Combination of Ring-Opening Polymerization and "Click" Chemistry for the Synthesis of an Amphiphilic Tadpole-Shaped Poly(ϵ-Caprolactone) Grafted by PEO

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ABSTRACT: A tadpole shaped poly(ϵ-caprolactone) (PCL; M_n = 24 500) was made amphiphilic by grafting the two PCL tails with PEO. In the first step, a macrocyclic PCL was synthesized by ring-opening polymerization of ϵ-caprolactone (ϵCL) initiated by a cyclic tin(IV) dialkoxide and stabilized by local intramolecular photo-cross-linking. In the second step, the polymerization of a mixture of ϵCL and α-chloro-ϵ-caprolactone (αClϵCL) was resumed with formation of two activated chloride containing PCL tails. In the third step, the chlorides were converted into azides onto which alkynyl end-capped PEO was grafted by the copper-mediated Huisgen's cycloaddition [3 + 2], thus giving a "click" reaction. The thermal properties of the final copolymer and the precursors were analyzed by differential scanning calorimetry. The amphiphilicity of the final copolymer was confirmed by micellization in water.

Introduction

Nowadays, much attention is paid to the synthesis and study of copolymers with different compositions and chain architectures, such as linear, grafted, comb-shaped, star-shaped, hyperbranched, and dendrimeric chains with the purpose to establish architecture-property relationships in bulk and in solution.[1] The discovery of natural DNA macromolecular ring,[2] where the two strands of the double helix form a high order link, can account for the effort by the chemists to design and synthesize cyclic macromolecules.[3] Recently, Kricheldorf revised the classical theory of step-growth polycondensation and showed that macrocycles can be prepared under kinetic control provided that no side reaction takes place and that conversion is close to 100%.[4] Another approach relies on the synthesis of telechelic precursors by living/controlled polymerization techniques followed by the end-to-end coupling of the linear chains by any reaction known in the state of the art, such as nucleophilic substitution,[5,6] addition on unsaturations,[7−9] metathesis reaction,[10] amidification,[11] "click" reaction,[12] and electrostatic interaction followed by covalent fixation.[13] The main advantage of this route has to be found in the control of the molecular weight of the linear precursors of the macrocycles. This strategy was successfully implemented to synthesize a wide range of cyclic macromolecules, such as polystyrene,[5−7,9,14−17] poly(2-vinylpyridine),[18] poly(2-chloroethyl vinyl ether)s,[19,20] poly(tetrahydrofuran),[21] polyisoprene,[8,22,23] and polybutadiene.[24,25] However, in order to prevent any detrimental intermolecular polycondensation from taking place, the intramolecular coupling reaction must be performed under very high dilution, and the length of the linear precursors must be small enough for the intramolecular coupling to be effective. In spite of these restrictions, tadpole-shaped copolymers with one[26−29] or two side chains were synthesized.[27,30,31] Quite interestingly, Deffieux et al. explored the synthesis of highly branched macrocycles, i.e., cyclic poly(chloroethyl vinyl ether) onto which polystyrene chains are attached.[32]

Very recently, a novel strategy was reported for the synthesis of a high molecular weight macrocyclic PCL (∼20000).[33] First, a cyclic tin(IV) dialkoxide initiated the polymerization of ϵCL, followed by a few units (15−20) of ϵ-caprolactone α-substituted by an acrylate (compound **1**, Scheme 1). Finally, the intramolecular photo-cross-linking of the pendent unsaturations yielded the targeted macrocycles (compound **2**, Scheme 1). The propagating tin dialkoxide, that was untouched by photo-cross-linking, resumed the ring-opening polymerization of either ϵCL[33] or lactide,[34] with formation of a two-tail tadpole-shaped copolyester. In a version of this strategy, the macrocyclic PCL was substituted by pendent hydroxyl groups, that were esterified by carboxylic acid end-capped PEO, so leading to a sun-shaped copolymer.[35] Nevertheless, to the best of our knowledge, no example of tadpole-shaped polymer with grafted tails, has been reported in the scientific literature.

Recently, Riva et al.[36,37] and Parrish et al.[38] showed that PEO could be grafted onto linear aliphatic polyesters, such as PCL and PLA, by "click" Huisgen's cycloaddition [3 + 2] of azides and alkynes. Compared to other reactions previously used to graft PEO onto PCL,[39−43] the main advantage of "click" chemistry has to be found in very mild experimental conditions and minimized risks of degradation. For instance, PEO was successfully grafted onto polylactide without significant degradation of a nevertheless poorly stable polyester. The "click" cycloaddition was carried out in an organic solvent (THF, DMF) at a low temperature (35 °C).[36]

This paper aims at reporting on the synthesis of a two-tail tadpole-shaped copolyester, whose the tails are grafted by hydrophilic PEO according to the strategy shown in Scheme 1. The grafting is carried out by the "click" copper-mediated cycloaddition [3 + 2][44] of alkyne end-capped PEO onto azides attached to the tails. The ultimate purpose is to make tadpole-shaped PCL amphiphilic and to compare this novel architecture to the traditional PCL-*b*-PEO diblock and PCL-*g*-PEO graft copolymers.[45] It may be noted that all these copolymers consist of two biocompatible components and that PEO is known for protein repellent properties.

