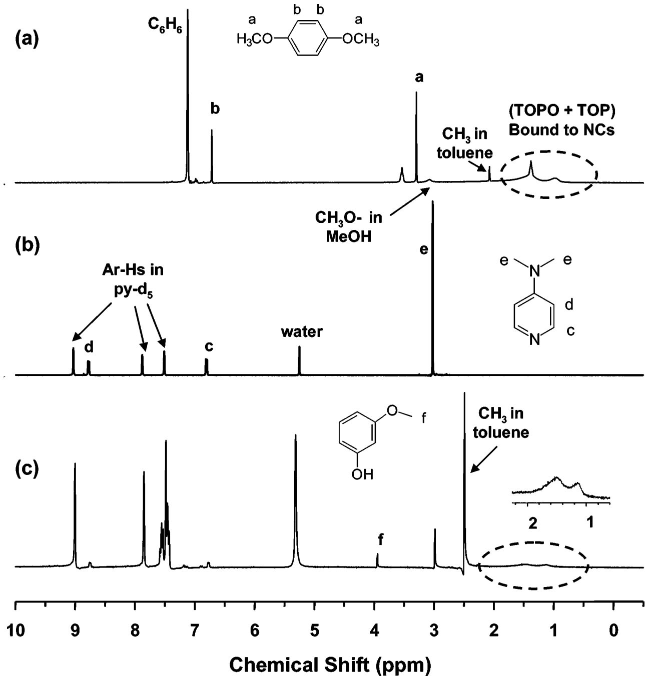

Figure 1. ^{1}H NMR spectra of (a) the purified TOPO-capped CdSe in C_6D_6, (b) DMAP in pyridine-d_5, and (c) purified DMAP-capped CdSe in pyridine-d_5, for comparison. Trace amounts of toluene and MeOH are present in the CdSe samples.

results are compared in Table S2 in the Supporting Information. The apparent molar mass determined using NMP is somewhat larger than that with THF/Et_3N for all four samples. This may reflect the possibility that compared to PS, PDMA has a larger hydrodynamic volume in NMP than in THF.

Evidence for Ligand Exchange. In this section, we describe experiments that monitor polymer adsorption to the NC surface and ligand exchange. By ligand exchange, we mean replacement of TOPO groups on the NC surface by an alternative ligand. We begin with experiments similar to those described by Emrick,[19,20] who described the complete replacement of TOPO, upon addition of 4-*N,N′*-(dimethylamino)pyridine (DMAP) to THF solutions of TOPO-capped CdSe. DMAP is a useful ligand for these studies, because its contributions to an ^{1}H NMR spectrum appear at distinctly different chemical shifts than those of TOPO. In our experiments, when excess DMAP (44 mg) was added to a solution of purified TOPO-capped CdSe, we observed that the optically transparent solution turned turbid after it was stirred at 70 °C for 4 h. The resulting dispersion was centrifuged to separate the precipitate from the clear supernatant. The dried solids, DMAP-capped CdSe, appeared to be insoluble in solvents such as toluene, chloroform, and THF, but were readily dispersed in pyridine to form a transparent solution. The change in solubility is an indication of displacement of the original surface ligands with DMAP.

In Figure 1c one can see that the ^{1}H NMR resonances for DMAP-capped CdSe in Py-d_5 are somewhat shifted compared to DMAP itself (Figure 1b) in Py-d_5. These samples also contained a small amount of *m*-methoxyphenol (MPOH), the methoxy protons of which serve as an internal standard. On the basis of integration of these peaks in Figure 1c, the amounts of TOPO and DMAP bound to CdSe are calculated to be 0.4 and 0.5 mg, respectively. Our results suggest that 90% of the TOPO was released from CdSe as a result of ligand exchange with DMAP. Moreover, the amount of DMAP (4.1×10^{-3} mol) bound to CdSe is much smaller than the amount of TOPO released from CdSe (9.6×10^{-3} mol). We would not be able to distinguish whether pyridine-d_5 molecules also served as surface ligands for the NCs. This experiment was repeated with another CdSe sample. Here we found that 91% of the TOPO was released upon exposure to DMAP at 70 °C. In Figure 2, we present TEM images of the DMAP-capped CdSe NCs, indicating that the particles did not aggregate as a consequence of the ligand exchange process.

