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Surface-Initiated Ring-Opening Polymerization: A Versatile Method for Nanoparticle Ordering

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ABSTRACT: The coordination−insertion ring-opening polymerization of ϵ-caprolactone was initiated from amine or hydroxyl groups spread over the surface of silica (ca. 30 nm) or cadmium sulfide (ca. 1.5 nm) nanoparticles, respectively. The initiation selectively occurred from the surface functional groups after activation into aluminum alkoxides species. The covalent grafting of the polyester chains was confirmed by the solubilization of the nanoparticles in organic solvents, e.g., $CHCl_3$ and THF for silica nanoparticles and toluene for CdS nanoparticles, at least when the surface-grafted PCL chains were long enough. In the case of silica nanoparticles, the linear dependence of the PCL molar mass as determined by ^1H NMR analysis on the initial monomer-to-amine ratio confirmed the controlled character of the polymerization. Transmission electron microscopy of thin films of PCL-grafted CdS revealed an homogeneous dispersion of the semiconducting nanoparticles throughout the polyester matrix.

Introduction

Composite materials that contain metal or semiconductor nanoclusters (1−10 nm size) are of interest owing to their applications in optics and electronics.[1,2] However, a major challenge in the preparation of such materials is to avoid both phase separation and clusters aggregation in the host matrix. Polymeric stabilizers have frequently been employed to control cluster size, morphology, and aggregation. Beside the chemical grafting of preformed functionalized polymers or the selective adsorption of copolymers onto the solid nanosized substrate,[3−7] an alternative strategy relies upon polymer grafting by direct initiation of the polymerization from the nanoparticle surface. This so-called "grafting-from" technique results in significantly higher grafting densities since the steric barrier to incoming polymers imposed by the in situ grafted chains does not limit the access of smaller monomer molecules to the active initiation sites.[8,9] By taking advantage of controlled/"living" polymerization mechanisms from ionic and radical initiators,[10−13] the "grafting-from" technique has been applied to grow polymer chains from the support surface using a variety of monomers, resulting in uniform, steady increase in the layer thickness. Living ring-opening polymerization (ROP) of lactones have proved to be very efficient in coating microparticles such as starch granules (5−40 μm)[14,15] and in patterning polyester films on large and planar Au/Si surfaces.[16,17] In this work, we show that ROP of lactones, e.g. ϵ-caprolactone (CL), can be readily initiated from nanoparticles surface, leading to a covalently attached polyester coating and nanoparticle ordering. The lactone ROP involves a "coordination−insertion" mechanism that is controlled in such a way that one can predetermine the number and length of polyester chains growing away from every nanoparticle. Two kinds of nanoparticles have been studied: silica and cadmium sulfide nanoparticles. The former used as model could act as a reinforcing filler to improve the mechanical properties of poly(ϵ-caprolactone) (PCL) and other polymeric matrices (PVC, ABS, SAN, ...) known to be miscible with PCL, while the latter, being semiconductor quantum dots, might display tunable electrooptical properties through their ordering in the polymer matrix.[18−20]

Experimental Section

Surface Functionalization of Silica Nanoparticles. Silica nanoparticles with a diameter of approximatively 30 nm have been kindly provided by Rhodia, France. 3-(2-Aminoethyl)aminopropyltrimethoxysilane was added to a solution of silica nanoparticles (2 g) in 20 mL of xylene. The reaction mixture was then stirred for 3 h at 120 °C. The particles were filtered and washed with xylene before being washed through Soxhlet extraction using a mixture of 1/1 methylene chloride/diethyl ether for 6 h. Finally, the particles were dried under reduced pressure at room temperature for 2−5 h. The grafting percentage was determined from elemental analysis. The weight percentage of silanol groups at the surface of the particles was previously determined by Karl Fischer titration, and the specific surface area of nanoparticles was calculated from BET measurements.

