Two General Methods for the Synthesis of Thiol-Functional Polycaprolactones

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ABSTRACT: We report here two different methods for preparing thiol-functional polymers. The first method consists of esterifying the hydroxyl-terminated polyesters with a thiol-protected mercaptoacetic acid. The Sangers reagent (2,4-dinitrofluorobenzene) was used to protect the mercaptoacetic acid and was removed with mercaptoethanol under mild conditions. The second technique involves the preparation of a protected thiol-functional initiator, the α-(2,4-dinitrophenylthio)ethanol, that could then be used in the polymerization of ϵ-caprolactone. This "functionalization from initiation" technique could also lead to the preparation of well-defined multibranched polymers with a thiol group at the focal point after the polymerization with a mercapto-initiator carrying dihydroxy or tetrahydroxy functionalities as initiating sites. The ultimate motivation in the preparation of such functional polymers is to elaborate nanocomposites by using the polymers as macroligands in the synthesis of nanoparticles.

Introduction

The manipulation and control of surface properties of polymeric thin films has been an important theme in many areas of research including biotechnology, microelectronics, microfabrication, and others.[1]

Our interest here is in using thin polymer films to tailor curved surfaces. In particular, we are interested in supramolecular arrangements based on nanoscopic entities, such as semiconductor nanosized clusters capable of self-assembly. Such heterosupramolecular entities should consist of macromolecular ligands attached to the cluster surface. One way to tailor surface properties is the deposition of thin polymeric films, and most examples are based on physisorption of either homopolymers or block copolymers.[2] Typically, for such films the interaction between the surface and the polymer is not strong, and desorption can occur in a good solvent or as a result of other compounds competing for the adsorption sites.

Alternatively, grafting of polymers to the surface by forming a covalent bond provides significantly greater adhesion of the polymer chains to the substrate.[3] This "grafting to" technique has been accomplished by end-functionalized polymers that react with a substrate, for example, silane-functional polymers grafting to silica surface,[3d,e] peptides grafting through the amide linkage to appropriately substituted substrates,[3f] and thiol-functional polymers grafting to gold-coated substrates.[3g] Indeed, the high reactivity of sulfur with many inorganic species such as gold or copper has brought interest to the use of molecules or macromolecules containing a free thiol.[4]

Although many synthetic routes for the preparation of organic thiols are well-known, only a few examples of well-defined polymers with thiol functionality have been reported.[4g,i,5] The limited synthetic procedures available may be a consequence of the stringent conditions thiols require for their preparation due to their high reactivity and their strong tendency to dimerize.

Ring-opening polymerization (ROP) methods allow the preparation of well-defined polyesters with functional end groups.[6] The "coordination-insertion" mechanism of the polymerization initiated by aluminum triisopropoxide ($Al(O^iPr)_3$) implies that a hydroxy end group is systematically present in the ω-position, as a result of the hydrolysis of the chain-growing site. Polycaprolactone (PCL) macromonomers have been obtained from the esterification of this ω-hydroxy end group with methacrylic acid.[7a] Likewise, we have reported preliminary studies on the conversion of the ω-hydroxy end group to a thiol group through a condensation reaction with a protected mercapto acetic acid, followed by a deprotection step.[7b]

Aternatively, an α-functionality can be introduced in a controlled way by the use of functional aluminum alkoxide initiators prepared by reaction of triethylaluminum ($AlEt_3$) with an alcohol.[7a,8] In addition, functional initiators have been synthesized through the exchange of the alkoxy groups of $Al(O^iPr)_3$ with the desired functional alcohol.[9] Here, we detail a similar approach to thiol-functional PCL using derivatives of mercaptoethanol as an initiator.

Both methods, used to functionalize linear polycaprolactone (PCL), are described in this paper. To this end, our objective is to prepare a series of polymers that serve as stabilizers for the controlled growth of the semiconductor nanoparticles. This should lead to the formation of heterosupramolecular structures where the particle spacing is controlled by the molecular weight and the particle size by the grafting density of the polymer chains.