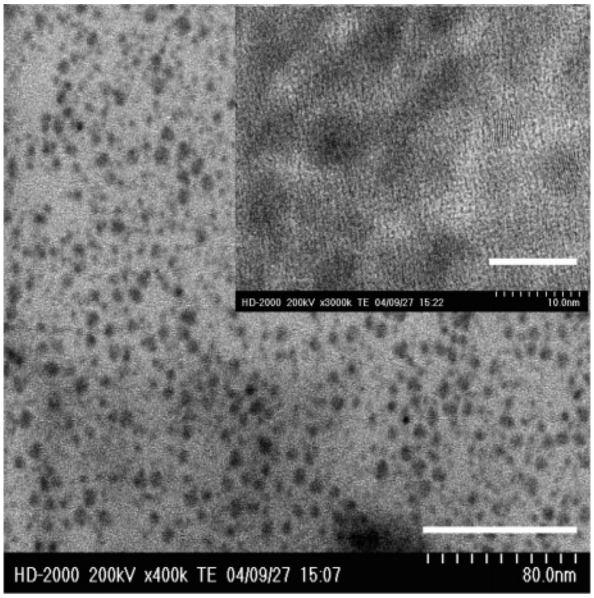

Figure 2. High-resolution TEM images of DMAP-capped CdSe nanocrystals, scale bar = 80 nm in the main figure and 10 nm in the inset. The TEM samples were prepared by placing a drop of the NC solution onto carbon-coated copper grids and allowing the solvent to evaporate.

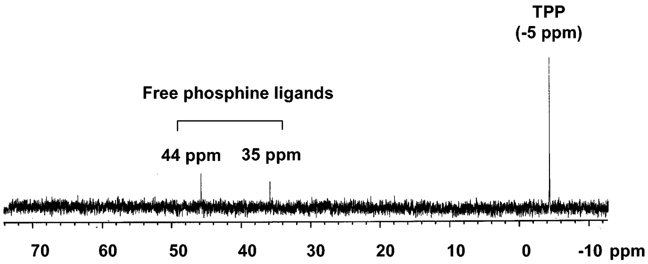

Figure 3. A ^{31}P NMR spectrum of the clear supernatant separated from the DMAP-capped CdSe in C_6D_6. A known amount of triphenylphosphine (TPP) was added as an internal reference.

The supernatant from the DMAP ligand exchange was examined by ^{31}P NMR to test for free phosphine ligands. The example presented in Figure 3 shows two weak signals at 35 and 44 ppm, which can be assigned to free phosphine ligands including TOPO released from CdSe, as well as a peak at −5 ppm that corresponds to triphenylphosphine as an internal standard. Unfortunately, this experiment was not very reproducible, and in some experiments, the peaks due to free TOPO were too weak to be detected.

Ligand exchange with PDMA took place under milder conditions than for DMAP. A sample of polymer was introduced into a toluene solution of purified NCs and stirred 4 h at room temperature. In almost every case, the release of free TOPO into the toluene could be detected by ^{31}P NMR. Another test for the successful adsorption of the polymer onto the particle surface was a pronounced change in colloidal properties. After treatment with the polymer, dried samples could be dispersed in methanol or acetonitrile to give transparent, fluorescent solutions. CdSe−TOPO NCs are known to be insoluble in those

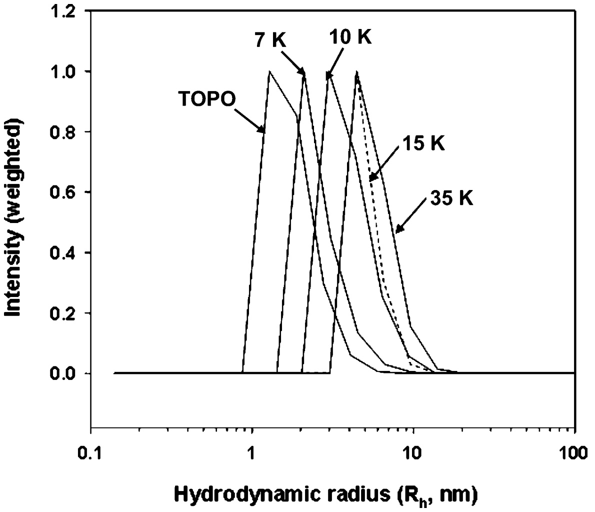

Figure 4. CONTIN plots of intensity vs Rh for CdSe−TOPO NCs before (TOPO) and after addition of M_{7K}−, M_{10K}−, M_{15K}−, and M_{35K}−PDMA in toluene.

solvents. More information is available from dynamic light scattering experiments described in the following section. We note as a final comment here, that we have not, up to this point, tried to purify these NCs from excess polymer in the solution.

Adsorption of PDMA of Different Molar Masses onto CdSe NCs. This section describes our investigations of PDMA chain length on the properties of CdSe−PDMA nanocomposites. Various PDMA samples were prepared and exchanged onto the surface of CdSe NCs and CdSe/ZnS core−shell NCs. We label those polymers M_n−PDMA, where the number-average molecular weight n = 7K, 10K, 15K, 19K, and 29K for samples synthesized by conventional solution polymerization. One sample, n = 35K was synthesized by ATRP. After the CdSe−PDMA samples were stirred at room temperature for a minimum of 4 h, they were examined by right-angle dynamic light scattering. A CONTIN analysis of the autocorrelation decay showed a single peak for each sample, and the (apparent) hydrodynamic radius R_h was calculated from the first cumulant of the relaxation rate of the particles. These data are combined in Figure 4. One can see that the value of R_h is shifted from ca. 1.9 nm for the TOPO-capped CdSe to 2.7, 4.7, 5.2, and 6.3 nm after addition of M_{7K}−, M_{10K}−, M_{15K}−, and M_{35K}−PDMA, respectively. These results not only confirm that a layer of polymer has been deposited on the particle surface, they also indicate that the corona thickness around the particles in solution increases with the length of the polymer chain.

