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Synthesis of Thiol-functional Polycaprolactones and their Use in the Preparation of CdS Nanoparticles

Géraldine Carrot[1], Christopher J. G. Plummer[1], Mikael Trollsås[2], James L. Hedrick[2], Jöns G. Hilborn[1*]

[1]Polymer Laboratory, Department of Materials Science, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

[2]Center of Polymeric Interfaces and Macromolecular Assemblies, IBM Research Division Almaden Research Center, 650, Harry Road, San Jose CA 95120-609, USA

SUMMARY: Nanosized CdS particles with diameters in the quantum confinement range (20 to 50 Å) have been prepared using thiol-functional polyesters as ligands. Well-defined polycaprolactones with mercapto end groups were synthesized by Ring Opening Polymerization (ROP). Functionality was introduced either by end coupling or by means of a functional initiator. We show that the ω-hydroxy end group can be converted to thiol through esterification with an aliphatic mercapto acid, provided that the thiol group is protected. Another approach made use of mercaptoethanol, protected in the same way, as a functional initiator for the polymerization of caprolactone. The CdS particle forming reactions have been carried out in DMF using thiourea as the sulphurizing agent and thiol-functional polyesters as the stabilizer. The resulting nanoparticles, with tunable size and optical properties, remained stable in solution for several months. After film casting, homogeneously distributed CdS single crystals could be observed by transmission electron microscopy.

Introduction

The synthesis of well-defined functional polymers has attracted considerable interest owing to their use in the structural control of material surfaces with great potential in applications such as adhesion, biotechnology and microelectronics[1)]. They permit better adhesion of the polymer chains to the surface by forming a covalent bond with the substrate[2,3)]. This is the physical basis for the construction of thermodynamically stable entities with nanoscale

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[*] To whom correspondence should be addressed

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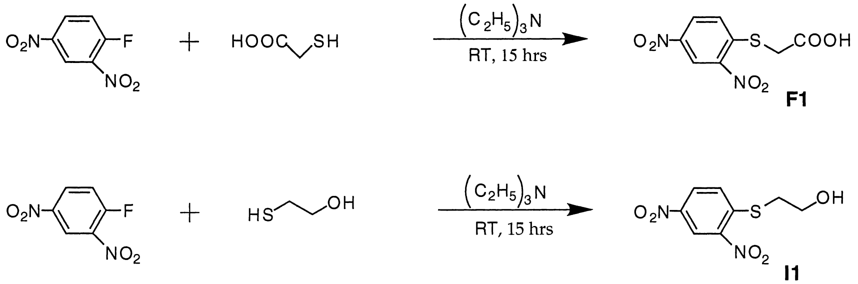
structure and order, consisting of a polymer on one side, and metal or semiconductor nanoparticles on the other. These new entites are particularly interesting since they combine the properties of the polymer and the nanoscale inorganic materials (mechanical properties, electronic and optical properties). They also offer the possibility of self-organization of semiconductor nano-sized clusters exhibiting quantum confinement[4-6)] in a polymer matrix.

The high reactivity of sulfur with many inorganic species such as gold, silver and cadmium has provoked interest in the use of molecules containing a free thiol[7-10)]. In this paper, we describe the synthesis of linear thiol-functional polycaprolactones (PCL) which are then used as polymeric ligands for the preparation of semiconductor CdS nanoparticles. We report on two versatile methods for the thiol-functionalization of polycaprolactone obtained from ring opening polymerization (ROP)[11)]. One consisted of the conversion of the ω-hydroxy end-group of the polyesters to a thiol group through esterfication with Sangers reagent protected mercaptoacetic acid, followed by a deprotection reaction. Polycaprolactone macromonomers have been synthesized using a similar approach with methacrylic acid[12)]. Alternatively, an α-functionality can be introduced by using functional initiators obtained from an exchange reaction of the alkoxy groups of $Al(^{i}OPr)_3$ with the desired alcohol[13,14)]. Likewise, the second method involved the use of an initiator containing a protected thiol group.