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Experimental Section

Measurements. Nuclear magnetic resonance spectroscopy was carried out using a Bruker ACP-200 FT-NMR spectrometer using deuterated chloroform or deuterated dimethyl sulfoxide (DMSO) as solvent and tetramethylsilane as internal reference. The number-average molecular weights were calculated from the intensity ratios of the OCH_2 methylene proton signal ($\delta = 4.05$) and the $HOCH_2$ methylene proton signal ($\delta = 3.65$) in the ^{1}H NMR spectra. IR spectra were taken on a Nicollet FT-IR spectrometer using KBr pellets, and a Dylor XY800 Raman spectroscope was used. Gel permeation chromatography (GPC) was performed on a HPLC Kontron system (with UV detector), equipped with Ultrastyragel columns ($10^5 + 10^4 + 10^3$ Å) and calibrated with standard polystyrene samples. The eluent (tetrahydrofuran (THF) or CH_2Cl_2) was used at a flow rate of 1 mL min^{-1}. Analytical thin-layer chromatography (TLC) was performed on Merck plates (0.25 mm thick) using a hexane/ethyl acetate mixture.

Materials. Toluene used for the ring-opening polymerization was dried by refluxing over sodium and distilled under a nitrogen atmosphere before use. ϵ-Caprolactone (ϵ-CL) was dried over CaH_2, distilled twice under reduced pressure, and then stored under a nitrogen atmosphere. Aluminum isopropoxide (Al(^{i}OPr)$_3$) was sublimated and then dissolved in toluene under nitrogen. Poly(ϵ-caprolactone) (PCL) was prepared by solution polymerization, isolated, and dried in vacuum.[6b] Benzyl alcohol, mercaptoacetic acid, and mercaptoethanol were distilled over CaH_2 just before use. All other reagents were used as received. (Dimethylamino)pyridine toluenesulfonate (DPTS) was synthesized according to a literature procedure.[10]

Synthesis of α-(2,4-Dinitrophenylthio)acetic Acid, 1. Mercaptoacetic acid (26 mmol) in 20 mL of $CHCl_3$ was slowly added to a solution of 5 g (26 mmol) of 2,4-dinitrofluorobenzene mixed with 7 mL of triethylamine at room temperature. Extractions were carried out with HCl (1 M) and then twice with water. The product was separated, dried over magnesium sulfate ($MgSO_4$), and filtered. Yellow crystals were then recrystallized from $CHCl_3$ with a yield of 6.1 g (88%).

^{1}H NMR ($CDCl_3$): δ 9.06 (s, 1H, −Ar, $J_m = 3.0$ Hz); δ 8.27 (dd, 1H, −Ar, $J_m = 3.0$ Hz, $J_o = 9.0$ Hz); δ 7.75 (d, 1H, −Ar, $J_o = 9.0$ Hz); δ 3.76 (s, 2H, −SCH_2COOH). Elemental analysis: (found) % C, 36.80; % H, 2.53; % N, 10.71; % S, 12.30; (calculated) % C, 37.21; % H, 2.34; % N, 10.85; % S, 12.42.

Synthesis of α-(2,4-Dinitrophenylthio)ethanol, 2. Mercaptoethanol (26 mmol) in 20 mL of $CHCl_3$ was slowly added to a solution of 5 g (26 mmol) of 2,4-dinitrofluorobenzene mixed with 7 mL of triethylamine at room temperature. The purification was performed as described above for **1**, giving a yield of 5.2 g (79%).

^{1}H NMR ($CDCl_3$): δ 9.06 (s, 1H, −Ar, $J_m = 3.0$ Hz); δ 8.27 (dd, 1H, −Ar, $J_m = 3.0$ Hz, $J_o = 9.0$ Hz); δ 7.75 (d, 1H, −Ar, $J_o = 9.0$ Hz); δ 4.05 (t, 2H, −SCH$_2$CH_2OH, $J = 6.0$ Hz); δ 3.30 (t, 2H, −SCH_2CH$_2$OH, $J = 6.0$ Hz). Elemental analysis: (found) % C, 39.18; % H, 3.34; % N, 11.37; % S, 13.12; (calculated) % C, 39.34; % H, 3.30; % N, 11.47; % S, 13.13.

End-Functionalization of PCL with 1 (1-PCL). One equivalent (equiv) of polymer was dissolved in 10 mL of CH_2Cl_2 in the presence of 1.3 equiv of **1** followed by the addition of 1.5 equiv of DCC and 0.3 equiv of DPTS. After 24 h of reaction at room temperature the solution was filtered, and the functionalized polycaprolactone was recovered by precipitation in cold methanol, filtered, and dried to give a yield of 95%.

