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## Research Article

# Polycation-Capped CdS Quantum Dots Synthesized in Reverse Microemulsions

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This paper is focused on the formation and recovery of cadmium sulfide (CdS) nanoparticles in two different types of polycation-modified reverse microemulsions using low molecular weight poly(diallyldimethylammonium chloride) (PDADMAC) and poly(ethyleneimine) (PEI). Both polymers were incorporated in a quaternary w/o microemulsion consisting of water, toluene-pentanol (1 : 1), and sodium dodecyl sulfate (SDS), as well as in a ternary w/o microemulsion consisting of water, heptanol, and 3-(N,N-dimethyl-dodecylammonio)-propanesulfonate (SB). UV-vis and fluorescence measurements in the microemulsion illustrate the capping effect of the polycations on the formation of the CdS quantum dots. The nanoparticles are redispersed in water and characterized by using UV-vis and fluorescence spectroscopy, in combination with dynamic light scattering. From the quaternary microemulsion, only nanoparticle aggregates of about 100 nm can be redispersed, but, from the ternary microemulsion, well-stabilized polycation-capped CdS quantum dots can be obtained. The results show that the electrostatic interactions between the polycation and the surfactant are of high relevance especially in the solvent evaporation and redispersion process. That means only that in the case of moderate polycation-surfactant interactions a redispersion of the polymer-capped CdS quantum dots without problems of aggregation is possible.

## 1. Introduction

The importance of small, monodisperse semiconductor particles has greatly increased in the recent years, due to the growing interest in technological applications of the resulting materials in electronic devices like solar cells or LEDs [1–4], medical diagnostics [5–7], and photo catalysis [8–10]. The optical, optoelectronic, and magnetic properties of such materials are strongly depending on the size according to the well-investigated size quantization effect [11–14]. Nanoscale semiconductors like cadmium sulfide show a size-dependent onset of light absorption, and a blue shift of the fluorescence band with decreasing particle size. Therefore, the formation of monodisperse cadmium sulfide (CdS), CdSe, or ZnS nanocrystals, so-called quantum dots, is of importance. For the preparation of such materials, different methods can be used, for example, sol-gel [15, 16] or solvothermal [17, 18] and irradiation processes [19, 20]. An important way to synthesize monodisperse nanoparticles of very small

dimensions is to use a template phase. The nanoparticles can be formed in block copolymer micelles or polymer microgels [21–24] in dendrimers or microemulsions [25–31]. Especially microemulsion template phases are widely used as “nano-reactors” to make ultrafine particles [32, 33]. For this process, two w/o microemulsions are mixed together containing reactant A and reactant B, respectively. Hereby, the size of the droplets, and the bending elasticity as well as the rigidity of the droplet film is of importance, due to the fact that droplet diffusion and fusion is the rate-determining step in the microemulsion and not the reaction between the components A and B [31]. Two different mechanisms for the droplet exchange process are discussed in the literature, that is, the water channel mechanism and the droplet coalescence mechanism [34].

By adding polymers one can influence the droplet size [35–37], the droplet-droplet interactions [38–40], and the stability [41] and rigidity [42–44] of the surfactant film in w/o microemulsion due to polymer-surfactant interactions.

Our own experiments have shown that polyelectrolytes can be incorporated into water-in-oil microemulsions, too [45–47]. Molecular dynamic simulations of inverse micelles in presence of a cationic polyelectrolyte have shown that the polymer is located nearby the surfactant film [48]. The polyelectrolyte-modified water-in-oil microemulsions can be used as a template phase for the formation of different types of very small nanoparticles, for example, BaSO<sub>4</sub>, ZnS, gold, and magnetite [49–52].

It has to be mentioned here that it is possible to produce ultrafine CdS nanoparticles inside the microemulsion droplets with a narrow size distribution in absence of an additive [26, 32, 53], but an efficient recovery of the nanoparticles from microemulsion is still an open problem [54]. There are different approaches, for example, water or temperature-induced separation [55, 56], precipitation by antisolvents [57] or surfactants [58], or a so-called cloud point extraction [59], but due to their high surface energy the ultrafine particles tend to coagulate irreversibly during the separation process. Therefore, it is necessary to protect the nanoparticles during the separation and recovery process. To overcome this problem organic molecules can be added to stabilize the particles during the recovery process. Agostiano et al. have used, for example, thiophenol as a capping agent to redisperse CdS nanoparticles in pyridine [26], and Tamborra et al. immobilized octylamine-capped CdS nanocrystals in polymers, that is, poly(methylmethacrylate) or polystyrene [60].

To stabilize nanoparticles in water, polyelectrolytes are of special relevance due to their electrosterical stabilization effect [61, 62]. Therefore, polyelectrolyte-modified microemulsions are of special interest, because of the fact that the polyelectrolytes are already present during the process of particle formation, solvent evaporation as well as during the process of redispersion in water.

This paper describes the influence of two polycations incorporated into microemulsions on the CdS nanoparticle formation process and the possibility to recover the nanoparticles after solvent evaporation and redispersion in water.