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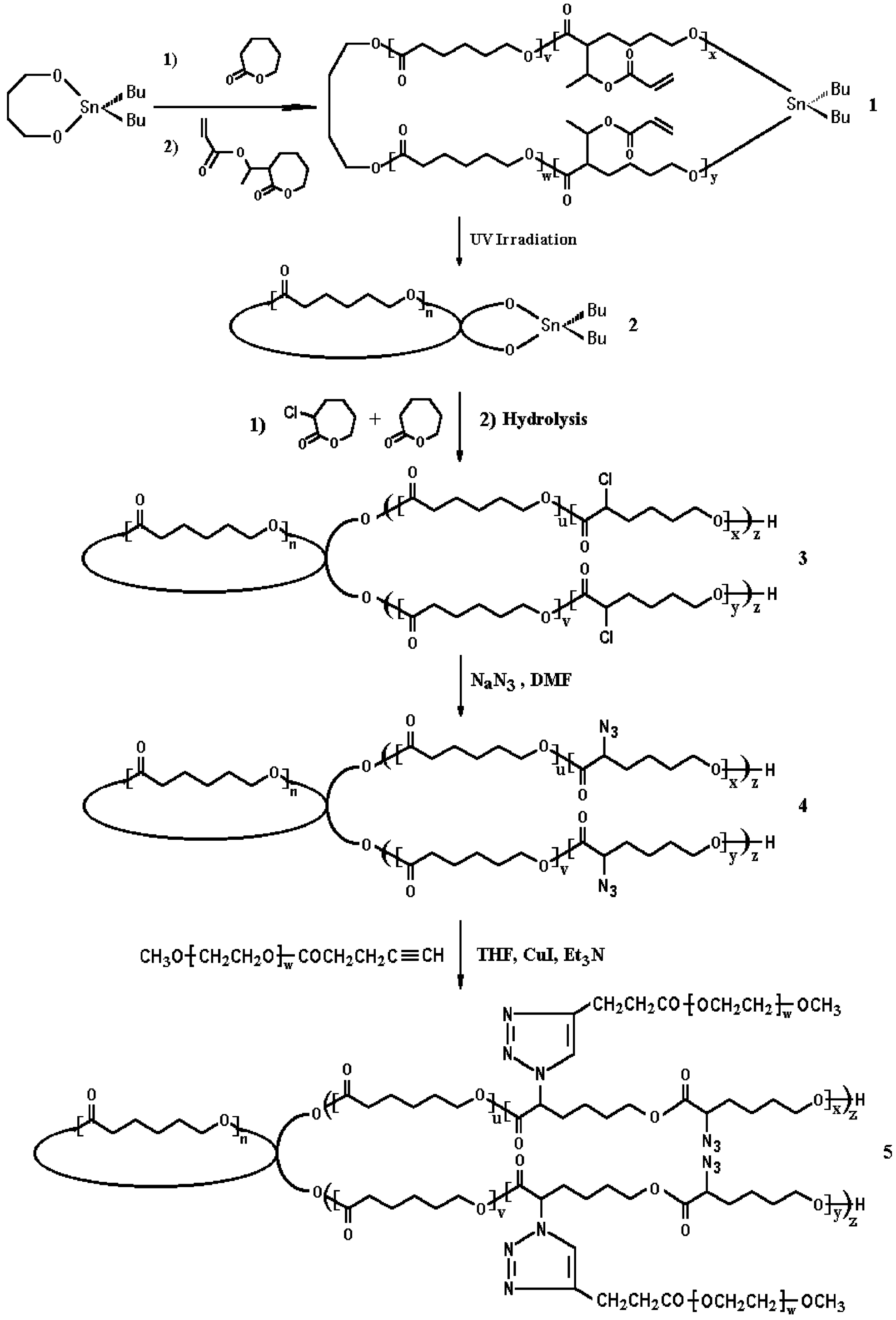
Scheme 1. Synthesis of an Amphiphilic Copolymer by Grafting of PEO onto a Tadpole-Shaped Precursor