This thiol-functional polymer was then used as ligand capable of reacting in-situ with the CdS particles during synthesis, becoming covalently bound to the cadmium surface ions. Distinct supramolecular entities (CdS-g-PCL) of several nanometers in size consisting of a CdS crystal core surrounded by covalently end-linked PCL chains of controlled molecular weight, have been obtained.

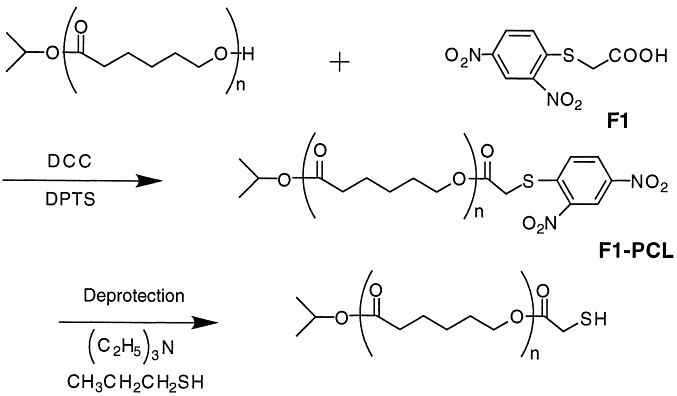
Synthesis of the polycaprolactone ligands

Both methods, end-functionalization and functionalization from initiation, necessitate the protection of the thiol group prior to the esterification or the polymerization. 2,4-Dinitrofluorobenzene, known to selectively protect the sulfhydryl group in cysteine in the presence of an amine[15,16], was selected as the protecting group since it can be quantitatively removed from an exchange reaction using mild conditions[17]. In addition, it does not interact with the polymerization process and it provides an excellent handle for characterization of the degree of functionality by ^{1}H NMR and IR spectroscopies. The protection itself involved the aromatic nucleophilic substitution of the activated fluoride of 2,4-dinitrofluorobenzene by the thiol of mercaptoacetic acid or mercaptoethanol catalyzed by triethylamine (Scheme 1)[18]. Recrystallization of the crude product from $CHCl_3$ gave **F1** and **I1** as yellow crystals in high yields.



Scheme 1: Synthesis of α-(2,4-dinitrophenylthio)acetic acid, **F1** and α-(2,4-dinitrophenylthio)ethanol, **I1.**

Functionalization was then carried out through the esterification of **F1** with hydroxyl-terminated polycaprolactone (PCL) in the presence of DCC (Scheme 2). After filtration of the urea, due to the dissociation of DCC, the thiol-functional PCL (**F1-PCL**) was recovered by precipitation in cold methanol. Analysis from ^{1}H NMR and infrared spectroscopies showed that the extent of functionalization was close to quantitative (Table 1).



Scheme 2: Esterification of the PCL hydroxy end group with **F1.**

Table 1. Characteristics of the functionalized polymers from end-functionalization (esterification with F1)

Sample	Precursor		Type	M_n	I (M_w/M_n)	%
	M_n	M_w/M_n		NMR	GPC	-S- function
3A3CL1	3600	1.16	protected	3500	1.22	98
3A3CLS1	3600	1.16	deprotected	3750	1.25	89
3A3CL2	2850	1.23	protected	2900	1.25	98
3A3CLS2	2850	1.23	deprotected	3200	1.26	90
5A4CL1	5700	1.14	protected	5600	1.22	89
5A4CLS1	5700	1.14	deprotected	5800	1.26	78

The deprotection of **F1-PCL** involved an exchange reaction between the protected thiol chain-end and a large excess of mercaptoethanol in the presence of triethylamine (Scheme 2)[19]. Table 1 gives the characteristics for the various **F1-PCL** which have been prepared. The molecular weights and the polydispersities (M_w/M_n =1.2) of the initial hydroxy terminated polyesters was essentially not affected by the coupling reaction demonstrating the selectivness of the reaction and the absence of disulphide formation. The degree of functionalization and the exact molecular weight have been determined from ^{1}H NMR spectroscopy.