CL Polymerization onto Silica Nanoparticles. The surface-modified nanoparticles (0.15 g) were dried under vacuum before being dispersed in dried THF (8 mL) under stirring. Triethylaluminum ($AlEt_3$, 0.086 mmol) was then added, and the mixture was heated to 40°C under an inert nitrogen atmosphere for 4 h before the addition of CL (0.8 mL, 6.87 mmol). After 24 h, the polymerization was terminated by adding a slight excess of aqueous HCl (1 N). Then, the crude reaction mixture was precipitated in an 8-fold volume excess of heptane. Aluminum residues were extracted by washing the PCL-coated silica nanoparticles in $CHCl_3$ once with a solution of ethylenediaminetetraacetic acid disodium salt buffered at pH 4.8 and twice with demineralized water. After drying, the yield and the monomer conversion were calculated to be respectively 92% and 90.5%.

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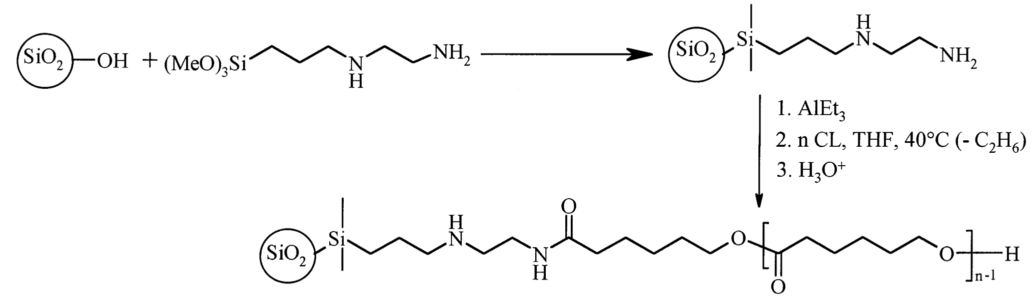
Scheme 1



Preparation of CdS Nanoparticles. In a three-necked round-bottom flask fitted with a condenser, the thio-functionalized ligand (Mercaptoethanol, ME: 18.5 mmol, 1.45 g, 1.30 mL or thioglycerol, TG: 18.5 mmol, 2.0 g, 1.54 mL) was added to a solution of cadmium acetate (18.5 mmol, 4.95 g) in 50 mL of DMF. The temperature was raised to 90 °C, and thiourea (9.25 mmol, 0.28 g) in 5 mL of DMF was then added through a septum. The CdS nanoparticles were recovered either by solvent evaporation (in the case of CdS particles prepared with ME) or by precipitation of the reaction mixture from an excess of acetone/methanol mixture (50/50 v/v) followed by filtration (in the case of TG as a thiol-functionalized ligand).

When TG was used as ligand, the nucleation step and accordingly the thiourea dissociation were very fast. Subsequent growth of CdS particles, which was referred to the propagation step by analogy with polymerization reaction, was in competition with the surface capping reaction by the thiol-functionalized ligands and was also found to be very rapid. In contrast, these steps were slower when using ME as evidenced by both a discrete shift of the maximum absorption wavelength as the nucleation proceeded and the time dependence of the UV−vis absorption.

After their growth, the CdS nanoparticles were recovered either by solvent evaporation in the case of CdS particles prepared with ME or by precipitation of the reaction mixture from an excess of acetone/methanol mixture (50/50 v/v) followed by filtration (in the case of TG thiol-functionalized ligand). The content in surface hydroxyl functions has been determined by a modified Gilman's titration using *n*-BuLi. CdS nanoparticles washed twice with methyl alcohol and acetone were first dried at 90°C under vacuum and then twice trough azeotropic distillation with toluene. CdS nanoparticles were suspended in toluene and reacted with a known excess of *n*-butyllithium. After reaction (2 h at 50 °C), careful filtration was carried out, and the surnatant was hydrolyzed with distilled water. Titration of LiOH was performed with oxalic acid. The content of surface hydroxyl groups was calculated by subtracting the LiOH content from the starting *n*-BuLi content. Actually, the surface hydroxyl concentration is an average value resulting from three separate titration experiments.

CL Polymerization onto CdS Nanoparticles. After an intensive drying under reduced pressure for 16 h at 90°C, CdS nanoparticles (1.48 g) were treated with $AlEt_3$ (5.7 mmol) in 15 mL of dried toluene for 4 h at 50 °C. After sedimentation of CdS nanoparticles, unreacted $AlEt_3$ and solvent were removed out through a stainless steel capillary under a slight overpressure of nitrogen flow. Previously dried toluene (15 mL) and CL (12.6 mL) were then added through a septum, and the polymerization was conducted at 65 °C for 1 week. The polymerization was terminated by adding a slight excess of HCl (1 M), and the suspension was filtered off. The soluble fraction was poured into a 8-fold excess of petroleum ether. The resulting precipitate was filtered off and dried under reduced pressure.