The aim of this paper is to learn more about the role of electrostatic interactions in the nanoparticle recovery process.

Therefore, two microemulsions were used: one containing the strong anionic SDS and the other the amphoteric SB.

The formation of CdS in both types of microemulsion is possible by mixing microemulsions containing the corresponding salts, that is, CdCl<sub>2</sub> and (NH<sub>4</sub>)<sub>2</sub>S [63]. The nanoparticle formation was investigated by means of UV-vis and fluorescence spectroscopy, and the redispersed particles were also characterized by UV-vis and fluorescence measurement, as well as dynamic light scattering (DLS).

## 2. Experimental Part

**2.1. Materials.** The poly(diallyldimethylammonium chloride), with a molecular weight of Mw = 21.000 g/mol, was synthesized by radical polymerization. DADMAC (N,N'-Diallyl-N,N'-dimethylammonium-chloride) (65 wt. % in

water) was purchased from Sigma-Aldrich and used as received. The branched Poly(ethyleneimine) with a molecular weight of Mw = 25.000 g/mol was obtained from the BASF. Toluene (>99%; Fluka), pentanol (>99%, Fluka), and heptanol (>99%, Merck) were used without further purification. Sodium dodecylsulfate (SDS) (>99% Fluka), cadmium chloride (CdCl<sub>2</sub>) (>99%, Fluka), and a 20 wt% aqueous solution of (NH<sub>4</sub>)<sub>2</sub>S are used as obtained. 3-(N,N-dimethyl-dodecylammonio)-propanesulfonate (SB) (>97%) was obtained from Raschig company. Water is purified with the Milli-Q Reference A+ water purification system (Millipore).

**2.2. Phase Diagram.** The determination of the isotropic phase range of all systems mentioned above has been carried out by titration of the pseudobinary oil-cosurfactant/surfactant, or oil/surfactant mixture with a 1 wt. % aqueous polymer solution. The mixture was shaken or treated by ultrasonification and optically tested in order to survey a transparent phase region of reverse microemulsions (L<sub>2</sub>-phase).

**2.3. Preparation of CdS Nanoparticles.** CdS nanoparticles are prepared by mixing two microemulsions: one containing 40 mmol/L CdCl<sub>2</sub> and 2 wt% polymer and the other 40 mmol/L (NH<sub>4</sub>)<sub>2</sub>S. The spontaneous induced formation of the nanoparticles in the w/o microemulsion droplets occurs after shaking the received microemulsion mixture of the corresponding precursor salts. Afterwards the mixture was dried under vacuum at 40°C for one week to remove the solvents (water, toluene, pentanol, and heptanol). The received powder was redispersed in water by ultrasonification for further characterization.

### 2.4. Characterization of CdS Nanoparticles

**2.4.1. UV-Vis Spectroscopy.** Absorption spectra are obtained by using a Cary 5000 UV-vis NIR spectrophotometer (Varian) in a wave length range between 200 and 800 nm. For this, the microemulsion samples, as well as the redispersed samples, were placed in a quartz cuvette with a path length of 1 cm.

**2.4.2. Fluorescence Spectroscopy.** Fluorescence measurements are carried out by using a FluoroMax-3 spectrometer (Horiba) in the wave length region between 370 and 700 nm at the excitation wavelength between 340 and 370 nm.

**2.4.3. Dynamic Light Scattering and Electrophoretic Light Scattering.** The determination of the particle size and the particle size distribution by dynamic light scattering measurements is carried out at a fixed angle of 173° (backscattering) at 25°C using the Zetasizer Nano ZS (Malvern), equipped with a He-Ne laser and a digital autocorrelator. The averaged particle diameters were obtained from five separate measurements by using a peak analysis by number, volume, or intensity.

The zeta potential that means the electrokinetic potential at the effective shear plane between the moveable and