Polymerization of PCL from 2 (2-PCL). The initiator was the aluminum trialkoxide obtained from the reaction of Al(^{i}OPr)$_3$ with **2** in toluene after a continuous toluene−2-propanol azeotrope distillation (three times). The polymerization of ϵ-CL from this new functionalized initiator was conducted in the melt at 110 °C in a previously flamed and purged with nitrogen for 20 h at room temperature. Functionalized polycaprolactones were dissolved in THF, precipited in cold methanol, and dried in vacuum (yield 98%).

General Deprotection Reaction. Triethylamine was added (pH 8) to a solution of the functionalized PCL (**1-PCL** or **2-PCL**) in mercaptoethanol or propanethiol (100 equiv). After 15 h of stirring the reaction mixture was precipitated into cold methanol or hexane to give the thiol-functional polymer in 95% yield.

Preparation of the Difunctional and Tetrafunctional Initiators, 3 and 4. The hydroxyl groups of bis-MPA and the second generation of bis-MPA can be protected by conversion to acetonide by reaction with dimethoxypropane,[11] leading to 2,2-bis((2,2-propyl)dioxymethyl)propionic acid and g2(−$CO_2C_7H_7$,−$(CH_3)_4$) in the pure form. Each of these compounds (7.5 mmol) was condensed at room temperature for 24 h with α-(2,4-dinitrophenylthio)ethanol (1.4 g, 7.5 mmol) in CH_2Cl_2 using DCC (1.78 g, 11.25 mmol) and DPTS (0.48 g, 1.125 mmol). After the removal of urea by filtration, both intermediates were purified using column chromatography (silica gel, hexane/EtOAc as an eluent). The acetonide groups were removed by dissolving each intermediate (3 g) in a mixture of 7 mL of THF and 5 mL of 1 M HCl(aq). The reaction mixture was stirred for 3 h, and the product was subsequently extracted with CH_2Cl_2 (15 mL) and then with water (20 mL). The organic phase was dried ($MgSO_4$) and filtered and the solvent removed to yield 2.52 g (84%, **3**) and 2.05 g (68%, **4**) of yellow crystals. Then, the initiators were subsequently stored until use and transferred in the glovebox.

^{1}H NMR ($CDCl_3$) (**3**): δ 9.06 (s, 1H, −Ar); δ 8.27 (dd, 1H, −Ar); δ 7.75 (d, 1H, −Ar); δ 4.46 (t, 2H, −CH$_2$CH_2O(CO)−); δ 3.36 (t, 2H, −CH_2CH$_2$O(CO)−); δ 3.73−3.92 (dd, 4H, C(CH$_2$O−)$_2$); δ 1.06 (s, 3H, −CH$_3$). (**4**): δ 9.06 (s, 1H, −Ar); δ 8.27 (dd, 1H, −Ar); δ 7.75 (d, 1H, −Ar); δ 4.33 (t, 2H, −CH$_2$CH_2O(CO)−); δ 4.07 (s, 4H, C(CH$_2$O−)$_2$);δ 3.48 (t, 2H, −CH_2CH$_2$O(CO)−); δ 3.34 (δ dd, 8H, C(CH$_2$O−)$_4$); δ 1.15 (s, 3H, −CH$_3$); δ 0.98 (s, 6H, −CH$_3$). Elemental analysis (**3**): (found) % C, 43.57; % H, 4.67; % N, 7.62; % S, 8.87; (calculated) % C, 43.33; % H, 4.48; % N, 7.77; % S, 8.90. (**4**): (found) % C, 47.48; % H, 5.62; % N, 4.71; % S, 5.38; (calculated) % C, 47.43; % H, 5.68; % N, 4.63; % S, 5.29.

Synthesis of the Branched Macromolecules, 3-PCL and 4-PCL. All branched polyesters were polymerized in the melt at 110 °C (20 h) in a previously flamed and nitrogen purged flask, using **3** or **4** as initiator with a catalytic amount of tin octanoate (Sn(Oct)$_2$). The resulting polymers were dissolved in THF (10%), precipitated in cold methanol, filtered off, and dried in vacuum. Finally, the thiol group of these polymers was deprotected according to the procedure described for the linear polycaprolactones (**1-PCL** and **2-PCL)**.