Measurements. FT-IR spectra were recorded on a Nicolet Magma IR-560 spectrometer. ^1H NMR spectra ($CDCl_3$) were recorded on a Bruker DPX-400 MHz. UV−vis absorption spectra were taken onto a Perkin-Elmer Lambda 900 UV−vis spectrophotometer. TEM images were recorded on thin films prepared by solvent casting by using a Philips EM430 scanning electron microscope. TGA thermograms were obtained with a Hi-Res TGA 2950 from TA Instruments.

Results and Discussion

Silica nanoparticles with a diameter of ca. 30 nm were first surface-functionalized by reaction between silanol groups and 3-(2-aminoethyl)aminopropyltrimethoxysilane in xylene at 120 °C for 3 h according to a modified literature procedure.[21] No ammonia or other basic catalyst was added since the condensation reaction is self-catalyzed by the amine groups of the silane derivative. The surface-modified nanoparticles were dispersed in dried THF and added with an equimolar amount of triethylaluminum ($AlEt_3$) with respect to the primary amine functions. The polymerization of CL was then conducted at 40 °C. After 24 h, the polymerization was terminated by adding a slight excess of aqueous HCl (1 N). Monomer conversion was determined by gravimetry after precipitation of the crude reaction mixture from heptane. The overall procedure is shown in Scheme 1.

The covalent grafting of PCL chains onto the nanoparticle surface through amide linkage contributes to the "solubilization" of silica nanoclusters in organic solvents such as $CHCl_3$ and THF, at least when the grafted polyester chains are long enough. Such a behavior demonstrates the efficiency of the "grafting-

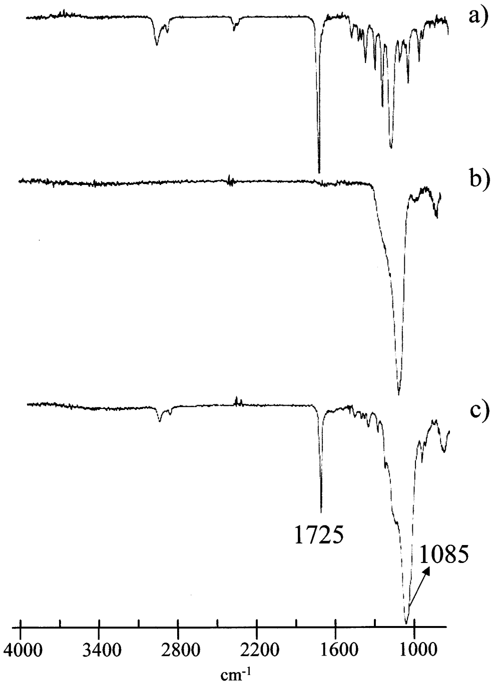


Figure 1. FT-IR spectra of (a) PCL, (b) amine-functionalized silica nanoparticles, and (c) PCL-grafted silica nanoparticles.

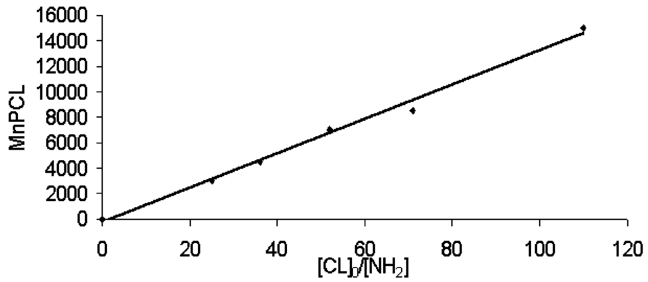


Figure 2. Dependence of the number-average molar mass (M_n) of PCL grafts on the initial monomer-to-amine ratio.