Figure 5 shows dark-field TEM images of samples of the CdSe NCs before and after addition of PDMA with different molar mass. Dark-field imaging is advantageous in that artifacts associated with the presence of polymers can be avoided, so that only the high-density CdSe particles can be seen in the TEM images. One can see that the diameters of the NC particles before and after surface modification are virtually identical, indicating that the particles remain discrete. Both the DLS and TEM measurements indicate that there is no aggregation or cluster formation of CdSe brought about by bridging polymer chains.

Passivation of CdSe and CdSe/ZnS NCs by PDMA: Spectroscopic Characterization. To examine the influence of polymer on the absorption and emission spectra of CdSe and CdSe/ZnS NCs, we prepared a series of samples of closely matched optical density. In Figure 6a, we show the UV−vis absorption spectrum of a solution of TOPO-capped CdSe NCs in toluene as well as spectra of this sample after ligand exchange with three PDMA polymers. Global features of the spectra are unchanged after ligand exchange with the polymer and, for a fixed concentration of particles, the magnitude of the absorbance was not affected. Closer inspection of the spectra show that the first exciton peak centered at 520 nm for CdSe−TOPO is blue shifted by a few nanometers for the NCs bearing polymer, as is often observed upon ligand exchange,[17] indicating a very small decrease in NC size. One can take this information, in conjunction with the TEM results, to conclude that polymer adsorption has little influence of the size of the NCs present in solution.

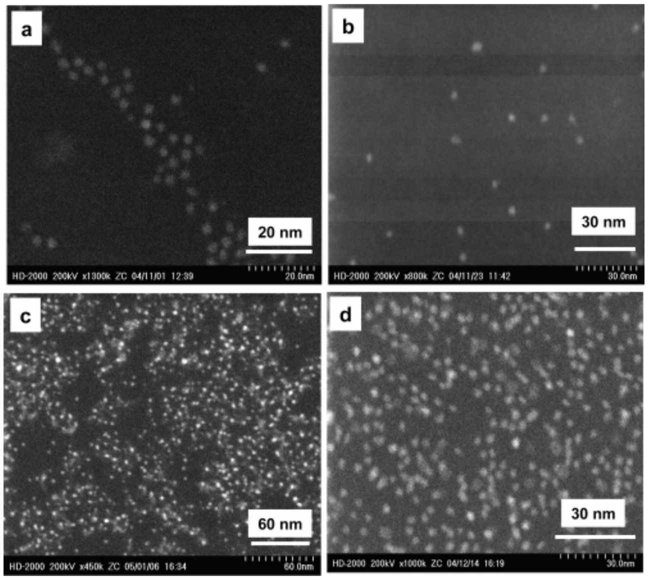

Figure 5. Dark-field high-resolution TEM images of CdSe NCs capped with (a) TOPO and (b) M_{7K}−, (c) M_{10K}−, and (d) M_{15K}−PDMA. The TEM samples were prepared by drying a drop of each NC solution onto a carbon-coated copper grid and allowing the solvent to evaporate.

In contrast to the almost imperceptible effect of surface-bound polymer on the UV−vis absorption spectra, the polymer had a striking effect on the photoluminescence (PL) intensity. We first consider the effect of the 10K and 15K polymers prepared by traditional solution polymerization. As one can see in Figure 6b, the presence of these polymers led to a 2.5-fold (15K) to 4-fold (10K) increase in PL intensity. The relative quantum yields (QY) were consistent, regardless of the excitation wavelength.[21] One can also note a small blue shift for the polymer-coated particles in the emission maximum centered at 530 nm for CdSe−TOPO. The results are summarized in Table 1. This effect is even more pronounced in a CdSe sample with a lower initial quantum yield (Figure 6c), indicative of poor surface passivation. The PL intensity increase after ligand exchange of purified CdSe−TOPO particles with the polymer samples indicates that the presence of the polymer on the particles improves the surface passivation of the CdSe NCs.