Experimental Section

Materials. ϵ-Caprolactone (ϵCL) (Aldrich) was dried over calcium hydride at room temperature for 48 h and distilled under reduced pressure just before use. Synthesis of 2-dibutyl-2-stanna-1,3-dioxepane (DSDOP),[46] α-chloro-ϵ-caprolactone (αClϵCL)[47] and the macroinitiator **2**[34] was reported elsewhere. Benzophenone (Aldrich) was purified by sublimation at 40 °C in vacuo and further 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. *N,N*′-Dimethylformamide (DMF) (ACROS) was dried over P_2O_5 for 5 days and distilled under nitrogen before use. Poly(ethylene glycol) monomethyl ether (M_n = 1050) (PEO) (Fluka), 4-pentynoic acid (Aldrich), dicyclohexylcarbodiimide (DCC) (Aldrich), 4-dimethylaminopyridine (DMAP) (Fluka), sodium azide (Aldrich), diethyl ether, heptane, and triethylamine (Aldrich) were used as received.

Preparation of Alkynyl End-Capped PEO. Poly(ethylene glycol) monomethyl ether (PEO) (M_n = 1000, 5 g, 4.7 mmol) was dissolved in dichloromethane (20 mL), followed by addition of a solution of 4-pentynoic acid (1 g, 9.4 mmol) and 4-dimethylaminopyridine (DMAP) (0.13 g, 1.18 mmol) in CH_2Cl_2 (5 mL) and finally 5 mL of a dicyclohexylcarbodiimide (DCC) (1.9 g, 9.4 mmol) solution in CH_2Cl_2. This mixture was stirred at room temperature for 16 h. After filtration, the solvent was eliminated under reduced pressure. The residue was dissolved in THF (8 mL), and the solution was filtrated before being poured in a mixture of diethyl ether and heptane (1:1). The precipitated product was

Table 1. Molecular Characteristic Features of 2 (Macrocyclic PCL), 3 (Tadpole-Shaped Copolyester), 4 (Azide-Substituted Copolyester), and 5 PEO-Grafted Copolymer) (See Scheme 1)

					composition of the tails			
samples	$M_{n,th} \times 10^3$	$M_{n,NMR} \times 10^3$	$M_{n,SEC}{}^a \times 10^3$	M_w/M_n	$F_{\epsilon CL}{}^b$	$F_{\alpha Cl\epsilon CL}$	$F_{\alpha N3\epsilon CL}$	F_{PEO}
2	25.6	24.5	20.6	1.40				
3	67.0	67.6	30.0	1.40	0.47	0.53		
4	68.0	66.6	31.0	1.40	0.47	0	0.53	
5	226.0	181.0	26.2	1.65	0.47	0	0.18	0.35

[a] Polystyrene (PS) standards were used for calibration together with the equation: $M_n(PCL) = 0.259 \times M_n(PS)^{1.073}$.[49] [b] $F_x = (DP_x)/(DP_{total})$, where DP_x (NMR analysis) is the polymerization degree of the comonomer x in the tails of the tadpole-shaped copolyester and DP_{total} is the sum of DP_x.

