Chapter 3

Synthesis of CdS 'smart' 'Q-Particles' by Amphiphilic Block Copolymers

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3.1. Introduction:

The synthesis of semiconductor nanoparticles or clusters is emerging in the fields of materials science and colloid science because of their wide range of optical and electronic properties.[1] Nanoparticles exhibit unique properties owing to quantum size effects[2] and the presence of a large number of unsaturated surface atoms. During the past decade, many synthetic methods based on polymer materials have been developed, among which synthesis of nano particles in polymer matrix has received significant attention.[3] In Cohen's group, semiconductor clusters were prepared within micro-phase separated diblock copolymer films.[4] Moffitt and Eisenberg also reported well defined CdS nano-clusters in the form of small ionic aggregates prepared from styrene-based random ionomers[5] and styrene-based diblock ionomers.[6] These particular types of nano-domains have been used as stabilizer[7] and nano-reactors.[3] But in the past decades, many people have prepared nanoparticles in micelles formed by amphiphilic block copolymers consisting of a hydrophobic block and a hydrophilic block.[8-9] Control of the location and distribution of the nanoparticles within the micelles is very important for a variety of applications. In most cases, nano particles are prepared in the core of micelles. However, in some cases, the location of the nano particles in the corona region (corona-embedded nano particles) is desired as well.

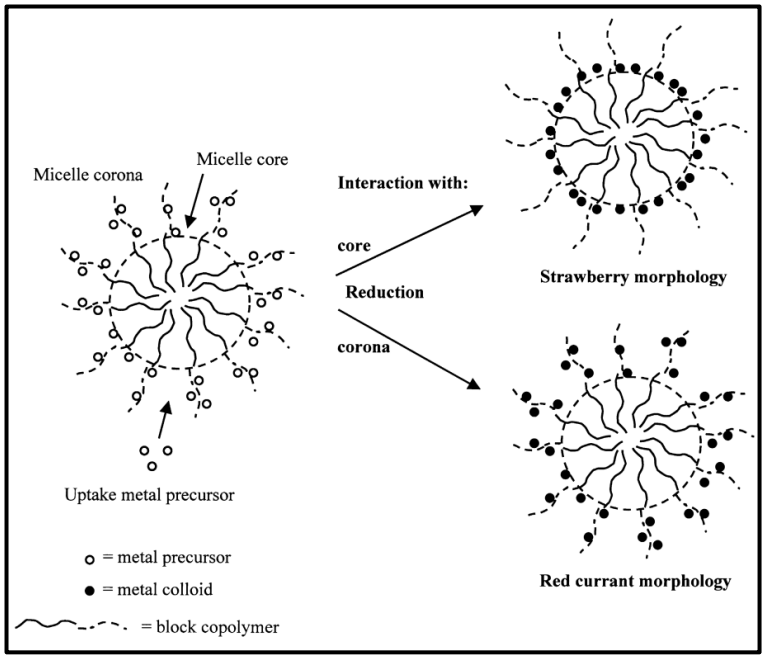
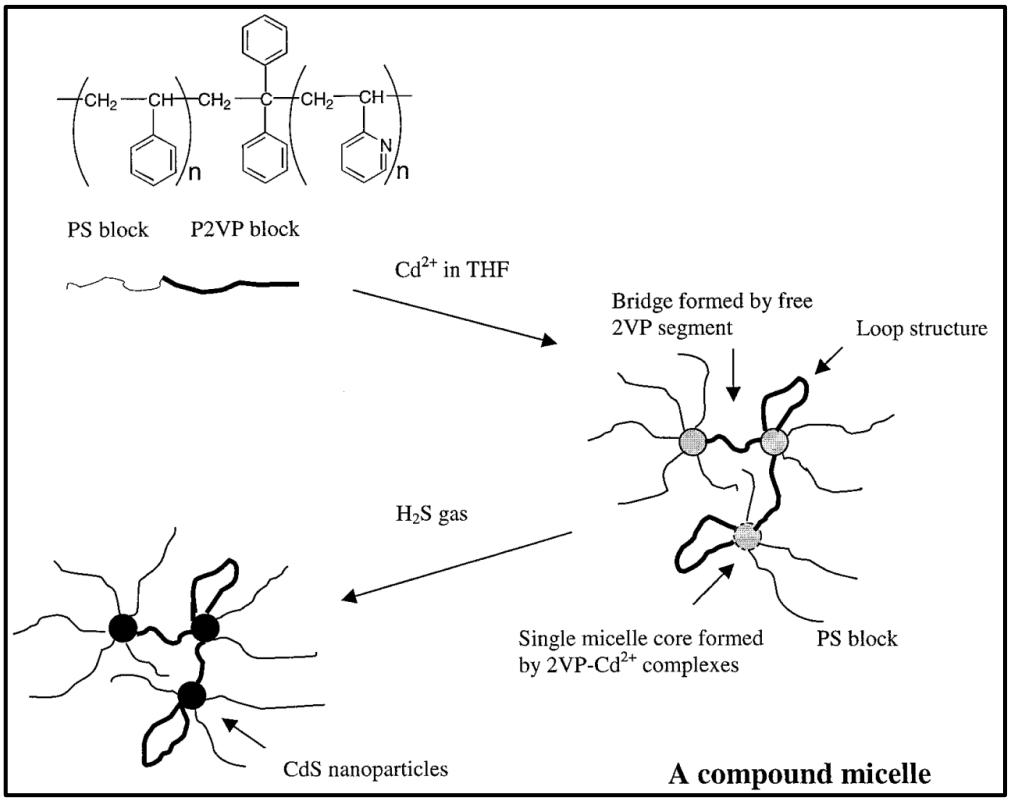