Results and Discussion

End-Functionalization. The first of the two approaches to introduce a thiol group at one end of a polymer chain consisted in the conversion of a hydroxy end functionality to the thiol. By protecting the thiol in mercaptoacetic acid, the possibility of a direct esterification between the acid and the hydroxy-functional polymer was envisaged. The protection of the thiol was done using 2,4-dinitrofluorobenzene (Sangers reagent). This compounds has been shown in the literature to have a high reactivity with a variety of functional groups such as sulfhydryl, phenolic, or imidazole contained in proteins and peptides.[12] It was found to be particularly suitable as a protecting group, since it may be removed using mild conditions.[12e] In addition, it does not interact with the polymerization process, and it provides an excellent handle for reaction monitoring and product characterization by ^{1}H NMR and IR spectroscopies. The protection reaction itself involved the aromatic nucleophilic substitution of the activated fluoride of 2,4-dinitrofluorobenzene by the thiol of mercaptoacetic acid catalyzed by triethylamine as a base according to Scheme 1.[13] The product α-(2,4-dinitrophenylthio)acetic acid (**1**) was formed in high yield.

Scheme 1. Synthesis of α-(2,4-Dinitrophenylthio)acetic Acid, 1, and α-(2,4-Dinitrophenylthio)ethanol, 2

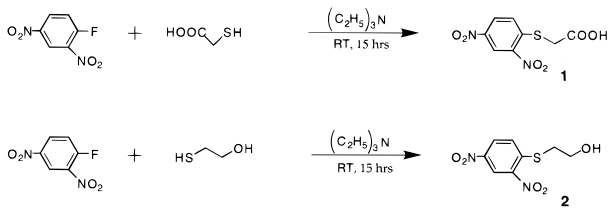
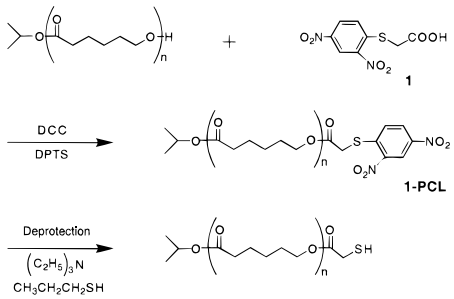


Table 1. Characteristics of the Functionalized Polymers from End-Functionalization (Esterification with 1)

	precursor			M_n	$I(M_w/M_n)$	% −S−
sample	M_n	M_w/M_n	type	NMR	GPC	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

Scheme 2. Esterification of the PCL Hydroxy End Group with 1



The polymer to be functionalized was prepared by ring-opening polymerization of ϵ-CL initiated by Al(^{i}-OPr)$_3$ in the bulk or in solution. The polymerization was arrested by hydrolysis of the active aluminum alkoxide bond which led to the formation of the hydroxy end group. The molecular weight of the produced polymers was close to that expected from the monomer-to-initiator ratio with narrow polydispersities (Table 1). Esterification of the hydroxy end group by condensation with **1** was done using DCC as previously reported in peptide synthesis.[14] The acid group was first converted to an active ester with DCC and then added to the hydroxy-functional PCL in methylene chloride (Scheme 2). As the reaction proceeded, the solution became opaque due to the dissociation of DCC leading to the formation of urea. Filtration easily removed the urea before the recovery of the polymer. ^{1}H NMR spectroscopy showed that functionalization of the polycaprolactone end group was close to quantitative (Table 1).

The spectrum in Figure 1a shows primarily four large peaks due to the repeating units of ϵ-CL. 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**). In addition, infrared spectroscopy confirmed the presence of the dinitrophenyl functionality by the asymmetrical and symmetrical stretching of the NO bonds at 1590 and 1535 cm^{-1}, respectively.