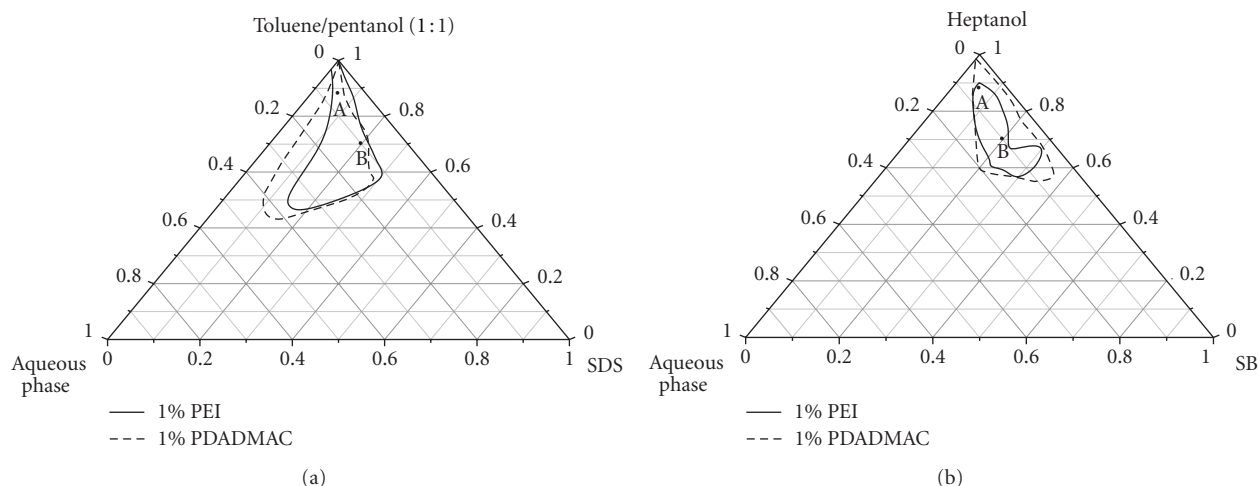


FIGURE 1: Partial phase diagram of the  $L_2$ -phase of the modified quasi ternary system toluene-pentanol (1:1)/SDS/water (a) and of the modified ternary system heptanol/SB/water (b).

nonmovable part of the double layer, was measured by means of the Zetasizer Nano ZS (Malvern) based on the principle of electrophoretic light scattering.

### 3. Results

**3.1. Phase Behaviour.** The partial phase diagrams with PEI and PDADMAC, determined at room temperature, show a transparent phase region of reverse microemulsions ( $L_2$ -phase) in the “oil” corner in all systems (Figures 1(a) and 1(b)). For the quasiternary system toluene-pentanol (1:1)/SDS/water, the  $L_2$ -phase is extended towards the water corner when PDADMAC is incorporated in comparison to the PEI-modified system. The phase range of the  $L_2$ -phase of the ternary system heptanol/SB/water is decreased by replacing PDADMAC with PEI. In both cases the reduction of the  $L_2$ -phase in presence of PEI is accompanied by lower interactions between the branched polymer and the surfactant film.

Furthermore, an extension of the phase range of the  $L_2$ -phase for both polymers in direction to the water corner can be observed in the quasiternary SDS-modified system. This effect can be explained by an enhancement of the bending elasticity of the surfactant film caused by interactions between the anionic surfactants and the polycations.

#### 3.2. Nanoparticle Formation

**3.2.1. Toluene-Pentanol (1:1)/SDS/Water Template Phase.** The formation of CdS nanoparticles has been carried out at Point A with a composition oil/surfactant/water = 88/6/6, that means at a water to surfactant ratio,  $R = 1.0$ . For checking the influence of the droplet size on the results, additional investigations were made at point B (composition oil/surfactant/water = 70/20/10), at  $R = 0.5$ . After elimination of the reference spectra, the absorption spectra are given in Figure 2(a) in absence and in presence of low molecular weight PEI and PDADMAC, respectively.

For poly(ethyleneimine) two pronounced absorption maxima, the first one at 324 nm and the second one at 348 nm, could be observed. Note, that the presence of two absorption maxima could be a hint for the existence of two different particle fractions. However, the fluorescence spectrum for the PEI modified system shows only one well defined band with a maximum at 508 nm (Figure 2(b)), which should be more asymmetric, if there are different particle fractions. Due to that, one can conclude that a surface modification or cluster formation with PEI influence the absorption behaviour of the particles in that characteristic way. Similar absorption and emission spectra were obtained by us with PEI of significant lower and higher molar masses [63].

In comparison a modification with poly(diallyldimethylammonium chloride) leads to a broad shoulder between 390 and 440 nm, similar to the unmodified water system, in good agreement to the results given in references [63, 64]. Fluorescence measurements (Figure 2(b)) show an expanded emission peak between 450 and 800 nm for PDADMAC with a maximum at 690 nm. In both systems the spectra indicate the formation of nanometer-sized CdS nanoparticles, taken into account that the position and the height of the absorption band are well related to the size of the semiconductor particles [26]. For that reason, one can assume a mean particle size range between 2 and 10 nm for the CdS nanoparticles formed in presence of PEI or PDADMAC. Nevertheless, the blue shift of the two absorption bands in the UV-vis spectrum indicates the formation of PEI-capped small CdS nanoparticles with a narrow size distribution, in good agreement with the shift of the emission peak towards the blue region.

Note that similar results were obtained at point B (compare Figure 8 in the Supplementary part), indicating that the droplet size is of minor relevance.

The blue emission colour of the PEI-modified and the orange colour of the PDADMAC-modified systems excited

TABLE 1: Experimental values of the band gap ( $E_g$ ) corresponding to the calculated diameter of the CdS nanoparticles.