Figure 3.1: Schematic illustration for the preparation of metal nanoparticles within the micelle corona of amphiphilic diblock copolymers, and the resulting system morphologies, "strawberry morphology" and "red currant morphology".[10-11]

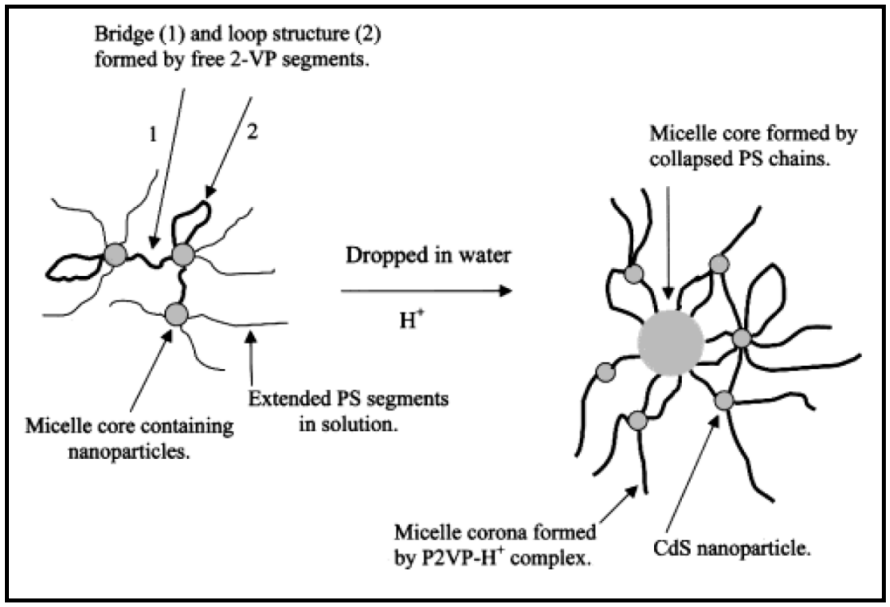
The location of the nano particles in a micelle is determined by the solvent type, the metal precursor type, the reaction conditions, and the interactions between the ions and the polymer.[10] Nowadays a new strategy *i.e.* salt-induced method has been used for the synthesizing of nano particles inside the core as well as within the corona region of polymers[10-11] where salt ions are diffused into the core of the micelle in a nonpolar solvent. Recently several groups have prepared nanoparticles in polymer micelles.[12-13] In this regards, synthesis of core-confined metal colloids in a polar solvent was reported by Mayer *et al*. which also proposed the "strawberry morphology" of the micelles.[10-11] This group also proposed a typical miceller morphology called "red currant morphology" where metal colloids are situated within the corona region.