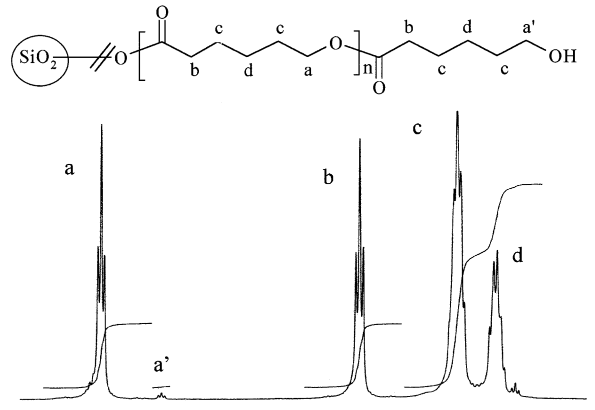
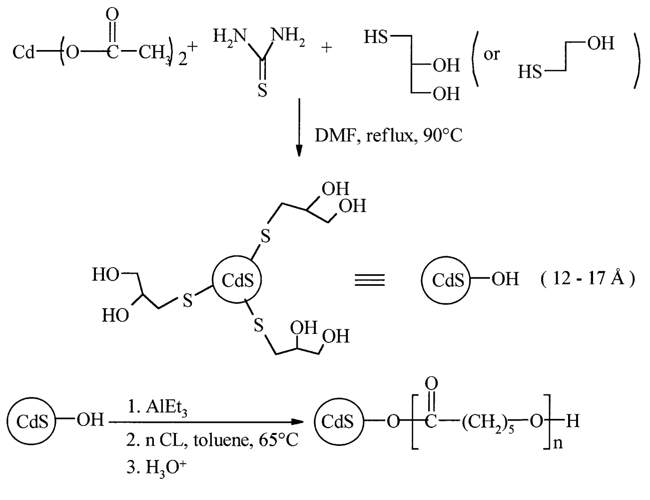


Figure 3. ^{1}H NMR spectrum of PCL-grafted silica nanoparticles in $CDCl_3$.

from" technique. It is confirmed by the FT-IR spectra of the PCL-grafted silica particles compared to the uncoated silica (Figure 1). Though silica particles are characterized by a single broad absorption centered at 1085 cm^{-1} (νSi$-$O) in the investigated frequency range, additional signals can be assigned to PCL vibration modes as assessed by νC$-$H at 2925 cm^{-1}, νC=O at 1725 cm^{-1}, and νC$-$O$-$C at 1000$-$1310 cm^{-1}.

Scheme 2



Actually, the ROP of CL initiated by primary amines, e.g. *n*-butylamine, in the presence of $AlEt_3$ has already been reported by some of us.[22] It has been shown that there is no ethane gas evolved upon mixing the amine with $AlEt_3$ at least under the investigated experimental conditions. Indeed, evolution of ethane requires the addition of CL, and the initiation reaction proceeds through the nucleophilic addition of the primary amine onto the carbonyl group of CL, which is activated by coordination to $AlEt_3$. That addition reaction promotes the ROP of the monomer and the simultaneous evolution of ethane. The propagation step takes place via the aluminum alkoxide end groups and has proved typically "living" when carried out in homogeneous solution. Interestingly, such a control is preserved when the ROP of CL is initiated by the amine functions grafted on the silica particles. Figure 2 shows that the molecular weight of PCL grafts increases linearly and proportionally with the initial monomer/amine molar ratio which gives credit to a well-controlled/"living" process.

Since the PCL chains are covalently grafted onto the silica nanoparticles, techniques such as size exclusion chromatography could not be used. Therefore, the PCL