System		Wavelength (nm)		$E_g$ (eV)		$d$ (nm) calculated [65]	
Microemulsion SDS based	PEI	324	348	3.83	3.57	2.2	2.5
	PDADMAC	420		2.96		3.6	
Microemulsion SB based	PEI	330	360	3.76	3.45	2.3	2.6
	PDADMAC	380		3.27		2.9	
Redispersion system SB based	PEI	320	350	3.88	3.55	2.2	2.5
	PDADMAC	415		2.99		3.5	

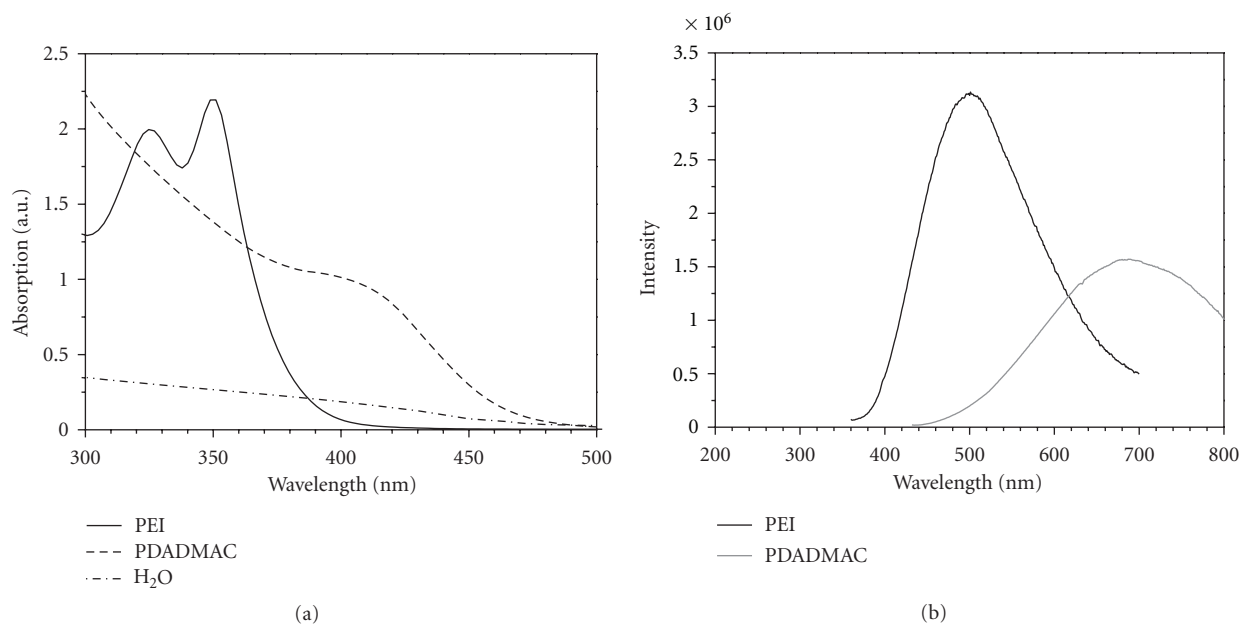


FIGURE 2: Absorption (a) and fluorescence spectra (b) of the microemulsion system toluene-pentanol (1:1), SDS, water after CdS nanoparticle formation in presence of PEI or PDADMAC at point A.

with a near-UV lamp (shown in Figure 9 in the Supplementary Material available online at doi:10.1155/2012/478153) underline the statements given before.

Summarizing the results, one can conclude that the PEI-modified nanoparticles are of about 2 nm, and the PDADMAC-modified ones of about 4 nm in size. This is in full agreement with calculated diameter based on the band gap according to reference [65] summarized in Table 1.

**3.2.2. Heptanol/SB/Water Template Phase.** To compare the characteristics of the CdS nanoparticles synthesized in the ternary system with the nanoparticles synthesized in the quaternary system, the formation of the particles has been carried out in all cases at point A and point B, respectively. In Figure 3(a) the absorption spectra (after elimination of the reference spectra) are given for CdS nanoparticles in presence of PEI and PDADMAC in comparison to the spectrum in absence of a polymer.

The absorption spectra for PEI show two absorption maxima, the first one, weakly distinctive, at 330 nm and the second one at 360 nm. In comparison to the results in the quaternary microemulsion a marginal bathochromic shift of both maxima can be observed. The shoulder,

obtained for CdS nanoparticles modified with PDADMAC, between 350 and 420 nm is shifted to lower wavelengths. The hypsochromic shift indicates the formation of smaller particles in case of the ternary microemulsion system. This can be explained by lower interactions between the amphoteric surfactant and PDADMAC located more in the inner core of the droplets. Due to this the particle growing process inside of the droplets is more restricted. PEI is not going to be affected by this effect, because of the branched structure of the polymer located more in the inner part of the droplet and significant weaker electrostatic interactions. Fluorescence measurements illustrated in Figure 3(b) show a broad emission peak with a maximum at 520 nm. The emission peaks are nearly in the same range already obtained in the quaternary microemulsion. According to these results one can conclude that PEI-capped CdS nanoparticles are formed in the same size range for both systems. This will be confirmed by the blue emission colour of the PEI-modified particles, which is quite similar in both microemulsions (Figures 9 and 10 in the supplementary part).