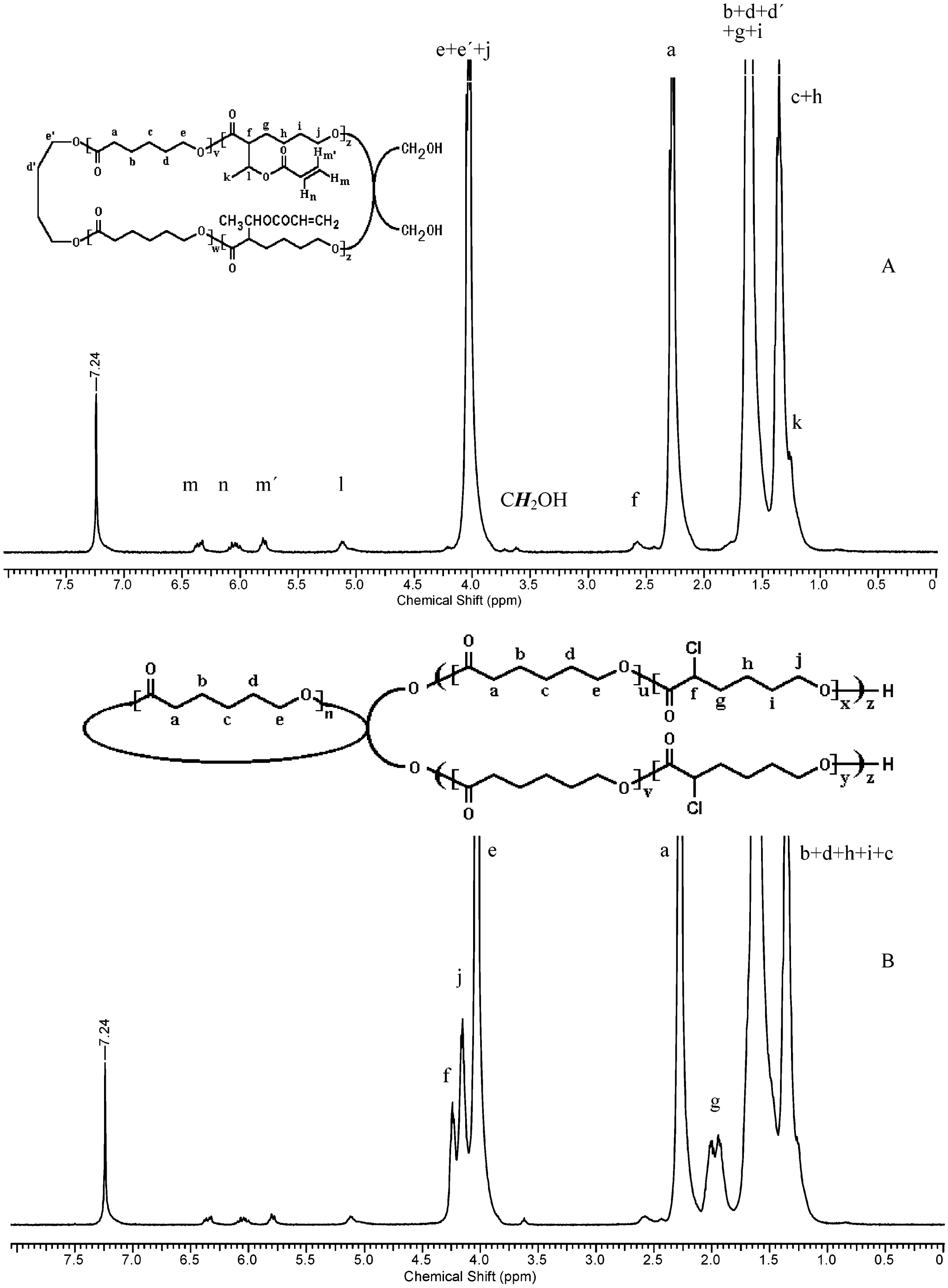


Figure 1. ^1H NMR spectra: (A) macrocyclic **2** after hydrolysis of the endocyclic tin dialkoxide; (B) tadpole-shaped copolyester **3**.

collected by filtration and dried in vacuo. Purification of the crude product by precipitation was twice repeated. Alkynyl end-capped PEO ($CH_3O(CH_2CH_2O)_{24}COCH_2CH_2C{\equiv}CH$) was analyzed by ^1H NMR and FTIR. ^1H NMR: δ 1.95 (t, 1H, $-C{\equiv}C\boldsymbol{H}$), 2.5 (m, 4H, $-C\boldsymbol{H}_2C\boldsymbol{H}_2C{\equiv}CH$), 3.34 (s, 3H, $C\boldsymbol{H}_3O-$), 3.6 ($-(C\boldsymbol{H}_2C\boldsymbol{H}_2O)_{24}-$), 4.22 (t, 2H, $-C\boldsymbol{H}_2OCO-$). IR: 1738 ($\nu_{C=O}$) cm^{-1}.

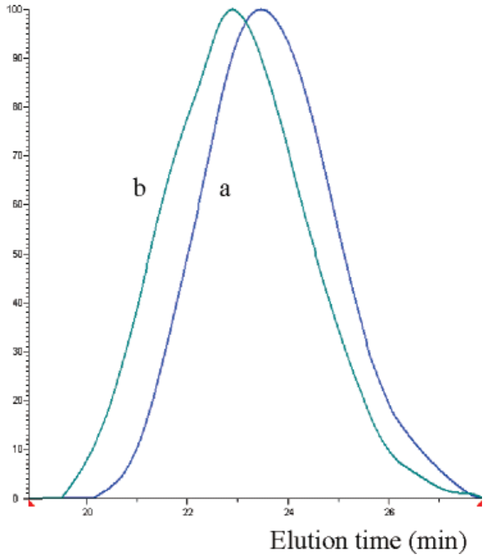


Figure 2. SEC traces for (a) the cyclic polyester after UV treatment and (b) the tadpole-shaped copolyester.