A different effect is seen with the 35K polymer prepared by ATRP. For the sample in Figure 6b, the PL intensity of the NCs coated with the 35K polymer is similar to that of the TOPO-coated particles, and the presence of the polymer is accompanied by a small enhancement of trap emission[17,22] seen at $\lambda > 600$ nm. For the more weakly emitting sample seen in Figure 6c, the presence of the 35K polymer led to a decrease in PL intensity compared to the TOPO-coated particles and a striking increase in the intensity of trap emission. Here we believe that there are two competing effects: enhanced surface passivation by the polymer as noted above, plus a parasitic effect

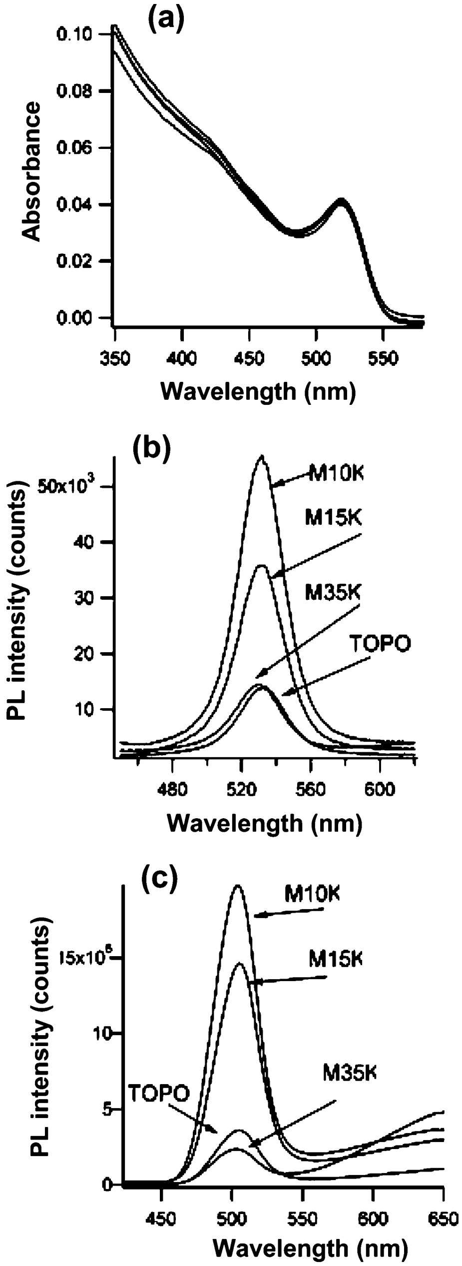

Figure 6. (a) UV−vis and (b) PL spectra of CdSe (sample 1) NCs and (c) CdSe (sample 2) NCs in toluene in which the NCs are capped with TOPO or with various PDMA polymers.

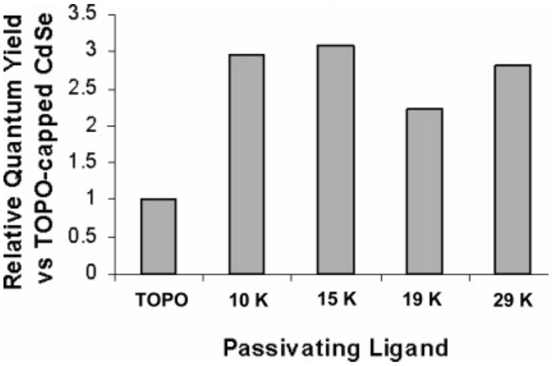

Figure 7. Quantum yield for CdSe passivated with different molecular weight PDMA vs TOPO-capped CdSe (sample 2) which has a quantum yield of ca. 3%.

Table 1. Spectroscopic Properties of CdSe and CdSe/ZnS in Toluene before and after Ligand Exchange with PDMA

CdSe Sample 1 Excited at 360 nm

	ligand = TOPO	10K	15K	35K
absorbance (at 360 nm)	0.085	0.093	0.097	0.093
max PL intensity (au)	1.32	5.23	3.36	1.37
relative QY	1	2.9	1.7	1.0

CdSe Sample 2 Excited at 470 nm

	ligand = TOPO	10K	15K	19K	29K	35K
absorbance (at 470 nm)	0.05	0.07	0.08	0.10	0.08	0.07
relative QY	1	3.0	3. 1	2.2	2.8	0. 2
% QY (vs rhodamine 6G)	3	7	8	6	7	1

CdSe/ZnS Sample Excited at 370 nm

	ligand = TOPO	10K	15K	35K
absorbance (at 370 nm)	0.21	0.22	0.22	0.21
relative QY	1	1.3	1.4	0.53
% QY (vs fluorescein)	36	46	48	18

Table 2. PL Decay Data for CdSe and CdSe/ZnS Capped with PDMA of Various Molecular Weights

	CdSe				CdSe/ZnS			
	τ_i (ns)[a]	A_i[a]	$\langle\tau\rangle$[b]	χ^2	τ_i (ns)[a]	A_i[a]	$\langle\tau\rangle$[b]	χ^2
TOPO	48.1	51.3	79.0	1.10	36.0	42.6	56.4	1.11
	158	33.1			14.3	38.7		
	13.3	15.6			191	18.6		
10 K	56.4	43.9	120.9	0.99	36.2	36.7	45.6	1.04
	202	46.8			14.9	48.6		
	17.3	9.4			172	14.6		
15 K	57.4	43.7	117.9	1.09	40.5	36.4	61.5	1.04
	201	45.2			15.1	47.1		
	17.9	11.2			239	16.6		
35 K	51.0	35.3	130.7	1.06	30.9	45.3	61.1	1.14
	194	57.7			11.6	27.8		
	11.4	7.0			163	26.9		