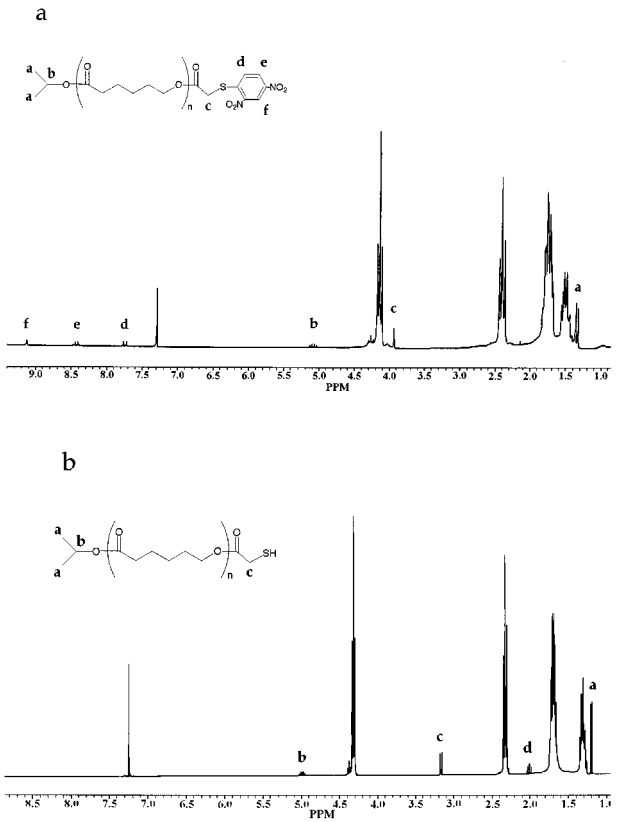


Figure 1. ^{1}H NMR of the thiol-functional PCL (**1-PCL**) prepared from end-functionalization, with the thiol protected (top, a) and deprotected (bottom, b).

The following deprotection reaction again involved an aromatic nucleophilic displacement reaction, this time as an exchange between the protected thiol chain end and a low molecular weight thiol such as mercaptoethanol or propanethiol (Scheme 2). Since the reaction is an equilibrium, it is necessary to add a large excess of the low molecular weight thiol in order to shift the equilibrium to the macrothiol. Mercaptoethanol was used when the molecular weight of the PCL was higher than 3000 as the polymer then could be recovered by precipitation in methanol, eliminating the excess of mercaptoethanol. Otherwise, propanethiol was utilized, and the functionalized PCL chains of lower molecular weight were precipitated in hexane. Removal of the α-(2,4-dinitrophenyl) group to regenerate the thiol functionality should be carried out carefully under a protective atmosphere, since thiols are known to readily undergo oxidation to form the corresponding disulfide. After this deprotection, ^{1}H NMR spectroscopy (Figure 1b) demonstrated the successful 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. Moreover, the presence of the mercapto group was confirmed by Raman spectroscopy, where the SH stretching was observed at 2600 cm^{-1}.

Table 1 summarizes the characteristics for the various **1-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 selectiveness of the reaction and the absence of disulfide

Scheme 3. Polymerization of ϵ-CL from 2

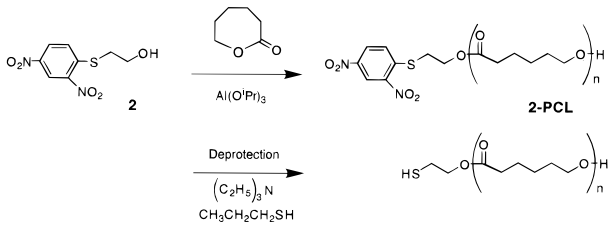


Table 2. Characteristics of the Polymers Functionalized from Initiation (2, 3, 4)

sample	initiator	catalyst	type	M_n NMR	$I(M_w/M_n)$ GPC
3I1CL1	2	$Al(O^iPr)_3$	protected	3000	1.25
3I1CLS1	2	$Al(O^iPr)_3$	deprotected	2900	1.28
5I1CL1	2	$Al(O^iPr)_3$	protected	4000	1.25
5I1CLS1	2	$Al(O^iPr)_3$	deprotected	4000	1.26
3I2CL1	3	$Sn(Oct)_2$	protected	3500	1.21
3I2CLS1	3	$Sn(Oct)_2$	deprotected	3500	1.20
5I2CL1	3	$Sn(Oct)_2$	protected	5600	1.24
5I2CLS1	3	$Sn(Oct)_2$	deprotected	5500	1.24
6I4CL1	4	$Sn(Oct)_2$	protected	6200	1.19
6I4CLS1	4	$Sn(Oct)_2$	deprotected	6150	1.22
10I4CL1	4	$Sn(Oct)_2$	protected	11200	1.20
10I4CLS1	4	$Sn(Oct)_2$	deprotected	10900	1.31

formation. Furthermore, this method of functionalization is not restricted only to PCL, but is general, and can be applied to most ω-hydroxy-functional polymers or copolymers. For instance, we have successfully prepared poly(ethylene oxide) with a mercapto end group using this method.[7b]

Functionalization from Initiation. The second approach for the synthesis of macrothiols is the use of an initiator containing a protected thiol. After polymerization deprotection could then be done as demonstrated above. The synthesis of such an initiator for the ROP of ϵ-Cl again involved the reaction with dinitrofluorobenzene, this time with mercaptoethanol to obtain α-(2,4-dinitrophenylthio)ethanol (**2**) (Scheme 1). During this reaction, the color of the solution evolved from slightly orange to reddish. Pure yellow crystals were obtained after recrystallization.