Fluorescence measurements for PDADMAC modified particles show a broad emission peak between 400 and 700 nm, with an emission maximum shifted to lower wavelengths at 590 nm. Our results show that in comparison

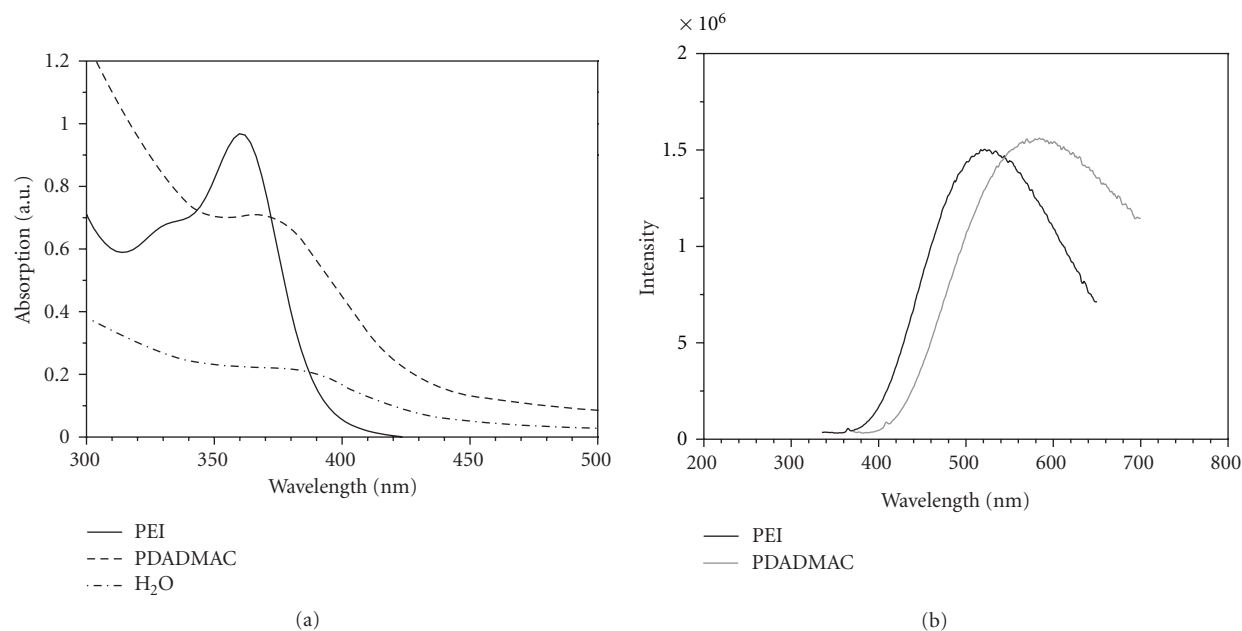


FIGURE 3: Absorption (a) and fluorescence spectra (b) of the microemulsion system heptanol, SB, water after CdS nanoparticle formation in presence of PEI or PDADMAC at point A.

to the PEI-modified system these particles are of course larger, but smaller in comparison to the quaternary SDS-based system. This corresponds with the yellow emission colour (Figure 10 in the supplementary part). Taking into account the emission colour and the fluorescence spectra one can conclude that PDADMAC-capped CdS nanoparticles of about 3 nm have been produced.

At point B similar results were obtained for the PEI-modified system, in contrast to a significant smaller absorption maximum in presence of PDADMAC, disappearing in absence of a polymer. These results underline the additional templating effect of the PEI in the SB-based microemulsion.

It is noteworthy that the different absorption and fluorescence behaviour cannot only trace back to different particle sizes. We also have to take into account that two different polycations, on the one hand branched PEI and on the other hand linear PDADMAC, in two different types of microemulsion, are used. Capping exchange at the nanoparticle surface can also influence the optical properties of the system, as already shown by Tamborra et al. [60]. In general one can conclude stronger electrostatic interactions (illustrated in Scheme 1) of the polycations with SDS, especially for the linear PDADMAC. Therefore, PDADMAC is located at the interphase and stabilize the surfactant film. In contrast, branched PEI, located more in the inner part of the droplet, influences the particle-growing process much more (additional templating effect).

