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Amphiphilic Sun-Shaped Polymers by Grafting Macrocyclic Copolyesters with PEO

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ABSTRACT: An amphiphilic sun-shaped copolymer was successfully prepared by esterification of carboxylic acid terminated PEO with the pendent hydroxyl groups of high molecular weight ($M_n = 28\,000$) cyclic PCL. The cyclic structure of the copolyester originally resulted from the polymerization initiation by a cyclic tin dialkoxide and was ultimately stabilized by the intramolecular cross-linking of a few unsaturated groups.

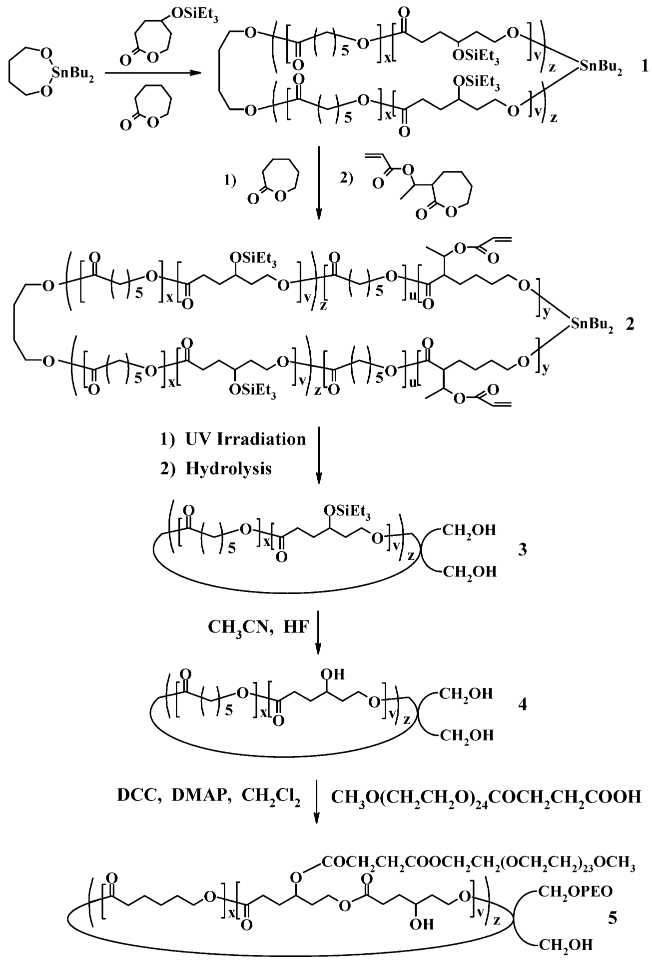
Introduction

The attention paid to the design and synthesis of macrocycles of various chemical structure, composition, molecular characteristics, and architectures is steadily increasing because of distinct properties from the linear counterparts, such as glass transition temperature, order−disorder transition, reduced viscosity, and lower hydrodynamic volumes.[1,2]

At the time being, only scarce examples of synthesis of sun-shaped macrocycles have been reported. Kricheldorf et al. reported on the synthesis of a sun-shaped poly(ether ketone) with cyclic arms by kinetically controlled polycondensation of an ab$_2$ monomer, i.e., 3,5-bis(4-fluorobenzoyl)phenol.[3] Deffieux et al. grafted living polystyryllithium onto pendant chloroethyl groups of cyclic poly(chloroethyl vinyl ether).[4] Very recently, an amphiphic sun-shaped copolymer [(cyclic PEO)-*graft*-PS, where PEO and PS stand for poly(ethylene oxide) and polystyrene, respectively] was synthesized by combination of anionic ring-opening polymerization and nitroxide-mediated radical polymerization.[5] Synthesis of tadpole-shaped polymers has been reported, thus macrocycles with either one[6−9] or two side chains.[6,10−14] According to Monte Carlo simulations, conformation of macrocycles should be modified by the side-chain grafting.[15] Clearly, this topic is basically unexplored and needs synthesis of model compounds for understanding and exploiting the impact of quite unusual architectures on the solution and bulk properties.