[a] Fitting parameters to $I(t) = \sum A_i \exp(-t/\tau_i)$. [b] Calculated according to eq 1.

caused by traces of residual copper ions from the initiator/catalyst in the ATRP polymer synthesis. We will provide further information about this effect later in the paper, when we present the results of time-resolved experiments.

In Figure 7, we show the QY of NC passivated with a wider range of molecular weights of PDMA, as compared to TOPO-capped CdSe. To rule out any preparation-related effects, all of these polymer samples were prepared by solution polymerization as described above. The TOPO-capped CdSe was prepared with a low QY to emphasize the extent of PL enhancement by the polymer ligands. This sample is similar to that shown in Figure 6c. The tail in the emission spectrum extending to the red of 550 nm is usually attributed to deep trap emission and is an indication of the poor passivation of the as-prepared NCs. From Figure 7, we can conclude that polymer molecular weight has little effect on the passivation of the NCs by PDMA.

In the preceding paragraphs, we saw that PDMA as a multidentate passivating ligand often leads to an increase in the PL intensity of CdSe quantum dots and can increase the PL of CdSe/ZnS quantum dots as well. The sample of CdSe/ZnS−TOPO (Table 2) that we examined had a quantum yield of 0.36. We report an increase in the QY when the NCs were passivated with the polymers (except for the 35K ATRP sample). We next compare these results to the effect on PL of ligand exchange with monodentate amine ligands as reported in the literature. Various amines have been shown to either enhance or suppress the PL of CdSe NCs. Talapin et al.[23] have reported that ligand

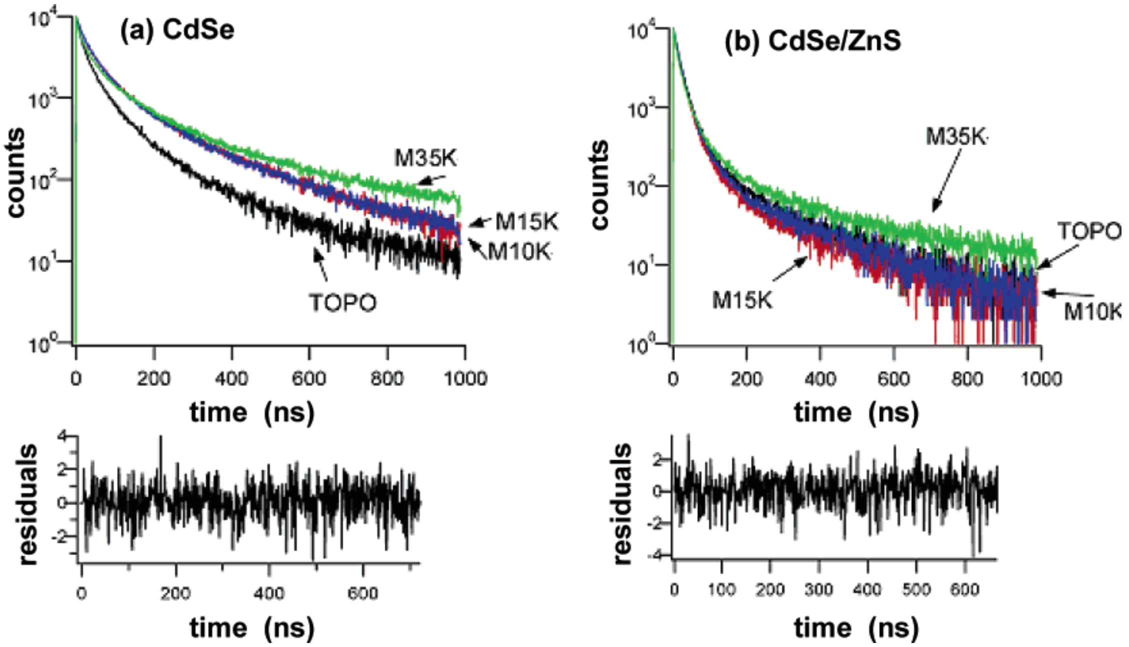

Figure 8. PL decays for (a) CdSe and (b) CdSe/ZnS NCs capped with TOPO or with various PDMA samples in toluene. All data are for dilute solutions in toluene. Weighted residuals are shown for the TOPO-capped samples.

exchange of TOPO with *n*-hexadecylamine, *n*-dodecylamine, and allylamine can result in an order of magnitude increase in QY. In contrast, Landes et al.[24] found that *n*-butylamine decreased the PL of CdSe NCs of a size similar to those in this paper. Addition of (dimethylamino)pyridine (DMAP) displaces the native TOPO ligands and reduces the PL.[24] It remains unclear what effect tertiary vs primary amine ligands have on the QY. The PL enhancement that we observe is likely to be a combination of improved binding of the pendant group itself (vs TOPO) and the cooperativity that the polymer affords.