The functional initiator was prepared via the reaction of **2** with $Al(^iOPr)_3$ using an azeotropic distillation of the toluene/2-propanol mixture, allowing a complete substitution (Scheme 3). It has been shown previously that the polymerization initiated by functional aluminum alkoxides keeps the living character of the polymerization.[15] In the present case, this was supported by the predictable molecular weight (from initial CL/initiator molar ratio) of the functionalized polyesters (**2-PCL**). Due to the poor solubility of new functional aluminum trialkoxides in solution, the polymerization was performed in the bulk, resulting in a polydispersity of 1.25 (Table 2).

Figure 2a shows the ^{1}H NMR spectrum of **2-PCL** where the methylene peak at 5.73 ppm denoted as (**a**) demonstrates that the hydroxyl group has initiated the polymerization. Again, the peaks from the protecting group (**d**, **e**, **f**) are clearly identified at low field. The two methylene groups (**b** and **c**) originating from **2** appear as triplets at δ 4.35 ppm and δ 3.31 ppm, respectively.

The mercapto group was deprotected using the same conditions as described above using an excess of mercaptoethanol. The ^{1}H NMR spectrum (Figure 2b) obtained after deprotection shows the absence of the (**d**, **e, f**) peaks; hence, the protecting group has successfully been removed. The **c** peak is shifted to higher field and appears as a multiplet due to coupling with the thiol hydrogen.

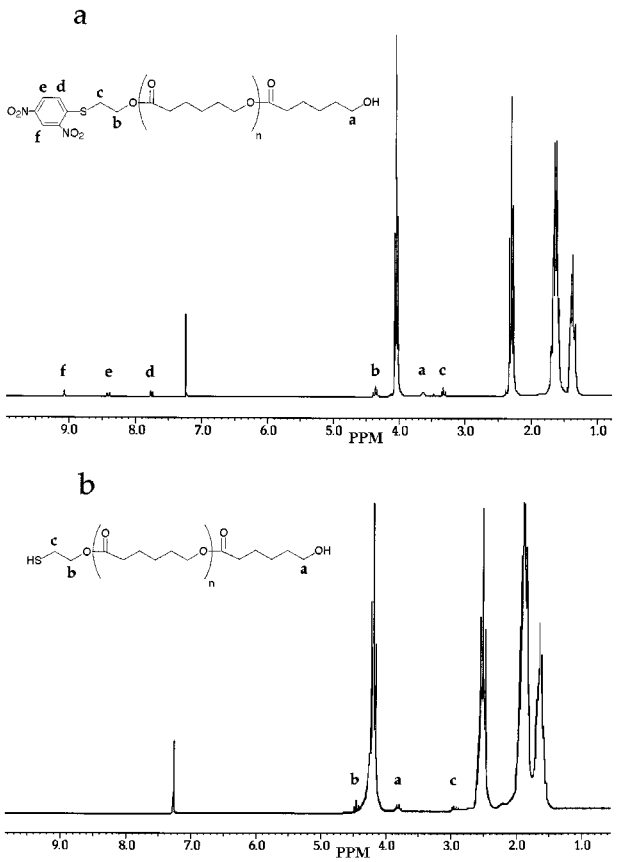


Figure 2. ^{1}H NMR of the thiol-functional PCL (**2-PCL**) obtained from initiation, with the thiol protected (top, a) and deprotected (bottom, b).