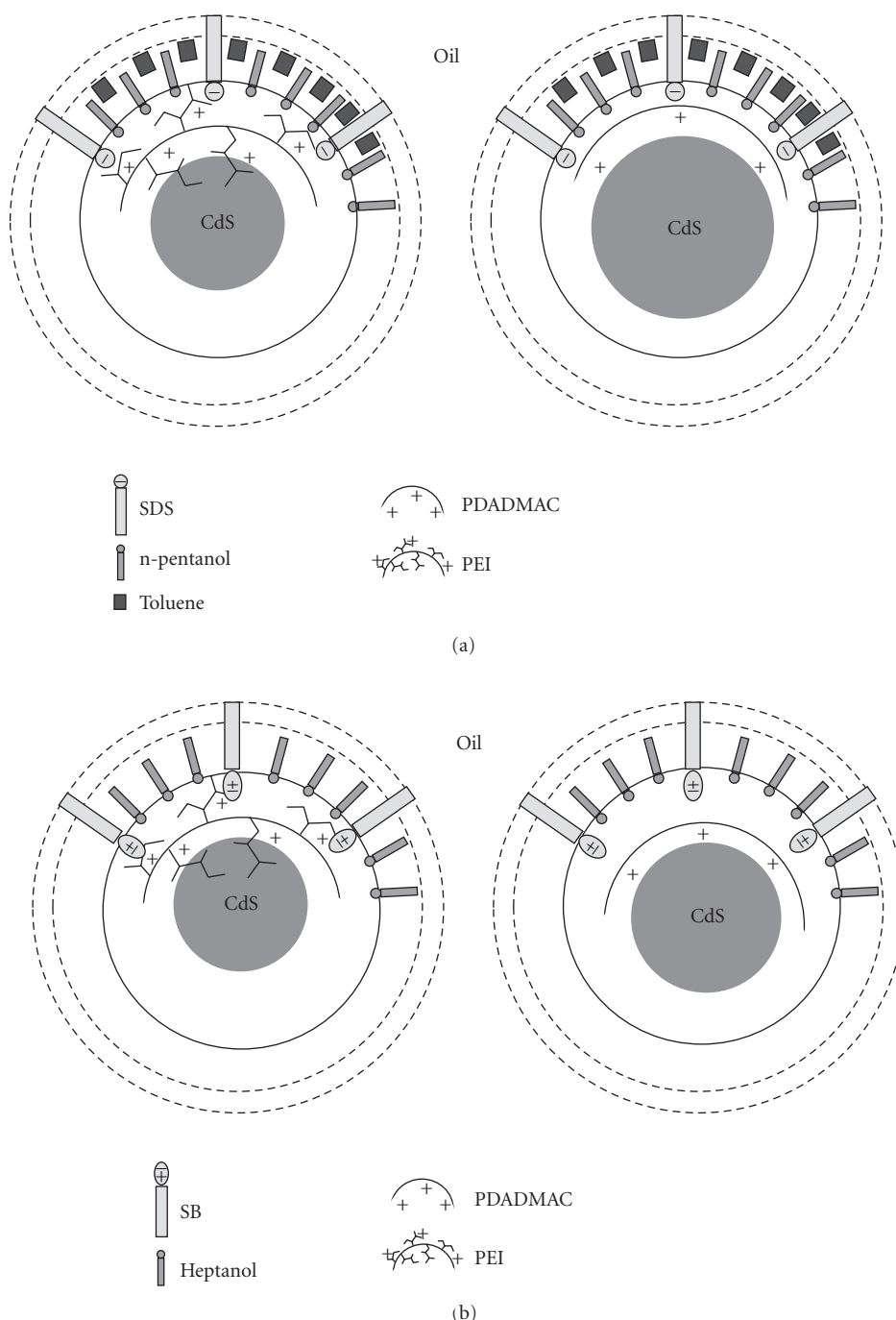
### 3.3. Characterization of the Redispersed Nanoparticles

**3.3.1. Nanoparticles Redispersed from the Toluene-Pentanol (1:1)/SDS/Water Template Phase.** After a complete solvent evaporation, the received powder was redispersed in water by ultrasonification. The obtained turbid solution was

filtrated to separate aggregates and bad stabilized individual nanoparticles. To get more information on the size and surface charge of the redispersed particles dynamic and zeta potential measurements were conducted. The results of dynamic light scattering shown in Figure 4 demonstrate that the diameters of the redispersed CdS nanoparticles are significant larger than the particle dimensions estimated in the microemulsion. Two main particle fractions with diameters of about 440 nm ( $\pm 120$  nm) and 120 nm ( $\pm 20$  nm) can be found for PEI, and of about 270 nm ( $\pm 140$  nm) and 65 nm ( $\pm 20$  nm) for PDADMAC, respectively. According to the results of UV-vis and fluorescence measurements in the microemulsion, one can conclude that individual-polymer capped CdS nanoparticles formed in the microemulsion droplets can be not redispersed after solvent evaporation without particle aggregation. Furthermore, zeta potential measurements show for both polymers a negative value of about  $-50 \pm 2$  mV. Taking into account that SDS (a strong anionic surfactant) is in excess, one can assume that the interactions between the surfactant and the polycations are strong enough to form polycation-surfactant complexes combined by a destabilization of the individual nanoparticles by stripping the polycation from the surface of the CdS particles.

**3.3.2. Nanoparticles Redispersed from the Heptanol/SB/Water Template Phase.** After solvent evaporation, the received powder can be completely redispersed in water by ultrasonification without problems of phase separation. Dynamic light-scattering experiments demonstrate that in the transparent solution only one fraction of nanoparticles can be obtained, with a mean diameter of 10 nm ( $\pm 3$  nm) in presence of PEI and 13 nm ( $\pm 4$  nm) in presence of PDADMAC, respectively (Figure 5).