Because biocompatible, permeable, and biodegradable linear aliphatic polyesters grafted with hydrophilic PEO are amphiphiles with widespread applications in medicine,[16−27] this work aims at reporting on the synthesis of amphiphilic polyesters with a sun-shaped architecture, i.e., macrocyclic copolyesters grafted with PEO. Very recently, Waymouth et al. reported on a very original approach for the synthesis of macrocyclic poly(3,6-dimethyl-1,4-dioxane-2,5-dione) [poly(lactide)] by zwitterionic ring-opening polymerization of 3,6-dimethyl-1,4-dioxane-2,5-dione [lactide] catalyzed by N-heterocyclic carbenes.[28] Kricheldorf et al. synthesized macrocyclic poly(oxepan-2-one) [poly(ϵ-caprolactone) or PCL] by ring-opening polymerization of oxepan-2-one (ϵ-caprolactone or ϵCL) by using cyclic tin dialkoxides as initiators.[29] The growing chains were closed by two endocyclic tin alkoxides prone to hydrolysis. Therefore, the rings were clipped by reaction with 1,3-dithian-2-one and formation of more stable carbonate groups.[30] Nevertheless, in none of these approaches functional groups were available on the macrocycles for further macromolecular engineering.

Scheme 1. Synthesis of Amphiphilic Copolymer with a Sun-Shaped Architecture



Our approach relied on the synthesis of macrocyclic PCL by ring-opening polymerization of ϵCL initiated by a cyclic tin dialkoxide, i.e., 2,2-dibutyl-2-stanna-1,3-dioxepane (DSDOP), followed by the addition and sequential polymerization of a few units of 1-(2-oxooxepan-3-yl)ethyl acrylate (αAϵCL).[12] The pendant acrylic unsaturations of the cyclic chains were intramolecularly cross-linked by UV irradiation in non very diluted

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Table 1. Characteristic Properties of the Linear (2 after Hydrolysis of Tin Alkoxides) and Cyclic (3) Copolyesters

samples	$M_{n,th}$	$M_{n,NMR}$	$M_{n,SEC}$	M_w/M_n	$\langle G\rangle$[a]	[η] (dL g^{-1})	T_g[b] (°C)	X_c[c] (%)	T_m[b] (°C)
L_{linear}	28 300	27 500	25 500	1.40		0.363	−64.5	32.6	41.38
$C_{marocycles}$	28 300	29 000	21 500	1.40	0.79	0.247	−56.8	27.2	35.92

[a] $\langle G\rangle = M_{p,SEC}(\text{cyclic})/M_{p,SEC}(\text{linear})$, where M_p is the molecular weight at the maximum of the elution peak. [b] T_g and T_m measured during the second heating run at a 10 °C/min rate. [c] $X_c = \Delta H_m/\Delta H_{100}$, where ΔH_m is the actual melting enthalpy and ΔH_{100} is the melting enthalpy for 100% crystalline PCL ($\Delta H_{100} = 136.4$ J g^{-1}).[35]

solution (~0.5 wt %), with formation of stable macrocyclic chains **3** (Scheme 1). Remarkably, tin alkoxides remained living after the intramolecular cross-linking step and thus available for further macromolecular engineering. For instance, two-tail tadpole-shaped copolyesters were easily prepared by resuming the ring-opening polymerization of ϵCL.[12−14]

In this work, ϵCL has been copolymerized with a monomer containing a protected hydroxyl group, i.e., 5-triethylsilyloxy-oxepan-2-one (γ-triethylsilyloxy-ϵ-caprolactone or γEt$_3$SiOϵCL). The triethylsilanolate groups were previously deprotected without significant degradation of linear copolyester chains, at least when the molar content of γEt$_3$SiOϵCL in the copolyester was lower than 30%.[31,32] This strategy has been extended to the cyclic copolyesters (molar content of γEt$_3$SiOϵCL = 10%) in order to make cyclic poly(γHOϵCL-*co*-ϵCL) **4** (Scheme 1) available, without degradation during deprotection. Moreover, carboxylic acid (−COOH) end-capped PEO was grafted onto the macrocycles by esterification. A very preliminary analysis of the self-assembly of an amphiphilic PEO grafted macrocyclic copolyester was carried out in water.