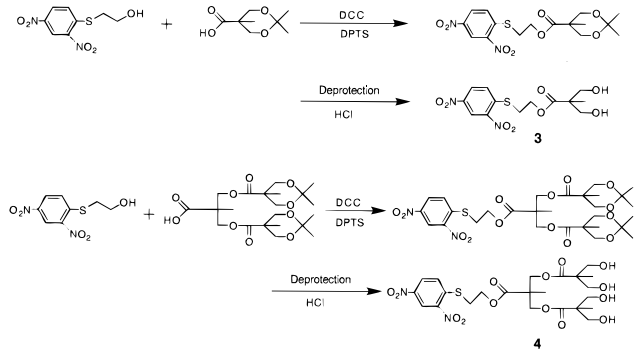
Undesirable side reactions could occur during this deprotection reaction and may lead to the formation of disulfides. But, we have shown previously that thiol-functional polycaprolactones presented no differences in the GPC spectra before and after the deprotection reaction.[7b] Conversely, poly(ethylene oxide) chains with a mercapto end group, functionalized in the same conditions, sometimes shows an extra shoulder with twice the molecular weight of the main peak, probably due to a partial dimerization of the macrothiols.

Thiol-Functional Multibranched Polymers. By applying the approach of growing living chains from a functional alcohol to give linear polyesters, branched polymers may also be prepared using multifunctional dendrons[16] containing several hydroxy functionalities used as initiation sites. After polymerization and deprotection the thiol will be situated at the focal point, thus providing highly controlled multiarm macrothiols.

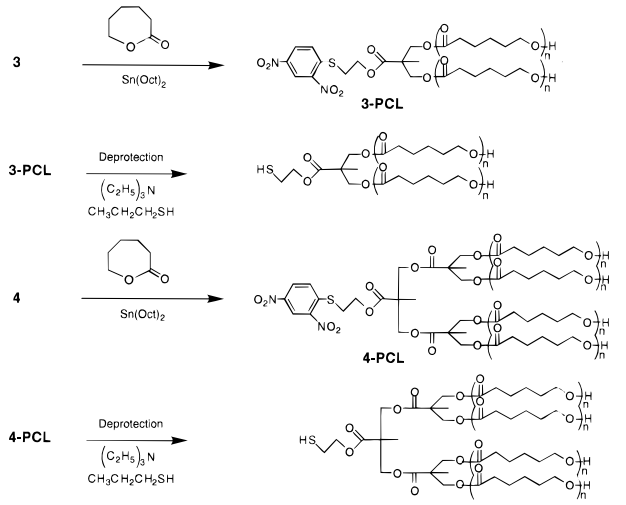
Scheme 4 shows the synthesis of the difunctional mercapto-initiator **3** from the condensation reaction of protected bis-MPA with **2** using DCC and DPTS. The tetrafunctional mercapto-initiator (**4**) was similarly obtained from esterification of the second-generation protected hydroxy-functional dendron of the bis-MPA with **2**. In both cases the initial protection of the hydroxyl functionalities by acetonide groups was necessary to avoid self-condensation reactions.

Removal of this protecting group allowed polymerization of ϵ-Cl from multifunctional mercapto-initiators

Scheme 4. Synthesis of the Difunctional and Tetrafunctional Initiators, 3 and 4



Scheme 5. Polymerization of ϵ-CL from 3 and 4



in the bulk at 110 °C using $Sn(Oct)_2$ as catalyst (Scheme 5). This catalyst has already been shown to be useful for the synthesis of polymers or block copolymers with narrow polydispersities and controlled molecular weights.[17] The optimal molar ratio of functional initiator to $Sn(Oct)_2$ has been found to be between 150 and 400.[17c] Similar to previous studies using this ratio, these multifunctional mercapto-initiators led to branched polymers with narrow polydispersity and molecular weights close to those expected from the monomer-to-initiator ratio (Table 2), demonstrating the livingness of the polymerization.

The spectra in Figure 3b shows the presence of the α-(2,4-dinitrophenylthio)protons' peaks (**a**, **b**, and **c**), as well as two peaks (**d** and **e**) of the two methylene groups adjacent to the thioether in **3-PCL**. The shifts of the singlet peaks **f** and **g** clearly show that both hydroxyl groups have initiated the polymerization (otherwise they would have been split). The degree of functionalization was fairly high and did not vary significantly after the deprotection reaction.

Similar analysis can be done from the tetrabranched polymer (**4-PCL**). In that case, peaks **h** and **i** are shifted as shown in Figure 4b, and peaks due to the protecting group of the thiol are still visible in the spectrum. After the deprotection reaction, peaks (**a**, **b**, **c**) due to the α-(2,4-dinitrophenylthio) protons have disappeared, and the methylene peak (**d**) next to the terminal thiol proton is slightly shifted to high field (2.8 ppm) and splitted to a quartet (spectrum not shown).