We also would like to comment that there is a sample-to-sample variability of this effect with different batches of quantum dots. Replacement of TOPO ligands with PDMA seems to have the most pronounced effect on NCs that were relatively poorly passivated with TOPO during synthesis. The magnitude of the effect varies with the quality of the nanocrystals.

Time-Resolved Experiments. Photoluminescence decay profiles for colloidal NC solutions are relatively easy to measure and very difficult to interpret. The decays are strongly nonexponential. Jones et al.[25] reported that they needed five exponential terms to fit the decays of CdSe/ZnS core−shell particles in toluene in order to obtain χ^2 values of 1.1 or less. This is an area still very much under investigation.[26,27] NC behavior is very different than that found for typical dyes in solution that exhibit exponential decays and for which weaker emission (for example, due to quenching) is accompanied by a decrease in the lifetime of the emission decay. Even in the case of dyes dissolved in glassy polymer matrices, where the emission decay can be strongly nonexponential, the PL quantum yields calculated from the integrated area under the normalized PL decay profiles are in good agreement with those measured by intensity measurements.

We wished to examine the effect of the polymer on the overall shape of the PL decay profile of the NCs and to see whether changes in intensity that resulted from binding of the polymer to the surface would in any way be reflected in the PL decay profiles. A selection of the decay profiles that we measured are shown in Figure 8a for a low quantum efficiency CdSe sample. Decay profiles for the CdSe/ZnS core−shell sample with a QY = 0.36 are shown in Figure 8b. For the weakly emitting CdSe samples, we find that the NCs with TOPO as the surface ligand have the fastest decay rate. The NCs with the 10K and 15K polymer have significantly slower decay components, particularly during the first 100 ns of the decay. That is consistent with the findings that surface trap states quench photoluminescence on short time scales.[28]

The particles passivated with the 35K polymer exhibit a faster decay rate during the first 50 ns than the particles passivated with the 10K and 15K polymer, but exhibit a long tail in the emission. We interpret the changes in the decay profile for this polymer-passivated NC sample to indicate the parasitic affects caused by traces of residual Cu ions in the 35K polymer prepared by ATRP. Alivisatos and co-workers,[29] for example, have shown that silver ions and copper ions in toluene solution can replace cadmium ions in CdSe NCs. A vestige of this effect may have occurred in our samples exposed to the ATRP polymer. We note that other researchers have encountered similar problems of loss of photoluminescence of CdSe NCs associated with the presence of copper ions used in ATRP reactions.[30]

It is immediately obvious comparing the decay profiles in parts a and b of Figure 8 that the CdSe/ZnS particles exhibit a much more rapid decrease in PL intensity over the first two decades of the decay compared to the CdSe particles. There are smaller differences in the detailed shapes of the decays, but the 35K-capped particles have the most pronounced tail in the emission at long times.

To proceed with a more quantitative data analysis, we fitted the decay profiles to sums of 3 exponential terms [$I(t) = \Sigma A_i \exp(-t/\tau_i)$]. As a note of caution, we comment that for decay profiles measured over longer times, it often becomes necessary to add additional terms to fit the data satisfactorily. In our experiments, in which we monitored three decades of decay for each of the samples and fitted them with χ^2 values of ca. 1.1, the three exponential terms most likely provide an adequate representation of the complete decay profiles.

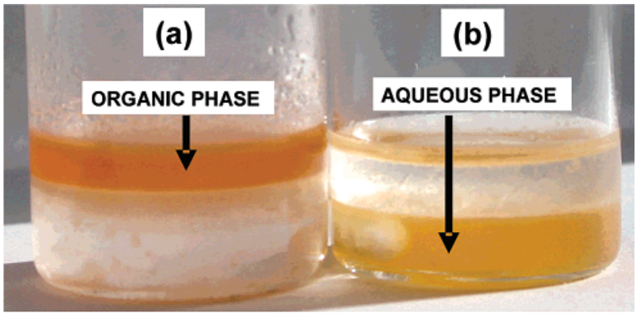

Figure 9. Transfer of polymer-modified CdSe NCs to an aqueous phase by polymer modification with CH_3I.