SCHEME 1: Schematic representation of the location and interactions of the polycations PEI and PDADMAC within the w/o microemulsion droplets of a SDS-based system (a) and a SB-based system (b).

The particles show a positive zeta potential of  $+8 \pm 3$  mV. From this data, one can conclude a polymer adsorption onto the surface of the CdS nanoparticles.

For further characterization UV-vis and fluorescence measurements were conducted. For PEI two absorption maxima could be observed in Figure 6(a), the first one at 320 nm and the second one at 350 nm. A broad shoulder between 390 and 450 nm can be observed in presence of PDADMAC, a hint for larger nanoparticle diameter.

A direct comparison, between the absorption peaks obtained in the microemulsion and the redispersed aqueous

system, shows no significant differences in the PEI system, but a marginal bathochromic shift of the absorption band for the PDADMAC modified system. According to this one can conclude that CdS nanoparticles could be redispersed without a significant change in the particle dimension much better in presence of PEI.

The fluorescence spectrum of the redispersed CdS nanoparticles in presence of PEI is shown in Figure 6(b); for PDADMAC the emission peak is very small and correspondingly not significant. One can see that the emission peak for PEI-capped CdS nanoparticles is shifted to lower

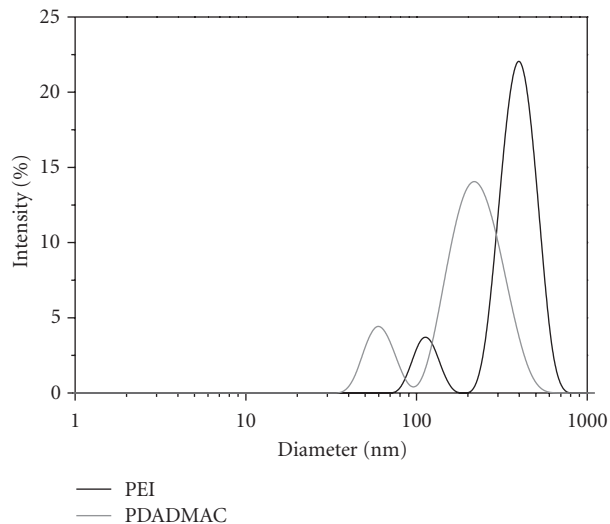


FIGURE 4: Size distribution of redispersed CdS nanoparticles produced in the microemulsion system toluene-pentanol (1:1), SDS, water (PEI) or (PDADMAC) at point A.

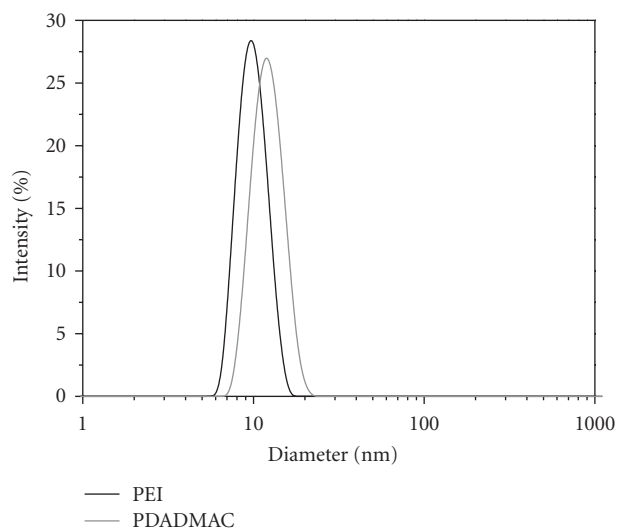
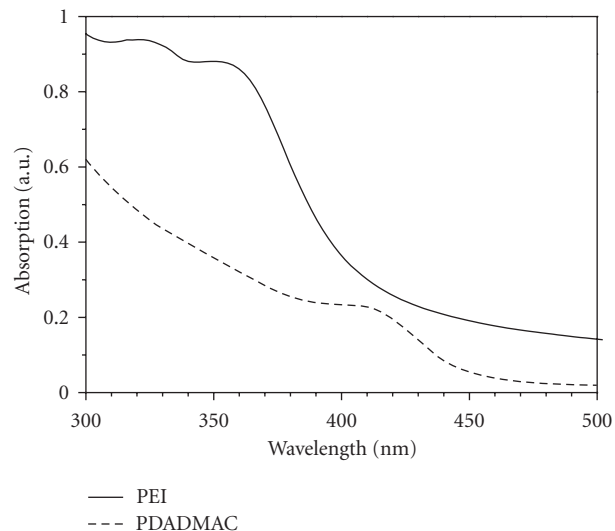