Experimental Section

Materials. ϵCL (Aldrich) was dried over calcium hydride at room temperature for 48 h and distilled under reduced pressure just before use. DSDOP was synthesized as reported in the scientific literature.[30] Synthesis of γEt$_3$SiOϵCL was reported elsewhere.[31] Synthesis of αAϵCL was also reported.[13] Benzophenone (Aldrich) was dried by azeotropic distillation (three times) of toluene. Dihydrofuran-2,5-dione (succinic anhydride), *N,N′*-dicyclohexylcarbodiimide (DCC), and *N,N*-dimethylpyridin-4-amine (4-(dimethylamino)-pyridine or DMAP) were dried by azeotropic distillation (three times) of toluene. Toluene (Aldrich, 99.5%) was dried over sodium benzophenone and distilled under nitrogen. Dichloromethane was dried over calcium hydride and distilled under nitrogen before use. Poly(ethylene oxide) monomethyl ether ($M_n = 1050$) (Fluka) (PEO) was used as received. Synthesis of the succinic ester of PEO monomethyl ether (PEO−COOH) was reported elsewhere.[33]

Synthesis of the Cyclic Precursor 2 and Intramolecular Cross-Linking (Scheme 1). In a typical experiment, 1.8 mL of ϵCL (16.2 mmol), 0.4 g of γEt$_3$SiOϵCL (1.64 mmol), 10.5 mL of dry toluene, and 3.0 mL of DSDOP solution (0.03 M in toluene) were successively added into a previously flamed glass reactor through a rubber septum with a syringe. After 2 h at 40 °C, 0.34 g of αAϵCL (1.6 mmol) in 3 mL of toluene was added to the reactor, and the reaction temperature was increased to 60 °C. After 2 h, 3 mL of the reaction mixture was picked out and hydrolyzed into the parent linear copolyester for characterization. The solution of the living cyclic precursor was cooled to room temperature under nitrogen, added with a benzophenone solution (2.3 mg, 15 μmol, in 0.5 mL of toluene), and finally diluted with dry toluene until 0.46 wt % of the copolyester. This solution was UV-irradiated (350−420 nm, 1000 W) at room temperature for 150 min. After evaporation of part of the solvent, a few drops of acetic acid (1 M in toluene) were added, and the polymer was precipitated in cold heptane, recovered by filtration, and dried in vacuo (yield: 92%).

Deprotection of the Macrocycles 3 and Grafting of PEO. The macrocycles **3** (0.5 g, 0.253 mmol of triethylsilanolate groups) were dissolved in 25 mL of acetonitrile (2 wt %), followed by the dropwise addition of hydrofluoric acid (40%, 0.06 g, 1.25 mmol). After stirring at room temperature for 20 min, the mixture was neutralized by sodium bicarbonate, filtered, dried over magnesium sulfate, and poured into cold heptane. The cyclic poly(γHOϵCL-*co*-ϵCL) **4** precipitated. It was collected by filtration and dried in vacuo (yield: 82%). This copolyester (0.2 g, 0.104 mmol to −OH groups) was dried further by azeotropic distillation (three times) of toluene and then added with dry dichloromethane (10 mL) and 2 mL of a solution of DMAP (0.08 g, 0.7 mmol) and triethylamine (0.1 mL, 1 mmol) in CH_2Cl_2. PEO−COOH (0.8 g, 0.7 mmol) was dried by azeotropic distillation (three times) of toluene and added with 5 mL of dry dichloromethane and 3 mL of a DCC (0.15 g, 0.7 mmol) solution in CH_2Cl_2. The two solutions were mixed upon stirring at room temperature for 24 h. The solvent was evaporated under reduced pressure, and the copolymer was dissolved in toluene and purified by dialysis against ethanol, followed by precipitation in diethyl ether (yield: 58%).