Preparation of the Tadpole-Shaped Copolyester 3, i.e., Macrocyclic Poly(ϵ-caprolactone) with Two Poly(αClϵCL-co-ϵCL) Tails (Scheme 1). In a typical experiment, the macroinitiator **2** (0.02 mmol, concentration: 6 wt %) was added to a mixture of α-chloro-ϵ-caprolactone (αClϵCL) (0.46 g, 3.16mmol) and ϵCL (0.35 mL, 3.16 mmol) in dry toluene (2 mL). After being stirred at 40 °C for 2 h, the polymerization mixture (concentration: 12 wt %) was hydrolyzed by acetic acid (1 M in toluene), precipitated in cold heptane, collected by filtration, and dried in vacuo (yield: 94%).

Grafting of PEO onto the Tadpole-Shaped Copolyester 4. First, 0.3 g of **3** (0.78 mmol of αClϵCL) was dissolved in 10 mL of DMF, followed by the addition of 0.15 g (2.34 mmol) of sodium azide. After the reaction was stirred at room temperature for 12 h, DMF was evaporated under reduced pressure, followed by addition of toluene (7 mL) and then filtration. The polymer **4**, i.e., the macrocyclic poly(ϵ-caprolactone) with two poly(αN_3ϵCL-co-ϵCL) tails, was precipitated in cold heptane, recovered by filtration, and dried in vacuo (yield : 93%).

Alkynyl end-capped PEO ($CH_3O(CH_2CH_2O)_{24}COCH_2CH_2C\equiv CH$) (0.70 g, 0.62 mmol) and 0.29 g of **4** (0.62 mmol of αN_3ϵCL) were dissolved in THF (12 mL), followed by the addition of triethylamine (0.1 mL, 0.68 mmol) and copper(I) iodide (0.06 g, 0.31 mmol). The reaction mixture was stirred at 35 °C for 4 h. After cooling to room temperature, the solution was dropwise added to cold diethyl ether and the precipitate collected by filtration. The conversion of pendent azide determined by ^{1}H NMR analysis is 65%. The polymer was dissolved in toluene and purified by elution through SiO_2 (toluene) in order to get rid of copper. Part of the solvent was evaporated, before the polymer was precipitated in diethyl ether, collected by filtration, and dried in vacuo. Purification of **5** by precipitation was twice repeated (yield = 53%).

Micellization of 5. First 25 mg of **5** was dissolved in 1.5 mL of THF, followed by the dropwise addition of water (1 mL) under vigorous stirring for 2 h. Then 2 mL of water was added in order to freeze in the micelles, the organic solvent (THF) being eliminated by dialysis against water. The micelles were observed by TEM.

Characterization. Size exclusion chromatography (SEC) was performed in THF at a flow rate of 1.0 mL min^{-1} at 45 °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 and the $M_n(\text{PCL}) = 0.259 \times M_n(\text{PS})^{1.073}$ equation[49] were used for calibration. ^{1}H NMR spectra were recorded in $CDCl_3$ with a Bruker AN 400 apparatus at 25 °C. Differential scanning calorimetry (DSC) was carried out with a TA DSC Q100 thermal analyzer calibrated with indium. The melting temperature (T_m) was measured after cooling the sample down to −90 °C and heating it up to 150 °C at 10 °C/min. Transmission electron micrographs (TEM) 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 of **5** (0.5 wt % polymer). The excess of solution was removed with a filter paper, followed by washing with water and drying in air. IR analysis was performed with a Perkin-Elmer Spectrum One FTIR spectrometer.

Results and Discussion

Although the molecular architecture of the copolymer envisioned in this work is complex, a five-step strategy has been devised (Scheme 1), in which the two polymerization steps are controlled and the substitution (conversion of chlorides into azides) and the "click" cycloaddition reactions are easily implemented and quasi quantitative.