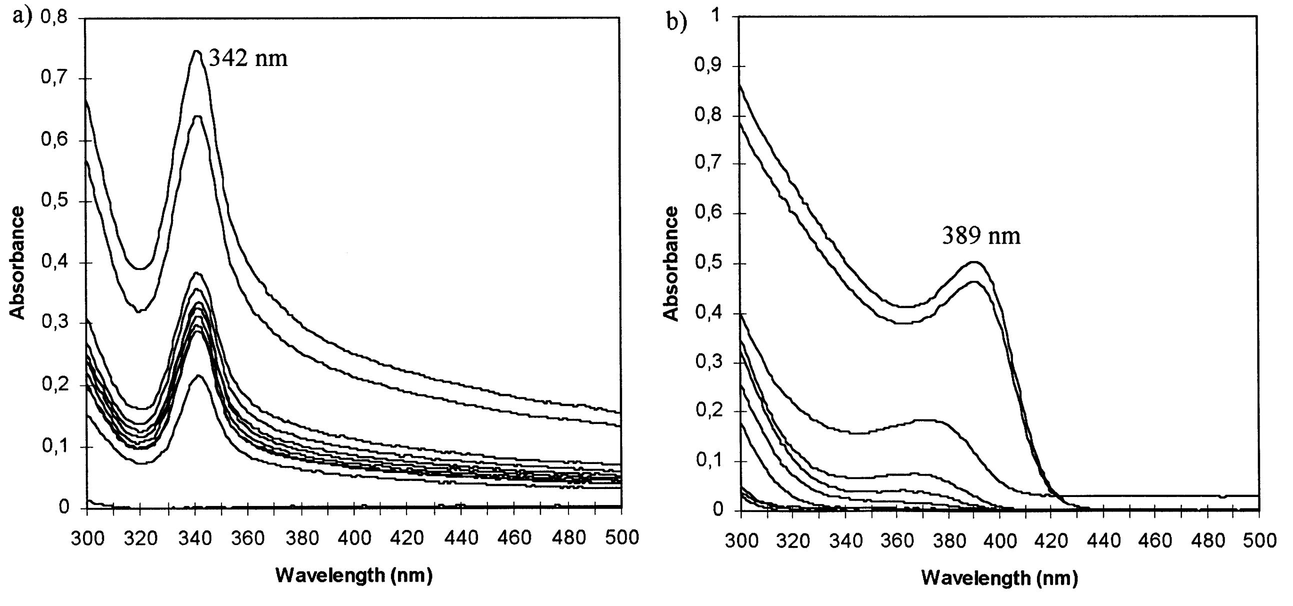


Figure 4. Time dependence of the UV$-$vis absorption spectra of CdS nanoparticles all along their growth with (a) TG (from 0 to 26 h) and (b) ME thiol-functionalized ligands (from 0 to 25 h, absorbance increases with reaction time) (solvent: DMF, 1 mg/mL).

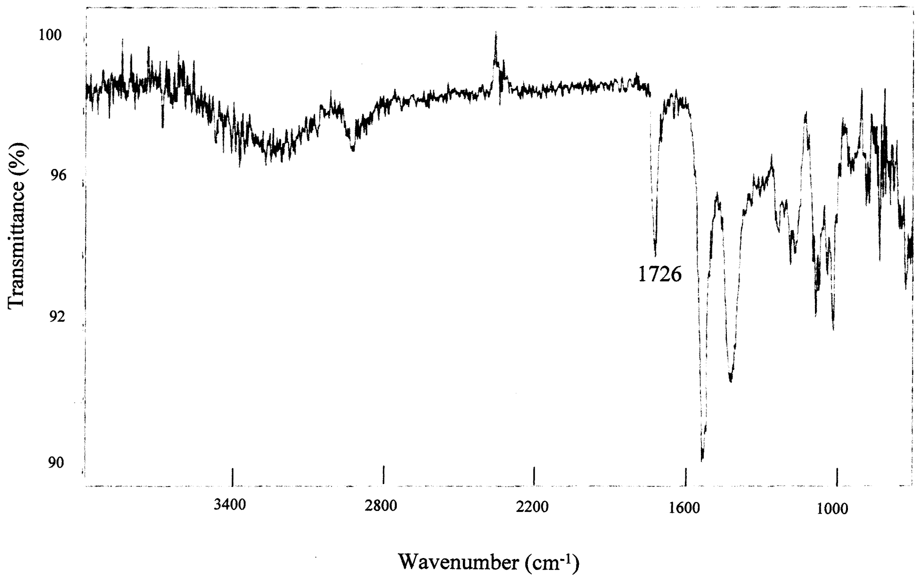


Figure 5. Typical FT-IR spectrum of PCL-grafted CdS nanoparticles.

molecular weight has been determined by ^{1}H NMR spectroscopy (in $CDCl_3$) from the relative intensities of the methylene protons of the repetitive units at 4.06 ppm ($\delta CH_2{-}O{-}C(O){-}$) and the α-hydroxymethylene protons at 3.63 ppm ($\delta CH_2{-}OH$) (Figure 3). It also has to be emphasized that there are as many anchored amide functions as hydroxyl end groups within the limit of experimental errors (±10%).