Scheme 3.1: Schematic representation of the formation of a core-confined micelle and preparation of CdS nano particles in a compound micelle.[14]

In a similar way Zhao and Douglas also reported a synthetic approach for the preparation of semiconductor nanoparticles by salt induced technique where metal colloids are situated both inside the core and within the corona region. They had chosen poly(styrene-b-2-vinylpyridine) (PS-b-P2VP) copolymer for the synthesis of core-confined metal colloids on complexation with cadmium ions (Cd^{2+}) in THF medium.[14] The core confined nano

particle was then prepared on introduction of H_2S gas into the solution. Later, this same group synthesized corona-embedded semiconductor nano particles by transforming the solvent phase from THF to water at low pH. In water, the hydrophobic polystyrene chains get collapsed in the core and each compound micelles associated with poly(2-vinylpriridine) chains resided at the corona region to from a relatively large single micelle (**Scheme 3.1 and Scheme 3.2**).[15]

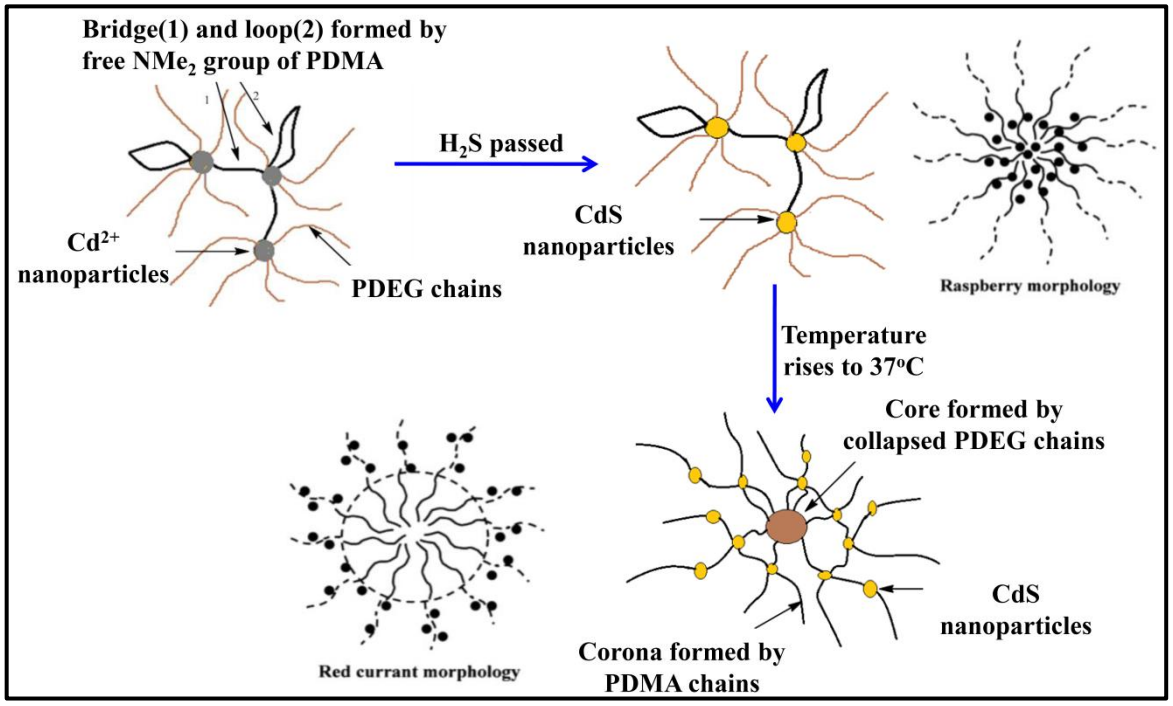


Scheme 3.2: Schematic illustrations for the transition of core-embedded CdS nano particles to corona-embedded CdS nano particles.[15]

Despite well-defined synthesis and stability of both the core-confined and corona-embedded micelle of the above copolymers it has some restriction during application *e.g.* sensor application as change in orientation of the nano particles in the micelle structures is induced by change of solvent.