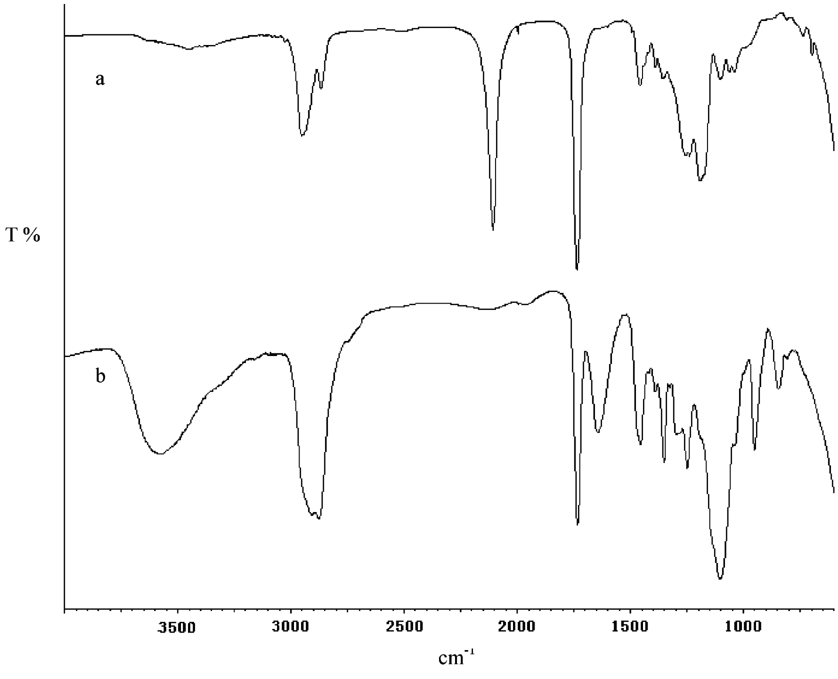


Figure 3. FTIR spectra: (a) tadpole-shaped copolyester **4** containing azide groups; (b) PEO-grafted copolymer **5** (Scheme 1).

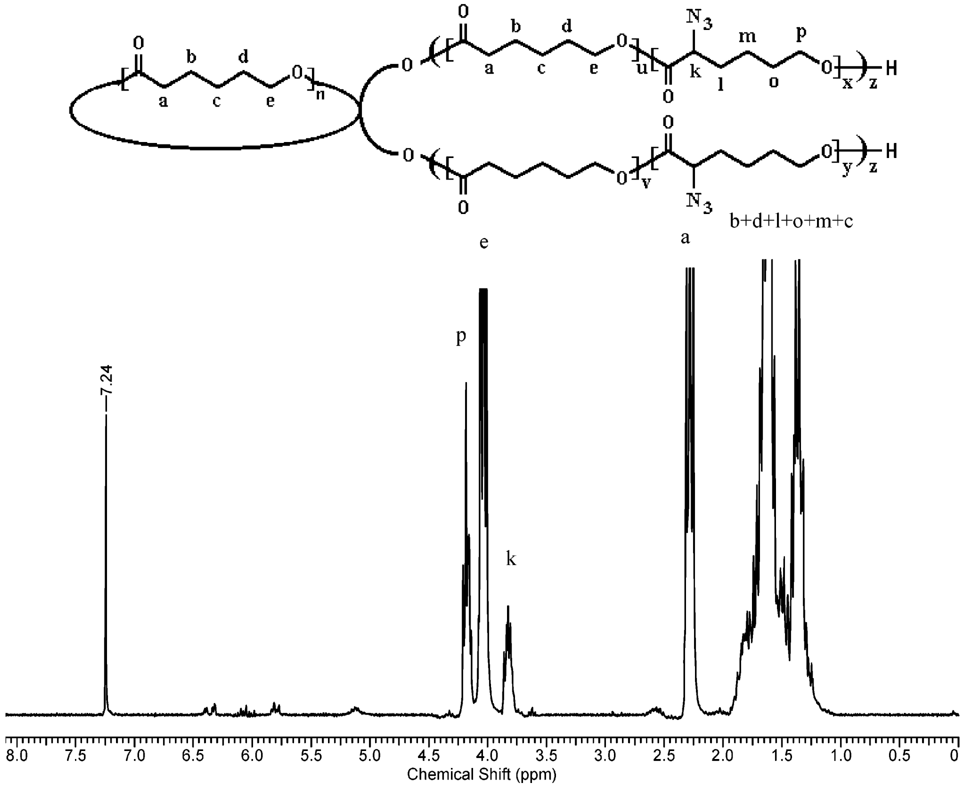


Figure 4. ^1H NMR spectrum for the tadpole-shaped copolyester **4**.

Synthesis of the Tadpole-Shaped Copolyester 3, i.e., Macrocyclic Poly(ϵ-caprolactone) with Two Poly(αClϵCL-*co*-ϵCL) Tails (Scheme 1). Recently, Lenoir et al. showed that tin(IV) dialkoxide is able to initiate the ring-opening copolymerization of ϵCL and αClϵCL.[48] In this work, quite an unusual macrocyclic tin(IV) dialkoxide (***2*** in Scheme 1) was used to initiate the copolymerization of ϵCL and αClϵCL. This macroinitiator was synthesized as reported elsewhere.[33] It contained 215 ϵCL units and 10.5 unsaturations, as an average. Molecular weight ($M_{n,NMR} = 24\,500$; $M_{n,SEC} = 20\,600$) and polydispersity ($M_w/M_n = 1.4$) remained unmodified upon the UV treatment used to cross-link the intramolecular acrylate groups and to stabilize the macrocycle accordingly (Table 1). The concentrated macroinitiator **2** solution (concentration = 6 wt %) was added with a solution of ϵCL and αClϵCL in dry toluene. The polymerization mixture was stirred at 40 °C for 2 h. The resumption of the ϵCL and αClϵCL copolymerization was confirmed by ^1H NMR (Figure 1). Indeed, the resonances typical of the protons of the αClϵCL units were clearly observed at 4.25 ($-COC\boldsymbol{H}Cl-$), 4.1 ($-C\boldsymbol{H}_2O-$), and 2.0 ppm ($-CHClC\boldsymbol{H}_2-$). The experimental average degree of polymerization of ϵCL and αClϵCL in the tails was 154 and 173, respectively, as calculated from the integration of the resonance peaks at 4.25 ppm for αClϵCL and 2.25 ppm for ϵCL, in line with the theoretical value ($DP_{th,\epsilon CL} = DP_{th,\alpha Cl\epsilon CL} = 158$).