Plots of the weighted residuals for these fits for the particles with TOPO ligands are shown beneath the two sets of decay profiles in Figure 8. We calculated the intensity-weighted mean lifetimes $\langle\tau\rangle_I$ for each sample from the expression

$$\langle\tau\rangle = A_1\tau_1 + A_2\tau_2 + A_3\tau_3 \qquad (1)$$

The fitting parameters and the values of $\langle\tau\rangle_I$ are collected in Table 2. These mean decay times are on the order of 60 ns for the CdSe/ZnS NCs, and there is relatively little variation among the samples. We find much longer mean lifetimes for the CdSe particles, and, as one might expect, based on the decay profiles seen in Figure 8a, a much greater sample-to-sample variation. The main conclusion that can be drawn from the PL decays is that the adsorption of polymer does, indeed, change the surface chemistry of the quantum dots. Slowing down of the short time decay is observed in Figure 8 when the polymer is added, consistent with the picture that the polymer is passivating the surface and removing surface traps.

Corona Modification for NCs with Polymer Ligands. In the preceding sections of this paper, we have shown that PDMA, acting as a multidentate ligand, is effective at surface passivation for both CdSe and CdSe/ZnS NCs. An even more attractive feature of polymers adsorbed to the surface of NC is that they provide robust colloidal stability in various environments. Thus, they can be used to modify or control compatibility of NCs with different media. In our preliminary communication, we reported that CdSe/ZnS NCs passivated with PDMA of M_n = 4700 could be dispersed in methanol to form highly luminescent solutions. The TOPO-capped precursor particles were insoluble in methanol. Although PDMA itself is soluble in water, the NC−PDMA particles could not be dissolved (dispersed) in aqueous solutions.

Here we demonstrate that post-modification of the polymer bound to the NC can have a profound effect on solvent−NC compatibility. In Figure 9a, we show a digital photograph of a solution in toluene of CdSe NCs (sample 1) stabilized by PDMA (10K) floated on a layer of water. The aqueous phase is clear and the photoluminescent particles remain in the toluene phase. Addition, with stirring, of a small excess of methyl iodide (10 mol % excess based upon total amount of Me_2N- groups) into the solution leads to a pronounced change. The toluene layer becomes clear and the lower aqueous phase becomes colored and photoluminescent. It appears as if the methyl iodide has reacted with a fraction of the dimethylamino groups to convert them into alkyltrimethylammonium groups, rendering the particle−corona combination soluble in water.

To obtain more quantitative information about this process, we repeated the experiment using methyl tosylate (MTS) instead of methyl iodide as the methylating agent, carefully controlling the mole ratio of MTS to Me_2N- groups in the solution. A sample was prepared by mixing excess PDMA (solution polymerization, 27K, PDI = 3.9, 1.59×10^{-2} M Me_2N- groups) with 4.7×10^{-7} M CdSe−TOPO in toluene. Then the mixture was divided into three equal parts. Different amounts of MTS were added to the solutions to yield MTS/Me_2N- mole ratios of 1:1, 1:2, and 1:10. After the samples were stirred overnight, an equal volume of distilled water was added to each sample. We found that for higher ratios of MTS/Me_2N- (1:1 and 1:2), the transfer of NCs from toluene to water occurred within several minutes under stirring. In contrast, it took around 7 h for the sample containing 1:10 MTS/Me_2N- to transfer to the aqueous phase.

One indication that transfer of the NCs to the aqueous phase was complete for all three samples is that the toluene phase became clear and the aqueous phase developed a color similar to that seen in Figure 9. The UV−vis absorption spectra seen in Figure 10c provide quantitative confirmation of identical NC concentration in the three samples.

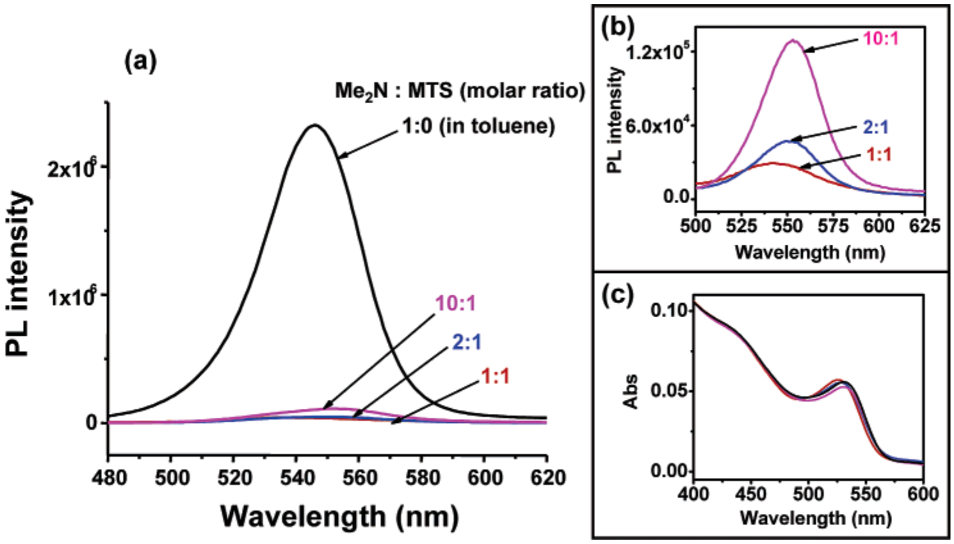

Figure 10. Photoluminescence (PL) and UV−vis absorption spectra of CdSe/PDMA in water following treatment in toluene with various amounts of methyl toslylate (MTS) and subsequent transfer to water. The ratios in the figure are Me_2N- groups in the polymer to MTS added. Key: (a) PL intensities for matched absorbance at λ_{max} compared to the starting CdSe/PDMA NCs in toluene; (b) PL intensities of MTS treated samples on an expanded scale; (c) absorbance spectra of all samples.