As far as the cadmium sulfide (CdS) nanoparticles are concerned, their synthesis involves the reaction between cadmium acetate and thiourea in the presence of thiol-functionalized molecules as stabilizers.[23] The core of these nanoparticles is essentially CdS while ligands are covalently and selectively bonded at the surface. In the present work, mercaptoethanol (ME) and thioglycerol (TG) were studied as new ligands capable to in situ react with cadmium acetate and thiourea for producing hydroxy-coated nanoparticles (Scheme 2).

Typically, the reaction was conducted in DMF at 90 °C and monitored by taking aliquots for UV−vis spectrometry analysis until no further changes were observed in the absorption spectra (Figure 4). The relative absorbance of the lowest energy exciton is proportional to the number of formed particles but is independent of the particle size.[24] The mean diameter of the nanoparticles has been determined from the position of the maximum absorption band following the Weller's model.[25] Depending on the nature of the thiol-functionalized ligand, the mean diameter has been estimated to 12 and 17 Å for TG and ME, respectively. In both cases the particle size distribution is monomodal although slightly narrower for TG-based nanoparticles.

The CdS surface hydroxyl groups were activated into aluminum alkoxide species by reaction with $AlEt_3$ (1 equiv) in toluene at 50 °C. The actual organic content was previously calculated from the weight fraction of ligands fixed on the CdS nanoparticles as determined by thermogravimetric analysis (TGA), i.e., 30 and 40 wt % for ME- and TG-based nanoparticles, respectively. To get more precise data on the content of the hydroxyl groups available at the CdS surface, a modified Gilman's titration with *n*-BuLi has been carried out. It comes out that TG-thiol-functionalized CdS contains 2.46 ± 0.68 mmol of reactive hydroxyl groups per gram of nanoparticles. Taking into account the CdS nanoparticle density (d = 4.82) and their mean diameter (12 Å), one can calculate that every particle is coated on the average by 9 ± 2 hydroxyl functions. The polymerization of CL was conducted at 65 °C and terminated by adding a slight excess of HCl (1 N). The suspension was filtered off, and the soluble fraction was precipitated from petroleum ether.

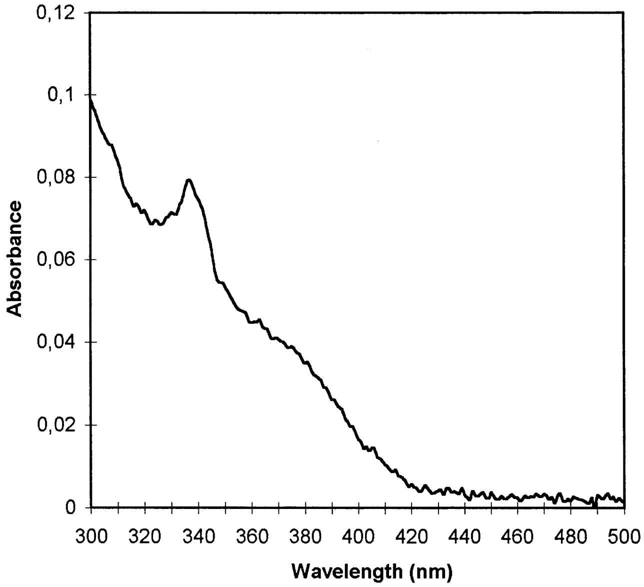


Figure 6. UV−vis absorption spectrum of typical PCL-grafted CdS nanoparticles (shown here for TG-functionalized ligand; in DMF, 1 mg/mL).

FT-IR and TGA analyses carried out on both recovered fractions showed the presence of PCL (Figure 5) with the soluble fraction more enriched in polyester chains. Such observations demonstrate the efficiency of the PCL grafting onto CdS particles and the occurrence of fractionation of PCL-grafted nanoparticles by filtration. Indeed, quantitative "solubilization" of surface-coated CdS particles in toluene can only be achieved when the number and/or the length of the grafted PCL chains are high enough, i.e., M_n above 2500.