The SEC trace of the copolymer ***3*** (Scheme 1) was shifted toward shorter elution times (Figure 2), while keeping the polydispersity index unchanged ($M_w/M_n = 1.40$). The apparent molecular weight was actually increased ($M_{n,SEC} = 30000$) compared to the macrocyclic precursor ($M_{n,SEC} = 20\,600$, $M_w/M_n = 1.40$). It can thus be concluded that the polymerization resumption by the macrocyclic **2** is effective and that a functional tadpole-shaped copolyester can be easily prepared. It must be noted that the number of arms cannot be directly determined by traditional NMR and SEC analyses. Nevertheless, it was previously shown that tin alkoxides were insensitive to UV irradiation and that the polymerization resumption was not perturbed by this treatment,[34] which gives credit to the formation of a tadpole-shaped copolyester with two tails.

Conversion of the Chloride Substituents of the Tails into Azides. Riva et al. previously reported that chloride substituents of linear copolyesters are quantitatively converted into azides by reaction with sodium azide, under nondegrading conditions for the polyester chains, i.e., in DMF at room temperature overnight.[36] This derivatization reactions was extended to the poly(αClϵCL-*co*-ϵCL) tails of the tadpole-shaped copolyester **3** (Scheme 1). A strong absorption characteristic of the azide groups was observed at 2107 cm^{-1} in the FTIR spectrum (Figure 3). The ^1H NMR spectrum for the tadpole-shaped copolyester **4** is shown in Figure 4. Two new resonances at 3.8 and 4.2 ppm were assigned to the $-COC\boldsymbol{H}N_3-$ and the $-C\boldsymbol{H}_2O-$ protons, respectively, of the $\alpha N_3\epsilon$CL units. At the same time, the signals at 4.25 and 2.0 ppm typical of the $-COC\boldsymbol{H}Cl-$ and the $-CHClC\boldsymbol{H}_2-$ protons of the αClϵCL units disappeared completely, and the signal at 4.1 ppm assigned to the $-OC\boldsymbol{H}_2$-COClCH$-$ protons was slightly shifted downfield upon substitution of chloride by azide, which confirms that the derivatization reaction was complete. Moreover, the molar composition of the tails was determined by ^1H NMR analysis ($F_{\alpha N3\epsilon CL} = 0.53$), in full agreement with the composition of the precursor **3** ($F_{\alpha Cl\epsilon CL} = 0.53$). Finally, the SEC traces (not shown) before and after the substitution reaction could be superimposed, as it should be for nondegrading experimental conditions.

Grafting of Alkynyl End-Capped PEO onto the Tadpole-Shaped Copolyester 4 by the "Click" Reaction. In a preliminary step, alkynyl end-capped PEO was prepared by esterification of the hydroxyl end group of PEO monomethyl ether by 4-pentynoic acid, in the presence of a condensation reagent, DCC, and a catalyst, DMAP, in dichloromethane at room temperature overnight. An IR absorption at 1738 cm^{-1} ($\nu_{C=O}$) and two triplets at 1.95 ppm for the terminal alkynyl proton