In our work,[16] I presented a novel method to prepare CdS nanoparticles within salt-induced micelle having controllable size and stability along with the reversibility. The stimuli dependent micelle formation and coordination capability of the (-NMe_2) groups of PDMAEMA block in $PDMAEMA_{10.5k}$-b-$PDEGMEM_{12.5k}$-Cl diblock copolymer have been used for the synthesis of 'smart' $PDMAEMA_{10.5k}$-b-$PDEGMEM_{12.5k}$-Cl/CdS ′Q-particles' hybrid nano structure. The synthesis of the CdS nano particles is carried out using the core of $Cd(OAc)_2$ salt induced $PDMAEMA_{10.5k}$-b-$PDEGMEM_{12.5k}$-Cl diblock copolymer micelle as template, in non-selective THF-MeOH medium. The salt induced micelles of the diblock copolymer is prepared at first in THF/MeOH [70/30 (v/v)] medium by reacting it with

$Cd(OAc)_2$, whereupon the (-NMe_2) groups of the PDMAEMA chains interact with the Cd^{+2} ions and hence remains directed towards the micelle core with PDEGMEM chains at the outside. Next, H_2S gas is bubbled through the medium resulting in the formation of CdS nano particles in the micelle cores. Finally, the 'core-confined' CdS nano particles are transferred into large volume of HPLC grade water (pH 7, at 5°C) and the organic solvent is evaporated off. Inside the miceller aggregates there may be different CdS core 'single' micelles which are interconnected by (-NMe_2) groups of bridging PDMAEMA chains to form compound micelle structures. The stabilized CdS nano particles thus remain directed towards the core of a compound micelle structure, forming a 'core-confined' CdS nano particle system.[14] At pH 7, PDMAEMA chains adopt a partially protonated form, hence non coordinated, protonated (–N^+HMe_2) groups of bridging PDMAEMA chains in a compound micelle structure should exert significant repulsion between positive charges which restricts agglomeration of the CdS cores (**Scheme 3.3**). Thus, 'Raspberry morphology' (**Scheme 3.4**)[10] for the diblock copolymer stabilized 'core-confined' CdS nano particle is proposed.



Scheme 3.3: Schematic illustrations for the formation and the transition of $PDMAEMA_{10.5k}$-b-$PDEGMEM_{12.5k}$-Cl stabilized CdS nano particles from core-confined micelle to corona-embedded micelle.

3.2. Experimental:

3.2.1. Materials:

$PDMAEMA_{10.5k}$-b-$PDEGMEM_{12.5k}$-Cl is used as synthesized. THF (GR, E-Merck, India & HPLC grade Spectrochem, India), Methyl alcohol (GR, E-Merck, India),$Cd(OAc)_2$ (E-Merck, India), Sodium Sulphide (H_2S, E-Merck, India), Hydrogen Chloride (HCl, India) and HPLC grade water are also used as received.

3.2.2. Preparation of diblock ($PDMAEMA_{10.5k}$-b-$PDEGMEM_{12.5k}$-Cl) copolymer:

In a typical sequential chain extension reaction in one pot, 1 ml (1.02 g., 5.42 mmol) of previously nitrogen purged DEGMEM monomer is injected into the septum sealed polymerization tube where $PDMAEMA_{10.5k}$-Cl is present after 9 h of polymerization (98% DMAEMA conversion). The content of the tube is stirred vigorously using vortex stirrer for about 60 min to mix DEGMEM properly with $PDMAEMA_{10.5k}$-Cl macroinitiator. The polymerization is then continued for 14 h at 30°C. The block copolymer, after dilution with THF is precipitated into petroleum ether, stirred well and then the petroleum ether present over the precipitated polymer is discarded. The block copolymer in the residue is redissolved in THF and reprecipitated in petroleum ether. This cycle is repeated for three times followed by drying of the polymer in a vacuum oven for 48 h and finally the monomer conversion is determined gravimetrically. The conversion of DEGMEM monomer in the second step is found to be 80%. The molecular weight of the block copolymer is determined through SEC which results a total $M_{n(SEC)}$ of 23,000 with dispersity (Đ)=1.09. The block copolymer prepared is therefore named $PDMAEMA_{10.5k}$-b-$PDEGMEM_{12.5k}$-Cl. In every similar cases of sequential chain extension experiments, prior to addition of the second monomer, small amount of PDMAEMA is withdrawn from the polymerization tube after opening the septum under constant nitrogen purging for SEC characterization.