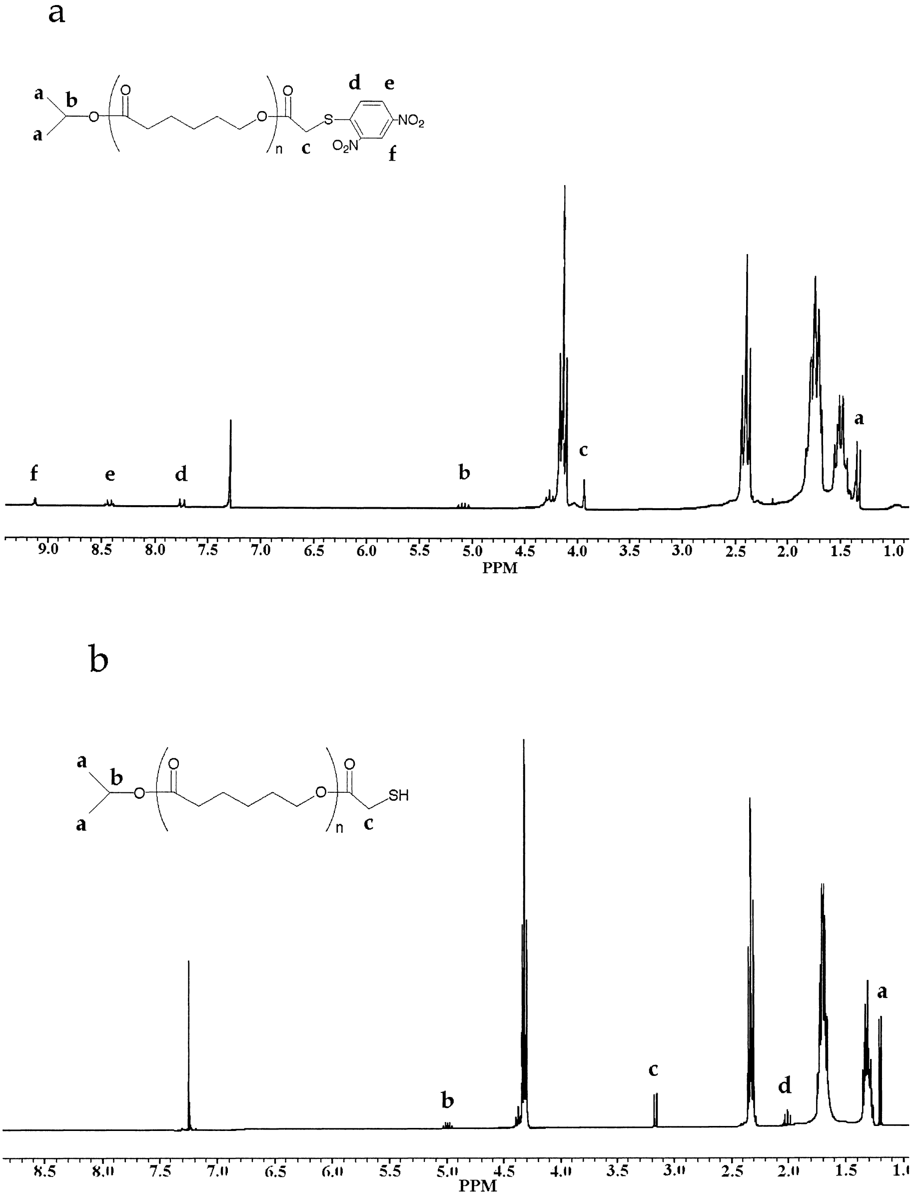
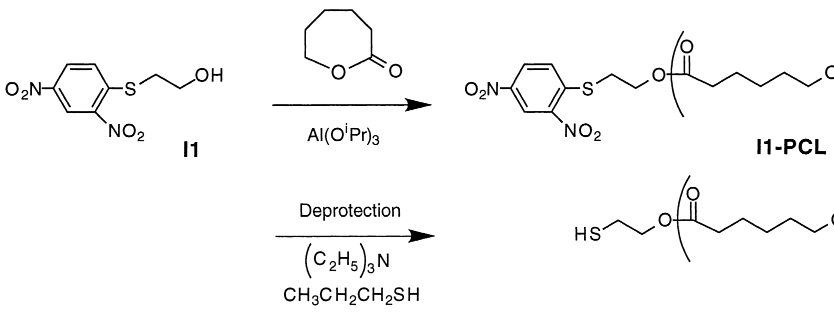


Fig. 1: ^{1}H NMR of the thiol-functional PCL (**F1-PCL**) prepared from end-functionalization, with the thiol protected (top, a) and deprotected (bottom, b).