Formation of Micelles by Self-Assembling in a THF−Water Mixture. 25 mg of **5** was dissolved in 1.0 mL of THF, followed by the dropwise addition of water (2 mL) under vigorous stirring maintained for 4 h. Then 3 mL of water was added in order to freeze in the micelles, the organic solvent (THF) being eliminated by dialysis against water. TEM was used to observe the geometry and size of the micelles.

Characterization. Size exclusion chromatography (SEC) was performed in THF at a flow rate of 1.0 mL min^{-1} at 40 °C with a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1073A refractive index detector and Styragel columns (HP PL gel 5 μm; pore size of 10^5, 10^4, 10^3, and 10^2 Å). Polystyrene (PS) standards were used for calibration, and the apparent molecular weights were converted into absolute M_n's for PCL by the $M_n(\text{PCL}) = 0.259 \times M_n(\text{PS})^{1.073}$ equation.[34] ^{1}H NMR spectra were recorded in $CDCl_3$ with a Brucker AN 400 apparatus at 25 °C. Differential scanning calorimetry (DSC) was carried out with a TA 2010 DSC thermal analyzer calibrated with indium. The melting temperature (T_m) was measured after cooling the sample to −90 °C and heating it to 150 °C at a 10 °C/min rate. The solution viscosity of the samples dissolved in toluene was measured with an Desreux−Bisschoff viscometer thermostated at 25 °C. Transmission electron microscopy (TEM) images were recorded with a Philips CM100 microscope equipped with a Gatan 673 CCD camera and transferred to a computer equipped with the Kontron KS100 system. Samples were prepared by dipping a Formar-coated copper grid into a dilute micellar solution (0.5 wt % polymer). The excess of solution on the grid was removed with a filter paper, followed by washing with water and drying in air.

Results and Discussion

The very first step of the synthesis of the envisioned sun-shaped macrocycles consists in copolymerizing ϵCL with γEt$_3$SiOϵCL, thus a protected hydroxyl containing ϵCL, whose polymerization and copolymerization with other lactones were successfully carried out in the recent past.[31,32] The complete polymerization of a mixture of γEt$_3$SiOϵCL (10 mol %) and ϵCL (90 mol %) initiated by DSDOP at 40 °C for 2 h was confirmed by gravimetry and ^{1}H NMR analysis of the collected copolymer. Then, a small amount of αAϵCL was added to the polymerization medium ($[\alpha A\epsilon CL]_0/[DSDOP]_0 = 18$) in order to end-cap the copolyester chains by a few acrylic unsaturations at both ends. After 2 h at 60 °C, the precursor **2**, temporarily cyclized by the endocyclic tin alkoxide, was permanently cyclized by UV irradiation. Nevertheless, a sample was previ-

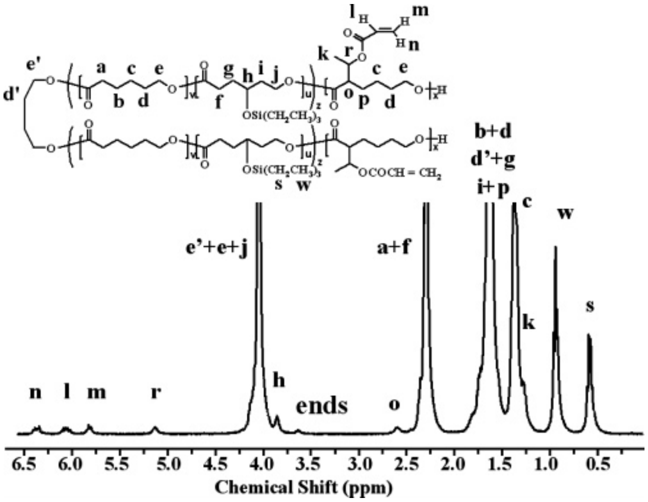

Figure 1. ^{1}H NMR spectrum for the linear counterpart of the precursor **2** (Scheme 1).