3.2.3. Preparation of diblock copolymer stabilized CdS nano particles in aqueous medium:

At first the $PDMAEMA_{10.5k}$-b-$PDEGMEM_{12.5k}$-Cl diblock copolymer (containing 58% of DMAEMA units by mole) is purified from Cu(II) complex contamination by passing a dilute THF solution of it through a basic alumina column and the polymer is isolated after evaporation of THF. Then 0.2 g of the purified $PDMAEMA_{10.5k}$-b-$PDEGMEM_{12.5k}$-Cl, containing 6.70×10^{-4} mol of DMAEMA units, is dissolved in 7 ml THF in a glass vial and the solution is sonicated for 15 minutes. In another glass vial $Cd(OAc)_2$ (3.35×10^{-4} mol) is dissolved in 3 ml MeOH. After that 3 ml of $Cd(OAc)_2$ solution is added to the 7 ml polymer solution in a drop wise fashion at 5°C. The freshly prepared stock solution having 0.02 g/ml

block copolymer concentration is again sonicated for 15 minutes. Then 3 ml of this solution (0.02 g/ml) is taken in another glass vial from the main stock solution and H_2S gas is passed through it very slowly. Thus a yellow colored diblock copolymer (0.02 g/ml) stabilized CdS nano particle system in THF/MeOH medium is prepared. Then 1 ml of this solution is added drop wise in 10 ml of HPLC grade water (pH 7) maintained at 5°C, taken in a different glass vial. The organic solvents are then allowed to evaporate and finally diblock copolymer stabilized CdS nano particles having a block copolymer concentration of 0.002 g/ml in aqueous medium is obtained.

3.3. Characterization:

The UV−VIS spectra of the block copolymer stabilized CdS quantum dots are observed in aqueous solutions (1 mg/ml) from 190 to 1100 nm using a UV−VIS spectrophotometer (Hewlett-Packard, model 8453) at different pH and temperatures. The sample is taken in a quartz cell of 1 cm path length.

The DLS experiments are carried out in a Malvern instrument. The laser source is a He-Ne laser at an angle of 173° equipped with a non-invasive back scatter detector using the method of cumulants. For temperature variation studies, aqueous solution of the diblock copolymer $PDMAEMA_{10.5}$-b-$PDEGMEM_{12.5}$-Cl (2 mg/ml)stabilized CdS quantum dots are heated from low to higher (10°C to 55°C) temperature at a rate of 3°C min^{-1} at pH 7 and the sample is allowed to stand for 5 minutes at every desired temperature, at which size measurement is done. Similarly, size measurement study of the same aqueous solution is done by increasing pH from 7 to 9.2 at 10°C.

The morphology of block copolymer stabilized CdS quantum dots is monitored by TEM instrument (JEOL, 2010EX) operated at an acceleration voltage of 200 kV and fitted with a charge-coupled device camera. A small drop of aqueous dispersion of sample is drop-casted on a carbon-coated copper grid at 5°C and 55°C and finally preserved at vacuum for 2 days before the TEM images are taken.

3.4. Result and discussion:

3.4.1. Analysis by UV/VIS Spectroscopy:

Figure 3.2a shows the UV/VIS absorption spectra of the 'core-confined' CdS nano particles in aqueous medium with variation of pH at 5°C. In neutral water (pH 7), the absorption edge (λ_e) appears at 435 nm with absorption peak (λ_p) at 361 nm. The significantly blue shifted λ_e compared to absorption onset of bulk CdS (515 nm) indicates quantum

confinement of CdS nano particles ('Q-Particles').[14] The CdS nano particle sizes estimated from λ_e value using Henglein's emperical curve indicates CdS nano particle sizes within 3.1 nm.[17] However, when the medium pH is increased to 9.2, the absorption signal becomes significantly broad and λ_e shows red shift to 470 nm [inset of **Figure 3.2a**] indicating increase in particle size up to 4.9 nm. At pH 9.2, largely deprotonated ($-NMe_2$) groups assisted by the flexibility of the PDMAEMA chains may induce extensive bridging interactions between different CdS cores in the compound micelle structure, leading to formation of soft-aggregates of CdS nano particles. This results in broader size distribution of CdS nano particles with red shift in the absorption edge. This structural reorganization of core confined CdS nano particles is however found to occur quite reversibly with variation in pH, as **Figure 3.2a** shows λ_e is again blue shifted to 435 nm when the medium pH is reduced to 7 after dilute HCl addition. The slightly increased absorption intensity with increasing medium pH from 7 to 9.2 might be due to the scattering of incident UV radiation by developed larger aggregates of CdS nano particles and formation of larger particles probably due to inter-miceller aggregates formation after deprotonation of ($-N^+HMe_2$) groups of PDMAEMA. However, upon lowering medium pH back to 7, disaggregation occurs and thus the absorption intensity again decreases. Similarly, a significant red shift in both of λ_p and λ_e to 374 nm and 455 nm respectively is observed when temperature of the 'core-confined' CdS nano particles is increased to 37°C (over LCST of PDEGMEM) from 5°C at pH 7 [**Figure 3.2b**].