Figure 1a shows the spectrum of the polycaprolactones with a protected thiol end-group. The peaks due to the methine proton in the isopropyl chain end give rise to a multiplet (**b**), while the two sharp peaks (**a**) come from the isopropyl methyl groups. The peaks corresponding to the α-(2,4-dinitrophenylthio)protons (**d**, **e**, **f**) are observed at δ 7.77 (d), 8.41 (dd) and 9.09 (s) ppm, respectively, while the methylene group located between the sulfur atom and the ester group appears in the spectrum as a singlet at δ 3.9 ppm (**c**). Spectrum in Figure 1b demonstrated the successful deprotection reaction with a complete disappearance of the α-(2,4-dinitrophenylthio)protons' peaks and a splitting of the **c** peak (methylene in the α-position to the ester) at 3.23 ppm due to coupling with the thiol proton. This latter (**d** peak) clearly appears as a triplet at 2.01 ppm.

The functionalization from initiation involved the use of a functional initiator which contains a protected thiol group. The polymerization can then be carried out from α-(2,4-dinitrophenylthio)ethanol, **I1** (Scheme 1) reacting with Al(^{i}OPr)$_3$, followed by an azeotropic distillation of the toluene/2-propanol mixture (Scheme 3). Because of the poor solubility of this new functional initiator, the polymerization was then performed in the bulk.



Scheme 3: Polymerization of ε-CL from **I1**.

Table 2 summarizes the characteristics of the polyesters obtained from the functional initiator, (**I1-PCL**). Again the thiol-functionalization could be controlled from ^{1}H NMR (spectrum not shown). The peaks due to the protecting group are clearly identified at low fields along with the two methylene groups originating from **I1** between 4.5 and 3 ppm.

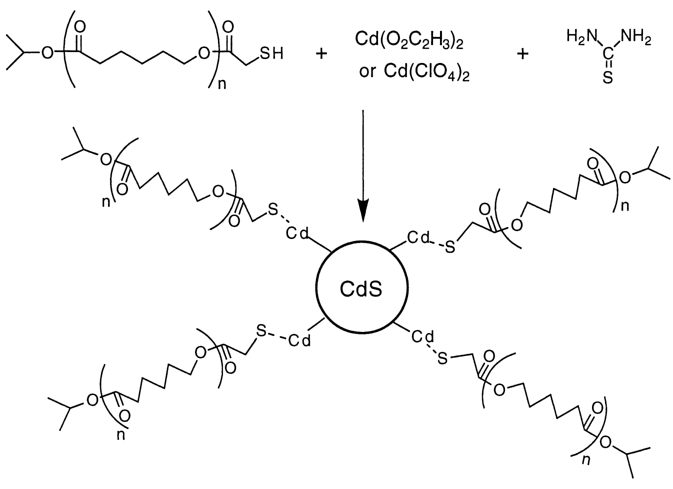
Table 2. Characteristics of the polymers functionalized from initiation (**I1**)

Sample	Initiator	Catalyst	Type	M_n NMR	I (M_n/M_w) GPC
3I1CL1	I1	$Al(O^iPr)_3$	protected	3000	1.25
3I1CLS1	I1	$Al(O^iPr)_3$	deprotected	2900	1.28
5I1CL1	I1	$Al(O^iPr)_3$	protected	4000	1.25
5I1CLS1	I1	$Al(O^iPr)_3$	deprotected	4000	1.26

The same deprotection reaction as described previously, was used here. The ^1H NMR spectrum of the resulting thiol-functional polymers confirmed the disappearance of the protecting group and the presence of the thiol functionality. GPC spectra presented no differences before and after deprotection that would account for disulphide formation.