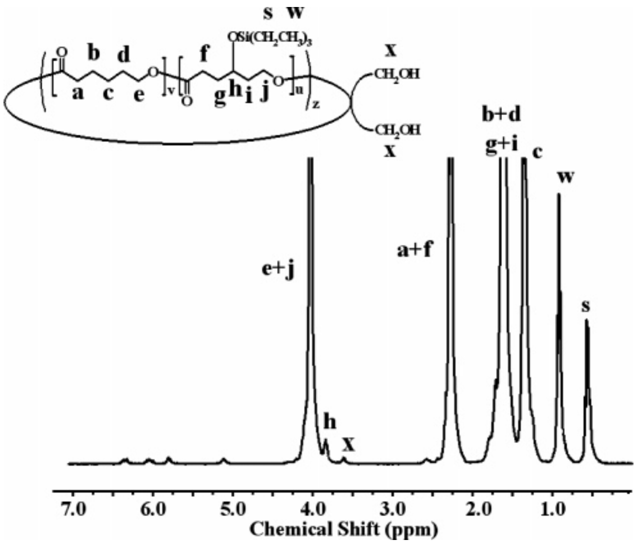

Figure 2. ^{1}H NMR spectrum of the macrocycle **3** (Scheme 1).

ously withdrawn from the medium and hydrolyzed into the parent linear counterpart for characterization, as reported in Table 1. The ^{1}H NMR spectrum of this linear copolyester is shown in Figure 1. The typical resonances of the two comonomer units are observed at 3.84, 0.92, and 0.56 ppm for the protons h, w, and s of the γEt$_3$SiOϵCL units and at 6.4, 6.1, and 5.8 ppm for the protons of the acrylic double bonds, respectively. From the integration of the signals at 0.92 ppm for γEt$_3$SiOϵCL, 6.4 ppm for αAϵCL, 2.25 ppm for ϵCL, and 3.6 ppm for the two $-$CH$_2$OH pendant groups, the experimental molar composition was calculated ($DP_{\gamma-Et3SiO\epsilon CL} = 17$, $DP_{\epsilon CL} = 175$, and $DP_{\alpha-A\epsilon CL} = 16$), which is close to the theoretical composition in the case of quantitative conversion, i.e., $DP_{\gamma Et3SiO\epsilon CL,th} = 18.2$, $DP_{\epsilon CL,th} = 180$, and $DP_{\alpha A\epsilon CL,th} = 18$. The number-average molecular weight (M_n) was determined accordingly (27 500). M_n was also measured by SEC, with polystyrene (PS) standards and conversion to M_n for PCL by the following equation: $M_n(PCL) = 0.259 M_n(PS)^{1.073}$.[34] Because the content of γEt$_3$SiOϵCL co-units is low, M_n(PCL) must be close to the absolute of M_n of the linear copolymer, which is confirmed by the good agreement with $M_{n,NMR}$ (25 500). The polydispersity index was in line with data reported by Kricheldorf et al. for the ring-opening polymerization of lactones.[29]

Because the reactivity of tin alkoxide derived from γEt$_3$SiOϵCL was observed to be lower than that of the ϵCL counterpart, a few ϵCL units were polymerized by compound **1** before adding αAϵCL, as shown in Scheme 1 (second step). Then the initiation of the αAϵCL polymerization is faster and allows to end-cap both ends of the chains with few pendant acrylic unsaturations while using a lower amount of this comonomer.

Intramolecular UV Cross-Linking of the Precursor 2. The precursor **2** was diluted by toluene ([Sn] = 1.9×10^{-4} M) and irradiated by UV light in the presence of 1 mol % of the benzophenone photoinitiator (with respect to the acrylic units) at room temperature for 150 min. The effectiveness of the intramolecular cross-linking has been assessed by ^{1}H NMR (Figure 2) analysis of the irradiated copolyester. The average number of the acrylic unsaturations decreased from 16 to 8.2, based on the relative intensity of the signals at 6.4 ppm for αAϵCL and at 2.25 ppm for ϵCL. Moreover, the molar content of the γEt$_3$SiOϵCL units remained unchanged, which indicates that the triethylsilanolate groups tolerate UV and are thus compatible with the photoinitiation and cross-linking processes.