While the CdSe NCs remain photoluminescent after transfer to the aqueous solution, the quantum yield decreased dramatically. Figures 10a and 10b show that there was more than an order of magnitude decrease in the PL intensity in water compared to a solution of the precursor PDMA-coated particles in toluene. The expanded scale in Figure 10b illustrates that the extent of residual intensity is also dependent on the mole ratio of MTS to amino groups. Since this ratio likely reflects the relative extents of methylation of the PDMA polymer, we surmise that more extensive methylation may reduce the number of Me_2N- groups available to passivate the NC surface.

Summary and Conclusions

Poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMA) samples with different molar masses were synthesized by conventional batch solution polymerization. Molar mass was controlled by the introduction of $C_{12}-SH$ as a chain transfer agent. For these samples, the molar mass distribution was relatively broad (PDI = 2−3). A third sample of higher molar mass but comparable PDI was synthesized by ATRP. These polymers were effective in toluene solution at displacing TOPO from the surface of CdSe and CdSe/ZnS NCs prepared in the presence of TOPO and purified to remove excess ligand.

One clear indication of polymer adsorption was the increase in hydrodynamic radius (R_h) of the particles as determined by dynamic light scattering. When these polymers bind to the particle surface, a fraction of the Me_2N- groups bind to the particle surface to act as passivating ligands. The remaining polymer segments form loops and tails that protrude into the solution. The polymer molecules attached to the particle surface cause an increase in R_h, because the corona chains are strongly swollen by solvent. The values of R_h increased with increasing polymer molecular weight, indicating that the overall length of the polymer chain has a strong influence on corona thickness. Upon drying, the corona chains collapse, and by TEM one cannot recognize any difference in diameter between TOPO-capped and polymer-capped nanoparticles. None of the samples showed any indication of particle aggregation.

The particles remain strongly luminescent. For CdSe and CdSe/ZnS, the intensity increased sharply in the presence of polymer. The effect of molecular weight was also investigated. We conclude that PDMA is a versatile polymer that can act as a multidentate ligand for both CdSe and CdSe/ZnS nanocrystals.

From a polymer perspective, there are two aspects of our experiment that merit comment and further investigation. The first is the possible selective binding of individual components from a polydisperse polymer solution. Longer chains (that contain more binding groups) tend to bind in preference to shorter chains. If this is the case for the samples examined here, we should find, if we had an appropriate analytical tool, that the longest chains in the samples would preferentially become bound to the particle surface. Another effect worth investigating in future experiments is whether long polymer chains are effective at displacing shorter chains from the particle surface.

The second aspect of interest is the detailed configuration of the polymer chains adsorbed to the surface. In the polymer physics community, it is understood that long polymers adsorbing to flat surfaces undergo a "pancake" to "brush" transition as a function of the density of adsorbed chains.[31] At low surface coverage, the polymers tend to lie flat on the surface so that many if not most of the pendant groups are in contact with the surface. At higher coverage, there is a relatively sharp transition to a polymer brush, in which only a fraction of the segments ("trains") are in contact with the surface. The remaining polymer protrudes from the surface as "loops" and "tails" that become stretched in the direction normal to the surface to minimize lateral coil−coil repulsion. Shorter polymers are less sensitive to this intercoil repulsion, and may in fact have a larger faction of their segments in contact with the surface. It would be very useful to know the number of Me_2N- groups in contact with the particle surface, and whether this number changes with a change in polymer molar mass.

As a concluding remark, we would like to comment that our finding that partial methylation of the PDMA bound to CdSe quantum dots effects transfer of the quantum dots from toluene into water opens the door to many new experiments involving corona modification of polymer-stabilized nanocrystals.

Acknowledgment. The authors thank the NSERC, through its I2I program, for their support for this research. T.E.D. thanks the NSERC for a graduate student fellowship. G.D.S. thanks the Alfred P. Sloan foundation. The authors thank T. Emrick for sharing with us his unpublished results.

Supporting Information Available: Text giving further details regarding the synthesis of the polymer samples, a table (Table S1) listing a recipe for the solution polymerization of DMA, and a table (Table S2) listing the molecular weights and polydispersities of all of the polymer samples synthesized. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0525740