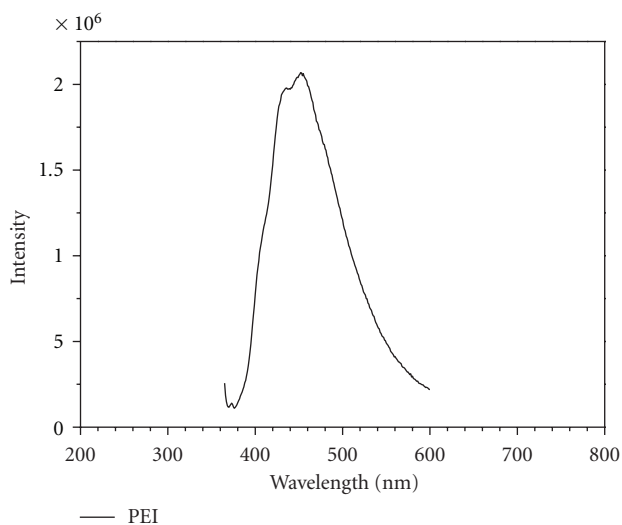
FIGURE 5: Size distribution of redispersed CdS nanoparticles produced in the microemulsion system heptanol SB, water (PEI), or (PDADMAC) at point A.

wave length and becomes more narrow in comparison to the microemulsion. The blue emission colour for PEI supports our finding that PEI-capped CdS quantum dots are redispersed without a change in the particle dimension. According to our assumption that redispersed PDADMAC-capped nanoparticles are larger than in the microemulsion, the emission colour is turned to orange for the redispersed particles, illustrated in Figure 11 in the supplementary part.

Based on the UV-vis spectroscopically obtained band gap the particle size of quantum dots can be determined according to Patidar et al. [65]. The calculated particle size is in the same range as expected according to UV-vis and fluorescence spectroscopy, as well as the observed emission colour (compare Table 1).



(a)



(b)

FIGURE 6: Absorption (a) and fluorescence spectra (b) of redispersed CdS nanoparticles produced in the microemulsion system heptanol, SB, water (PEI), and for the system with PDADMAC at point A.

In order to assure the size and the shape of the particles and explain the discrepancy between DLS and UV-vis data a supporting technique, like transmission electron microscopy (TEM), should be helpful as already shown by Pons et al. [66]. Unfortunately, it is not possible to get some micrographs of these systems with a TEM due to the excess of surfactants. Noteworthy, that CdS nanoparticles produced in a SB-based hexane-pentanol microemulsion could be successfully analyzed only by high-resolution transmission electron microscopy (HRTEM). The particle dimensions of 2-3 nm (shown in Figure 12 in the supplementary part) are also in that case in disagreement with the diameter of  $9 \pm 2$  nm observed in DLS. Inspired by these results we have synthesized in addition CdS nanoparticles in absence of surfactants, that means in a diluted aqueous PEI-solution. By this procedure we were able to produce PEI stabilized

CdS nanoparticles with quite similar properties. However, in that case, that means in absence of surfactants, TEM can be successfully applied. The TEM micrographs (Figures 7(a) and 7(b)) in the supplementary part clearly show that in addition to the individual nanoparticles of about 3 nm (Figure 7(a)) particle aggregates of about 10 nm (Figure 7(b)) exist.

In the heptanol-based microemulsion system investigated here, individual CdS nanoparticles of about 3 nm are redispersed, which aggregated to clusters containing 3–4 nanoparticles. Therefore, one can conclude that in the intensity plot of the DLS experiments predominantly the QD clusters are detected. The existence of two absorption peaks in the UV-vis spectrum can be related to QD's varying in the surrounding medium in dependence on the state of aggregation.

To underline the effect of the polyelectrolytes in the microemulsion template phase as well as in the recovery process we made two additional experiments.

In a “reference” experiment we produced CdS particles in the SB microemulsion in absence of a polyelectrolyte, followed by the solvent evaporation and redispersion in analogy to the procedure described above. In a second experiment we added the polyelectrolyte PEI during the redispersion procedure. The absorption and fluorescence spectra (given in Figure 13 in the supplementary part) clearly demonstrate that in absence of the polyelectrolyte quantum dots cannot be recovered. When the PEI is added during the redispersion procedure, only a marginal part of the nanoparticles can be stabilized.

#### 4. Conclusion

Our results show that the quaternary template phase consisting of water, toluene-pentanol (1:1), and the anionic surfactant SDS in presence of PEI or PDADMAC can be successfully used for the synthesis of polymer-capped CdS nanoparticles. Unfortunately a recovery of the quantum dots without a particle aggregation is not possible due to the strong surfactant polycation interactions.

When the ternary template phase with the amphoteric SB surfactant is used, the polymer-capped nanoparticles produced in the microemulsion template phase can be recovered. That means the individual polymer-capped quantum dots and QD clusters are stable during the process of solvent evaporation and can be redispersed.

The results show on the one hand that the recovery process is only successful when the electrostatic interactions between the polycation and the surfactant headgroups are moderate. On the other hand one can see that the polyelectrolytes should be incorporated already into the microemulsion, because of the additional templating effect of the polymer during the particle formation process, and the protecting effect during the recovery process.

#### Conflict of Interests

The authors declare no conflict of interests with Rashing company.

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