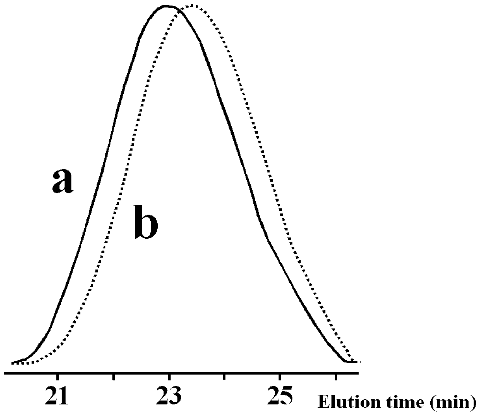

Figure 3. SEC traces for the (a) linear and (b) cyclic copolyester after UV treatment.

Figure 3 shows that the SEC trace after UV treatment and hydrolysis of the tin alkoxide is shifted toward higher elution time, compared to the linear counterpart. The apparent $M_{n,SEC}$ decreased indeed from 25 500 to 21 500 upon cross-linking, consistent with the lower hydrodynamic volume that the physically more compact cyclic macromolecules exhibit with respect to the linear counterparts.[1] This observation confirms that the macrocyclic copolyester is maintained after hydrolysis of the endocyclic tin alkoxide. The ratio of the molecular weights at the maximum of the elution peaks [$M_{p,SEC}$(cyclic)/$M_{p,SEC}$(linear)] is 0.79, in good agreement with the data published elsewhere for cyclic polymers.[1] The polydispersity index (M_w/M_n) (Table 1) before and after cross-linking remains unchanged.

Additional evidence for the successful cyclization is the ratio, g, of the intrinsic viscosity [η] of the copolyester after and before the UV treatment. This ratio ($g = [\eta]_{cyclic}/[\eta]_{linear}$) is 0.70 in toluene at 25 °C, which is again quite consistent with observations reported in the scientific literature for other macrocyclic (co)polymers.[1]

All these observations support that the cross-linking is typically intramolecular under the dilution conditions used (0.46 wt %) for the UV treatment. Moreover, the successful synthesis of the triethylsilanolate containing macrocyclic copolyester is additional evidence that this previously reported cyclization strategy is very effective.[12]

The thermal properties of the cyclic random copolyester and the linear counterpart were also analyzed by differential scanning

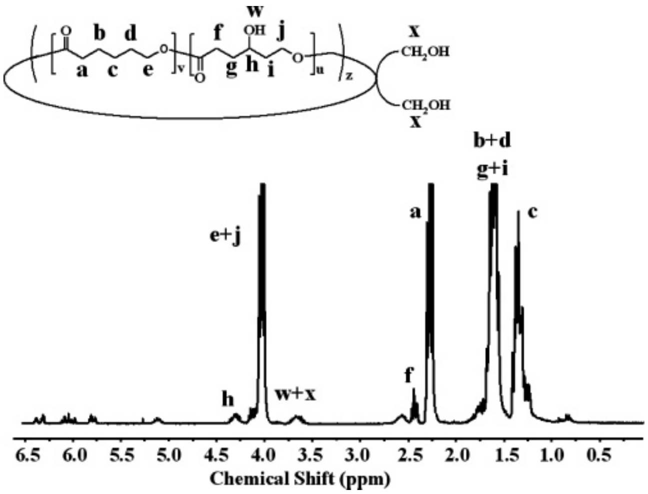

Figure 4. ^{1}H NMR spectrum for the macrocyclic copolyester **3** after deprotection.

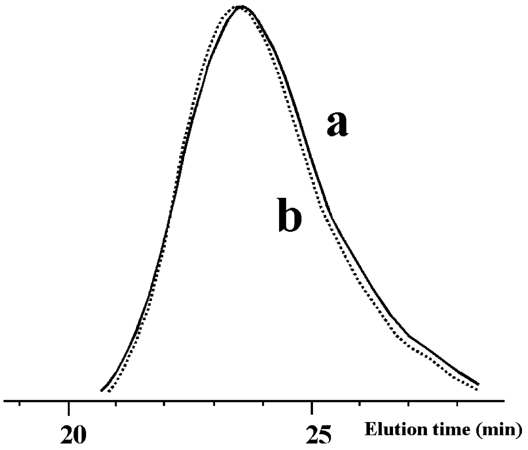

Figure 5. SEC traces for the macrocyclic copolyester before (a) and after (b) deprotection.