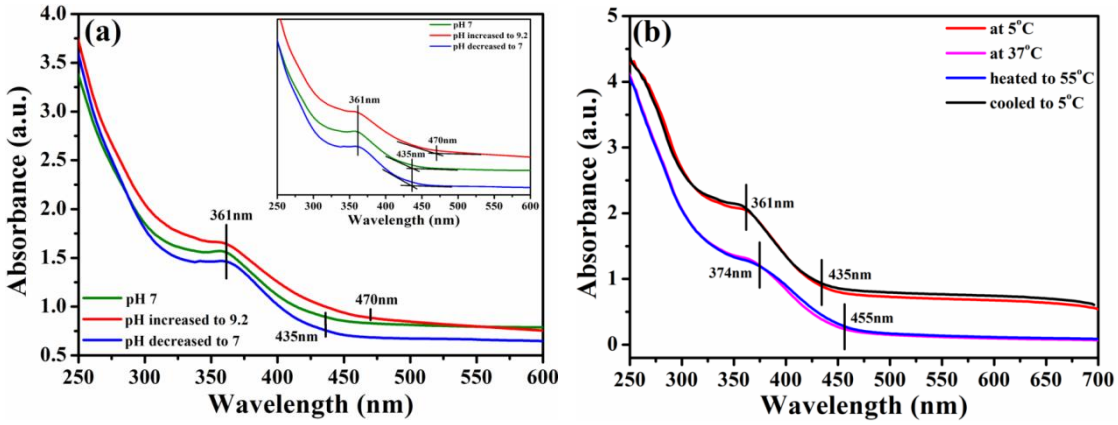


Figure 3.2: UV/VIS spectra of CdS nano particles stabilized by $PDMAEMA_{10.5k}$-b-$PDEGMEM_{12.5k}$-Cl copolymer in aqueous solution: (a) with variation of pH, and (b) with variation of temperature.[16]

However, no further change in absorption position is observed upon increasing the temperature to about 55°C. Furthermore, these changes in absorption positions have been found to occur quite reversibly, which is evident from getting an almost overlapping absorption profile when the temperature is again decreased to 5°C from 55°C. This is attributed to the reversible change in orientation of CdS ′Q-particles' from diblock copolymer micelle core to the corona.[15] Increase in temperature of the aqueous medium over its LCST at this pH value, triggers collapse of the PDEGMEM chains, leading to the formation of single micelles having hydrophobic PDEGMEM chains in the core and PDMAEMA stabilized CdS nano particles in the corona. Thus formation of a 'Red currant morphology'[10] for the diblock copolymer micelle corona embedded CdS nano particles is assumed at 37°C (at pH 7) due to columbic repulsion between positively charged ($-N^{+}HMe_2$) groups present in the PDMAEMA chains. The increase in size of CdS nano particles from 3.1 nm to 3.8 nm upon core to corona migration is attributed to the formation of soft aggregates of CdS nano particles due to inter-corona interactions between the single micelles through non-protonated free ($–NMe_2$) groups of PDMAEMA chains and CdS nano particles. Thermally triggered core to corona migration of CdS nano particles occur reversibly across the LCST of DEGMEM (32°C at pH 7) and further heating to 55°C does not show any change in absorption signals. It may be further noted here that the migration of CdS nano particles from core to corona or the reverse brings a significant variation in the structure and aggregation pattern of CdS nano clusters, which is reflected in the change in both λ_p and λ_e. However, as the CdS nano particles remain all through 'core-confined' during pH variation, only increase in maximum particle size and dispersity occurs due to aggregate formation. The temperature dependent particle size analysis by dynamic light scattering of the $PDMAEMA_{10.5k}$b-$PDEGMEM_{12.5k}$-Cl/CdS′Q-particle' hybrid nano structure is carried out in the temperature range of 10°C–55°C.