Synthesis of the polycaprolactone-grafted cadmium sulfide nanoparticles

Cadmium sulfide (CdS) particles (below a size of 10 nm) have been synthesized from cadmium acetate and thiourea in organic solvent such as DMF or THF using small molecules containing a thiol moiety as stabilizers[20-22)]. In this work, a similar reaction has been carried out using thiol functional polycaprolactones as "macroligands". The synthesis consists of a competitive reaction between CdS cluster growth and surface capping by the macroligands where the thiol is directly attached to cadmium (Scheme 4).



Scheme 4: Preparation of CdS-g-PCL clusters

When the particles are formed, they show an absorption maximum in the ultraviolet-visible (UV-vis) spectrum. In Fig. 2, it is shown that this absorption peak increases which is due to an increased number of particles. UV-vis absorption can then be used to monitor the reaction kinetics.

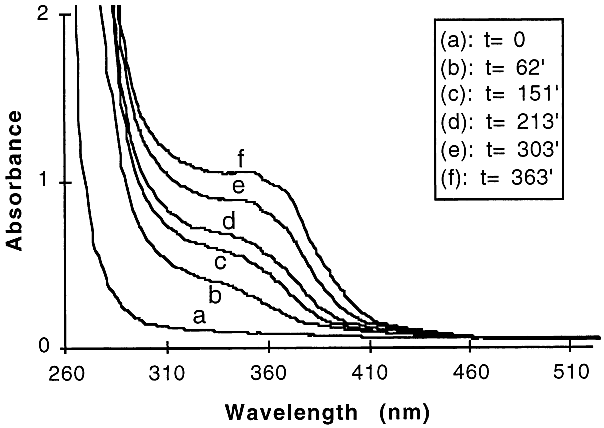


Fig. 2: Evolution with time of the absorption spectra of the CdS particles stabilized with thiol-functional PCL.

The position of the absorption peak may also be linked to the CdS particle size[23)]. We have shown that it was possible to control the particle size by adjusting the ratio thiourea to macroligand (S/SH ratio). By increasing this ratio, the synthetic procedure led to larger CdS particles[24)].

Characterization by gel permeation chromatography (GPC) permited the determination of the amount of chains effectively grafted to the particles. It was found that the refractometric response was different between the CdS-g-PCL and the corresponding PCL precursor, while the elution peak was the same in both cases indicating that only the free polymer left the column. From this difference, we can estimate the amount of non-grafted chains. Our first results showed that the number of grafted PCL chains increased when the amount of cadmium and also S/SH was increased. However, increasing S/SH to a certain extent led to less efficient stabilization then to partial agglomeration.

These soluble entities can also be cast into thin films demonstrating the self-organization and the success of the approach. Figure 3 shows the morphology of films cast from a CdS-g-PCL solution in THF. Homogeneously distributed nanometer-sized CdS particles are seen as black dots in the PCL matrix.

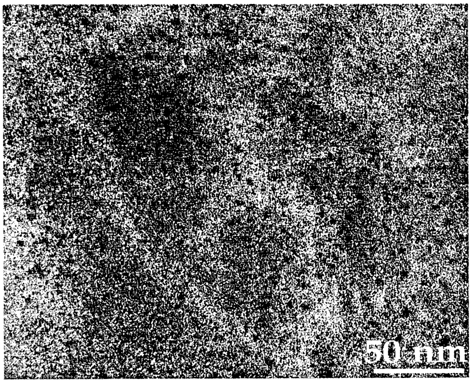


Fig. 3: Transmission electron microscopy (TEM) micrographs of CdS particles with PCL ligands cast from THF.

Conclusion

Successful new techniques based on ring opening polymerization for the synthesis of thiol-functional polymers have been presented. Well-defined PCL containing a mercapto end-group were then used for the stabilization of CdS semiconductor nanoparticles. Characterization showed that the preparation of these supramolecular entities could be performed with high degree of control (size of the particles, interparticle distance in the polymer matrix).

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