calorimetry (DSC). Both the samples are semicrystalline, which indicates that the γEt$_3$SiOϵCL counits (8.8 mol %) do not prevent PCL from crystallizing. However, the crystallinity degree, X_c, and the melting temperature, T_m, are lower for the cyclic copolyester than for the linear chains (Table 1). The reverse observation is reported for the glass transition temperature, T_g, which is higher for the cyclic than for the linear chains. Cyclization is thus responsible for a loss of chain mobility.

Chemical Modification of the Functionalized Macrocyclic Copolyester. The selective hydrolysis of triethylsilanolate groups of linear poly(γEt$_3$SiOϵCL-*co*-ϵCL) copolyesters of different compositions was previously carried out without any degradation of the backbone.[31] The same conditions were extended to the macrocycles, and the deprotection of the triethylsilanolate groups was complete as assessed by the disappearance of the ^{1}H NMR resonance peaks at 3.84, 0.92, and 0.56 ppm for the γ-CHOSiEt$_3$, -Si(CH$_2$CH_3)$_3$, and -Si(CH_2-CH$_3$)$_3$ protons of the γ-Et$_3$SiOϵCL units, respectively, and the appearance of two multiplets at 4.30 and 3.65 ppm assigned to the γ-CHOH and γ-CHOH protons of the γ-HOϵCL units, respectively (Figure 4 to be compared to Figure 2). The SEC traces could be superposed before (a) and after (b) deprotection (Figure 5), whereas the molar composition and M_n (21 000), determined by ^{1}H NMR analysis, remained unchanged after deprotection consistent with a nondegrading deprotection process.

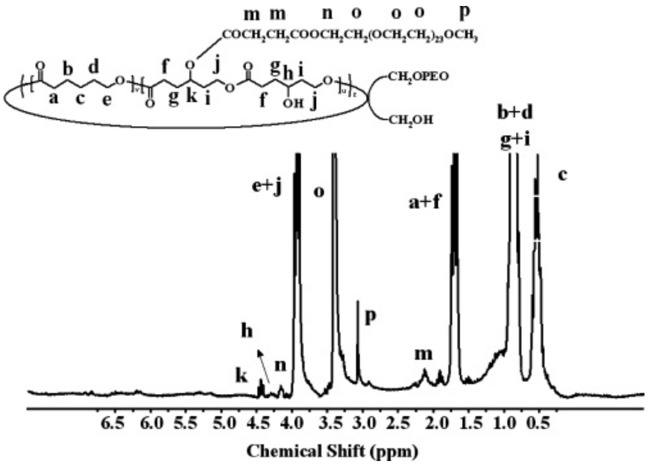

Figure 6. ^{1}H NMR spectrum for the PEO-grafted macrocyclic copolyester.

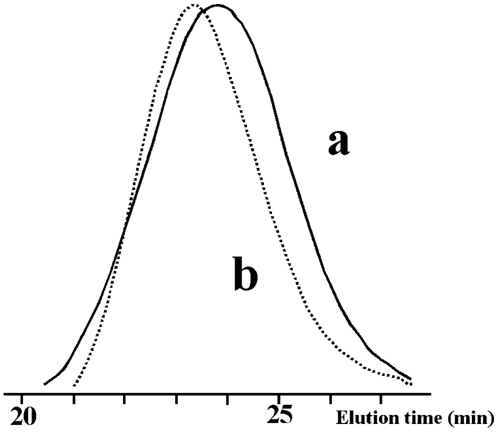

Figure 7. SEC traces for the cyclic copolyester before (a) and after (b) grafting of PEO.