3.4.2. DLS Analysis:

The plot is given in **Figure 3.3a**, which shows almost a steady Z-average particle size of about 87 nm up to 27°C during heating from 10°C. However, after this, a sudden decrease in Z-average particle size occurs and reaches to about 61 nm at 36°C which again remains steady up to 55°C. The observed shrinkage in the average size of the hybrid nano structure above the LCST of PDEGMEM further supports the view of change in miceller morphology from larger compound micelles with hydrated PDEGMEM chains in the exterior part to single micelles with dehydrated/hydrophobic PDEGMEM chains towards the micelle core.

Increase in medium pH from 7 to 9.2 at 10°C shows increase in Z-average particle sizes from 85 nm to 211 nm (**Figure 3.3b**), which is attributed to the proposed formation of soft aggregates of CdS nano particle cores inside the compound micelle, triggered by bridging interactions with increased number of deprotonated (-NMe_2) groups and inter-miceller aggregates leading to large particle formation after deprotonation of (-N^+HMe_2) groups of PDMAEMA.

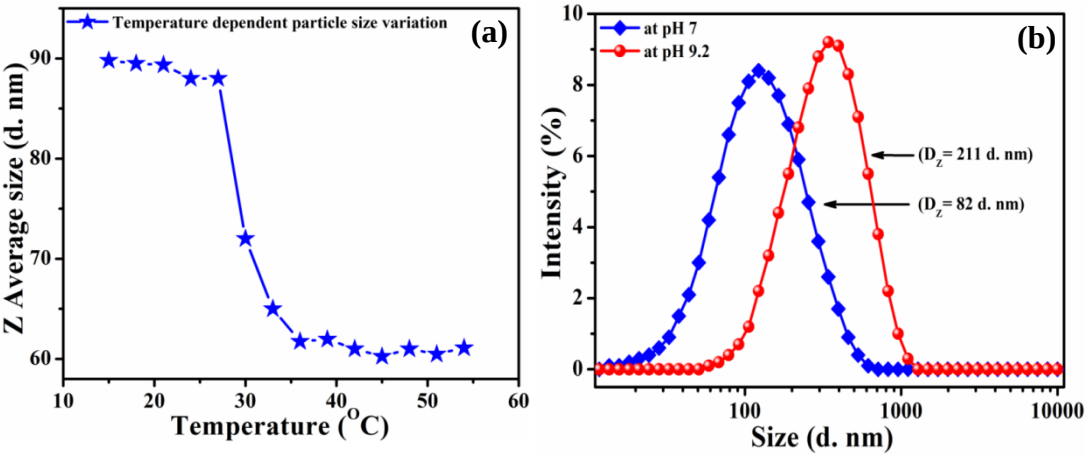


Figure 3.3: Particle size analysis by DLS of the PDMAEMA$_{10.5k}$-b-PDEGMEM$_{12.5k}$-Cl/CdS 'Q-particle' hybrid nano structure, in aqueous medium a) temperature variation in the range of 10°C to 55°C at pH 7, b) pH variation at pH 7 and pH 9.2 at 10°C.[16]

3.4.3. HRTEM Analysis:

Figure 3.4(a–c) shows the TEM micrographs for the above stated 'core-confined' and 'corona-embedded' CdS nano particles. In the 'core-confined' morphology, CdS nano clusters having sizes within 4 nm with individually discernible CdS quantum dots in the range of (0.5–1.5) nm are observed in the interior of large compound micelles having sizes in the range of 40–50 nm. The nano crystalline nature of the core confined CdS nano particles are observed from the fringe pattern or selected area diffraction pattern (SAED), as shown in **Figure 3.5**. This is observed when diblock copolymer stabilized CdS quantum dots is cast from aqueous dispersion (pH 7) at 5 °C. However, when the casting under similar conditions is done at 55°C, a different morphology results, where CdS nano particles are observed in the corona of much compressed micelles having sizes in the range of (10–15) nm as shown in **Figure 3.4(b and c)**. In the 'corona-embedded' morphology, single micelles are formed due to aggregation of PDEGMEM chains at higher temperature (over LCST of PDEGMEM). The presence of hydrophobic, aggregated PDEGMEM chains in the micelle core explain the

shrinkage in micelle size in 'corona-embedded' morphology unlike in the 'core-confined' morphology where rather loose micelle structures are formed due to the presence of water soluble PDEGMEM chains below its LCST. This is also indicated from DLS studies as discussed in the earlier section. **Figure 3.4c** shows enlarged view of aggregates of micelles formed through inter-corona interactions, which should explain the red shift observed in absorption signal during core to corona transition of CdS nano particles.