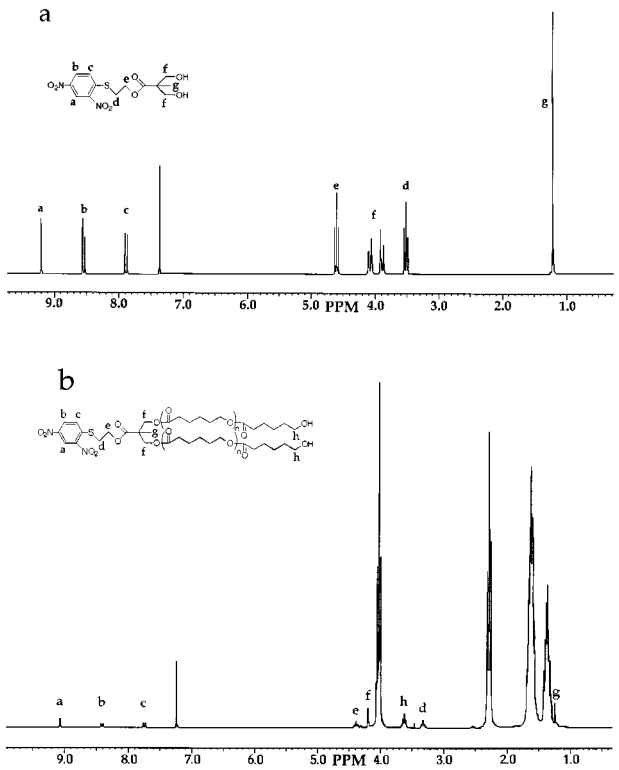


Figure 3. ^1H NMR of the difunctional initiator **3** (a, top) and the resulting polycaprolactone (**3-PCL**) (b, bottom).

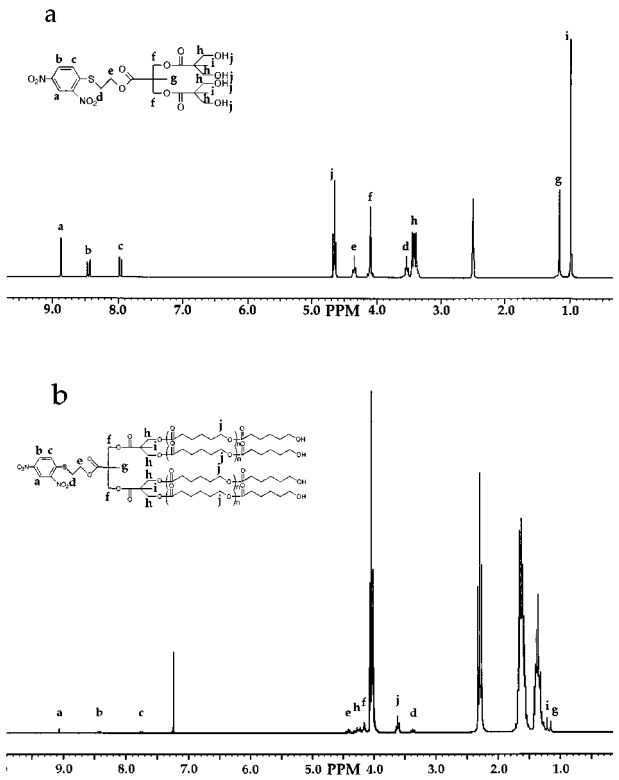


Figure 4. ^1H NMR of the tetrafunctional initiator **4** (a, top) and the resulting polycaprolactone (**4-PCL**) (b, bottom).

Conclusions

Nearly quantitative degrees of thiol terminal functionalities to living ring-opening polymerization of ϵ-Cl have been successfully achieved by end-coupling reactions with protected mercaptoacetic acid or by using initiators with a thiol group. Moreover, multibranched

polyesters have been obtained from mercapto-initiators with several hydroxy groups. These could lead to various potential applications such as the formation of thin-film composites.

Generally speaking, these results provide new prospects for the macromolecular engineering of asymmetric thiol-functional polymers. Some possible extensions of these reactions are the synthesis of dithiol polymers by combining both methods, i.e., controlling both the initiation and the end coupling steps. Moreover, the synthesis of α,ω-SH functional PCL seems to be feasible by coupling the parent asymmetric α-SH, ω-OH polymer.

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