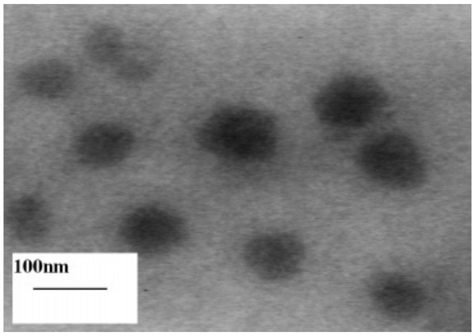

Figure 8. TEM picture of micelles of the cyclic poly(γ-HOϵCL-*co*-ϵCL)-*g*-PEO in water.

Grafting of water-soluble PEO onto the cyclic copolyester can decrease the hydrophobicity of the copolyester, which may be a requirement for biomedical application.

The pendant hydroxyl groups along the cyclic poly(γ-HOϵCL-*co*-ϵCL) backbone were esterified by PEO chain end-capped by a carboxylic acid, in the presence of a condensation reagent, DCC, and a catalyst, DMAP, in dichloromethane at room temperature. After purification by dialysis of ethanol solution, the copolymer was characterized by ^{1}H NMR and SEC techniques. The ^{1}H NMR analysis shows a decreased intensity for the multiplet at 4.3 ppm for the (γ-HO)$-$C$H-$ proton and the appearance of several new peaks at 4.2, 3.6, 3.35, and 2.6 ppm characteristic of the PEO grafts (Figure 6). Moreover, a new peak at 4.4 ppm is observed that corresponds to the (γ-PEO$-$COO)$-$C$H-$ proton and testifies to the esterification reaction. M_n (35 500) was determined by ^{1}H NMR by comparison of the relative intensity of the signals at 4.0 ppm [$-CH_2O-C(=O)-$] and at 3.6 pmm [$-CH_2O-$ of PEO grafts], the number of [$-CH_2O-C(=O)-$] units being known. The number of the grafted PEO chains (7−8 per cyclic chain) was estimated from the relative integration of the signals at 2.27 ppm ($-COCH_2-$, for the polyester) and at 3.65 ppm ($-CH_2CH_2O-$, for PEO), such that the grafting efficiency was 50−60%. The SEC trace after the PEO grafting remained unimodal and symmetric, with a slightly narrower distribution ($M_w/M_n = 1.30$, $M_n = 24\,000$) than the poly(γ-HOϵCL-*co*-ϵCL) macrocyclic precursor ($M_w/M_n = 1.40$, $M_n = 21\,000$) (Figure 7).

Additional, although qualitative, evidence for the successful grafting of PEO onto the macrocycles may be found in the formation of water-soluble micelles by self-assembly of the amphiphilic grafted macrocycles in water. Spherical micelles are observed by TEM (Figure 8) that consist of a hydrophobic core formed by the cyclic copolyester and a hydrophilic corona of PEO.

Conclusions

Random copolymerization of γEt$_3$SiOϵCL with ϵCL was initiated by DSDOP in toluene at 40 °C, followed by the addition and sequential polymerization of a few units of αAϵCL. The functionalized macrocyclic poly(γEt$_3$SiOϵCL-*co*-ϵCL) copolymer was prepared by intramolecular photo cross-linking of the unsaturations next to the propagating sites. An amphiphilic sun-shaped copolymer was thus successfully prepared by the selective hydrolysis of triethylsilanolate groups into hydroxyl ones, followed by their esterification by carboxylic acid terminated PEO. Micellization of this new type of amphiphiles was observed by transmission electron microscopy (TEM). A more detailed comparison of the micellization of sun-shaped and the parent linear PCL-*g*-PEO counterpart is under current investigation and will be reported in a forthcoming paper. It must be noted that the hydroxyl groups left unreacted could be reacted with a multifunctional compound (isocyanate or acyl chloride) in order to build up a network of macrocycles with dangling PEO chains.

Compared to the cyclization of linear chains by the coupling of their chain ends, the process reported here has the substantial advantage that the chain ends are continuously connected one to each other by a tin atom, which greatly facilitates the permanent (stable) coupling of the chains. Moreover, the macrocycles, grafted or not, are precursors of tadpole-shaped copolymers. This strategy is very flexible and paves the way to a variety of multicomponent cyclic architectures and to the investigation of the nanostructures and the macroscopic properties they can give rise to.

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