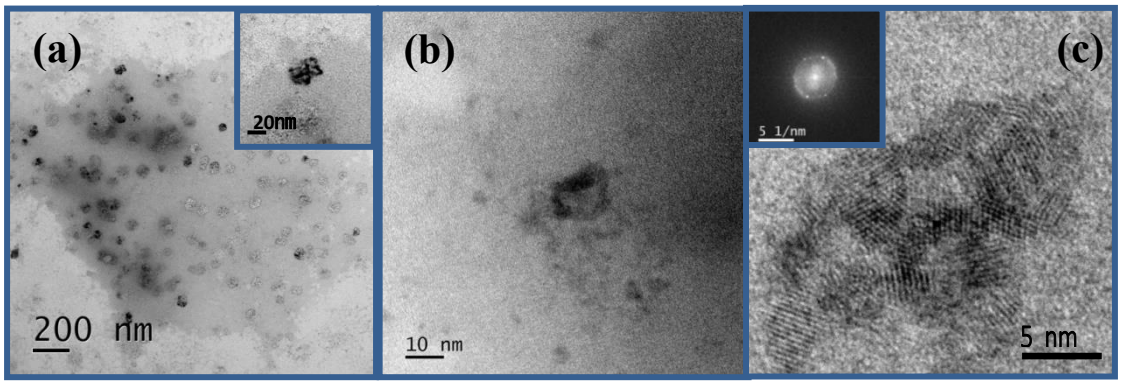


Figure 3.4: TEM micrograph of PDMAEMA$_{10.5k}$-b-PDEGMEM$_{12.5k}$-Cl diblock copolymer stabilized CdS 'Q' particles at pH 7: (a) 'core confined' CdS nano particles when casted from dilute aqueous dispersion at 5°C (b) 'corona-embedded' CdS nano particles casted from dilute aqueous dispersion at 55°C (c) aggregates of 'corona embedded' nano crystalline CdS nano particle as apparent from fringe pattern and SAED pattern (inset).[16]

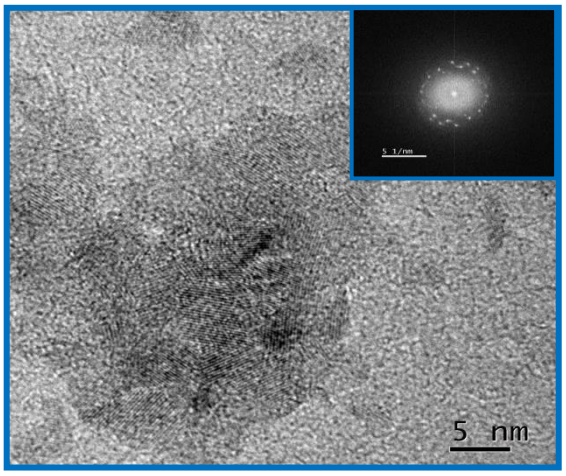


Figure 3.5: Fringe pattern observed in TEM picture of PDMAEMA$_{10.5k}$-PDEGMEM$_{12.5k}$-Cl diblock copolymer micelle core confined CdS nano particles. Inset shows SAED pattern.[16]

The fringe pattern observed along the periphery of the micelles in **Figure 3.4c** and the SAED pattern confirms the nano crystalline nature of the 'corona-embedded' CdS nano particles. Zhao *et al*. have previously reported preparation of 'core confined'[14] and 'corona-embedded'[15] CdS quantum dots using polystyrene-b-polyvinylpyridine (PSt-b-PVP) block copolymer in THF and in aqueous medium respectively. The present work demonstrates reversible migration of CdS 'Q-particles' from micelle core to corona in aqueous medium in a controlled manner with the variation of temperature at neutral pH.

3.5. Conclusion:

The dual stimuli responsive character (pH and temperature) and presence of highly coordinating pendant $-NMe_2$ groups in the block copolymer ($PDMAEMA_{10.5k}$-b-$PDEGMEM_{12.5k}$-Cl) have been exploited for the synthesis of stimuli responsive $PDMAEMA_{10.5k}$-b-$PDEGMEM_{12.5k}$-Cl/CdS ′Q-particle' hybrid nano structure in aqueous medium. The stabilized CdS quantum dots show shuffling of morphologies between 'core confined' and 'corona embedded' with the change of stimuli.

3.6. Reference:

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