Further evidence of the covalent grafting of PCL chains onto CdS surface is given by the UV−vis absorption spectrum of CdS particles after CL polymerization

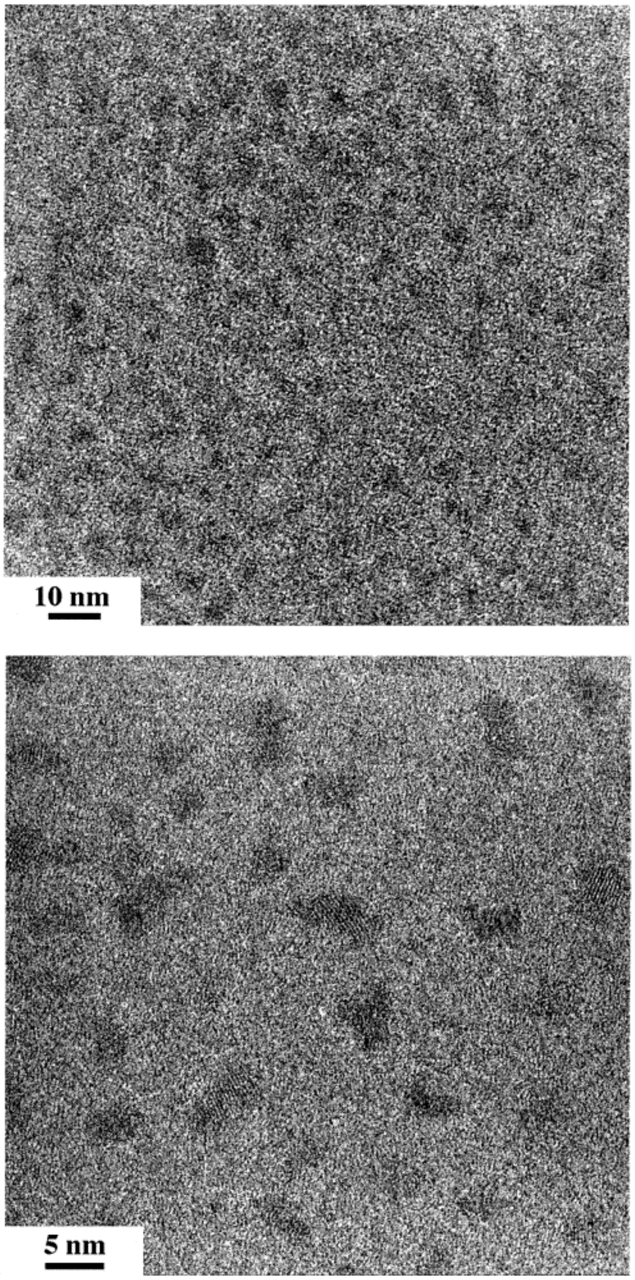


Figure 7. TEM images of a thin film of PCL-grafted CdS as obtained by solvent casting from THF (thiol-functionalized ligand: ME).

with a maximum absorption remaining located at about the same wavelength, e.g., for TG-functionalized nanoparticles (compare Figures 4 and 6).

Finally, transmission electron microscopy (TEM) images of thin films prepared by solvent casting allows to visualize the CdS nanoparticles homogeneously dispersed into the PCL matrix (Figure 7). A mean diameter of 1.5 nm can be estimated while a fine crystalline lamellar structure may be visualized in the dark CdS clusters.

Conclusions

In conclusion, this work shows that the ROP of lactones, and particularly CL, as promoted by the so-called "coordination–insertion" mechanism is a versatile method for stabilizing and ordering nanoparticles. The ROP of CL promoted by aluminum alkoxide active species allows for the polyester chains grafting onto nanoparticles with primary amine or hydroxyl functions spread over their surface. The grafting of PCL chains has been evidenced by the nanoparticles "solubilization" in organic solvents such as chloroform. Interestingly, TEM recorded over a thin film of the polyester-coated CdS nanoparticles displays homogeneous dispersion of CdS clusters within the polyester film.

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