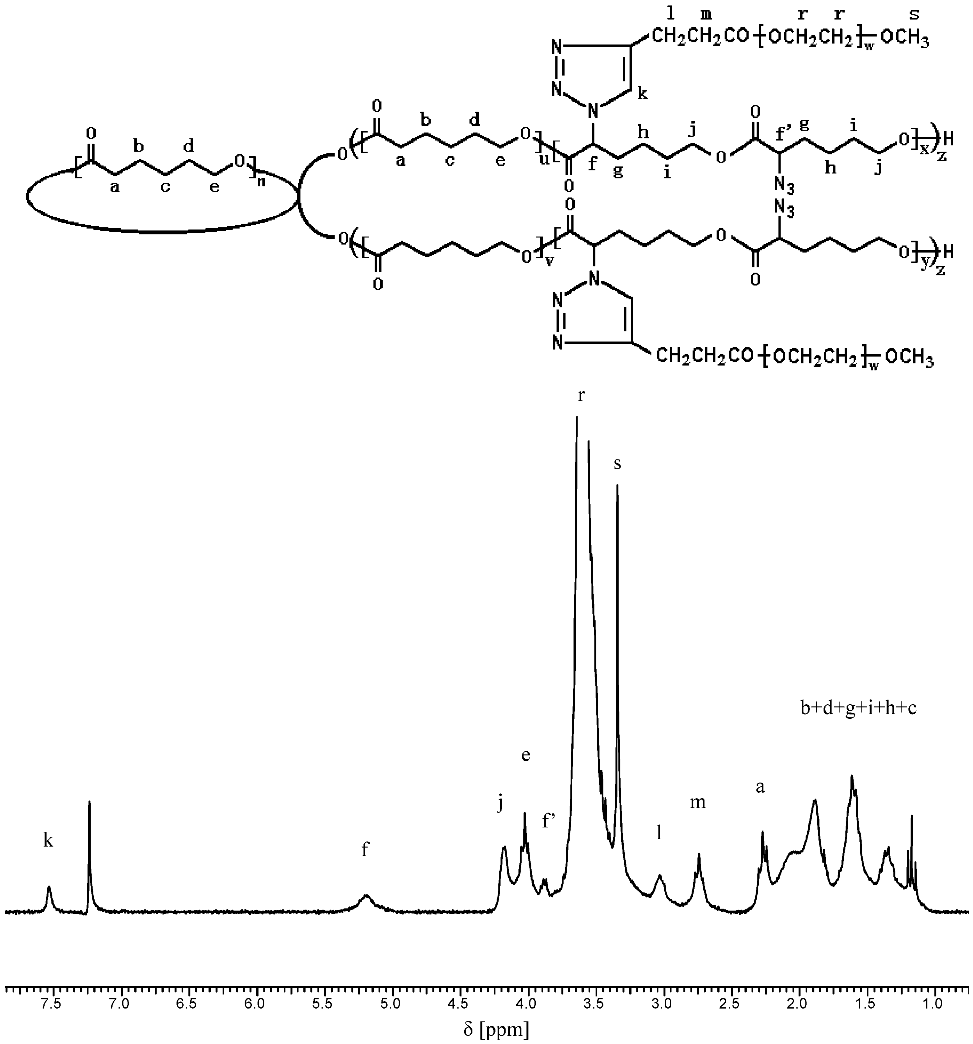


Figure 5. ^{1}H NMR spectrum for the amphiphilic copolymer **5**.

and at 4.22 ppm for the $-CH_2OCO-$ protons, respectively, confirmed the success of the esterification.

The tadpole-shaped copolyester **4** was reacted with 1.0 equiv (with respect to the $\alpha N_3\epsilon CL$ units) of alkynyl end-capped PEO, in THF in the presence of CuI and triethylamine at 35 °C. The reaction was monitored by FTIR spectroscopy. After 4 h, a significant decrease of the stretching frequency at 2107 cm^{-1}, typical of the azide, and the appearance of an absorption at 1646 cm^{-1}, typical of the triazole ring (Figure 3), showed that Huisgen's cycloaddition occurred as expected. The copolymer was precipitated in diethyl ether, and unreacted PEO was eliminated by repeating the precipitation three times. Figure 5 shows the ^{1}H NMR spectrum for the PEO-grafted tadpole-shaped copolyester. A set of new peaks was clearly observed at 7.5 ppm (singlet) typical of methine proton of the triazole ring, at 5.2 ppm assigned to the $-COC\boldsymbol{H}$(1-triazole)$-$ proton, at 3.6 ppm typical of the protons for the ethylene oxide units, at 3.3 ppm for the methoxy protons, at 3.0 ppm for the $-$(4-triazole)$-C\boldsymbol{H}_2CH_2CO-(OCH_2CH_2)_{24}OCH_3$ protons, and at 2.7 ppm for the $-$(4-triazole)$-CH_2C\boldsymbol{H}_2CO-(OCH_2CH_2)_{24}OCH_3$ protons (Figure 5 to be compared to Figure 4). The grafting efficiency (65%) was calculated from the relative intensity of the signals at 7.5 ppm for the triazole ring and at 2.25 ppm for the ϵCL units. Each arm of the tadpole-shaped copolyester was grafted by 53 PEO chains and M_n was 181000 g/mol as determined by ^{1}H NMR (Table 1).

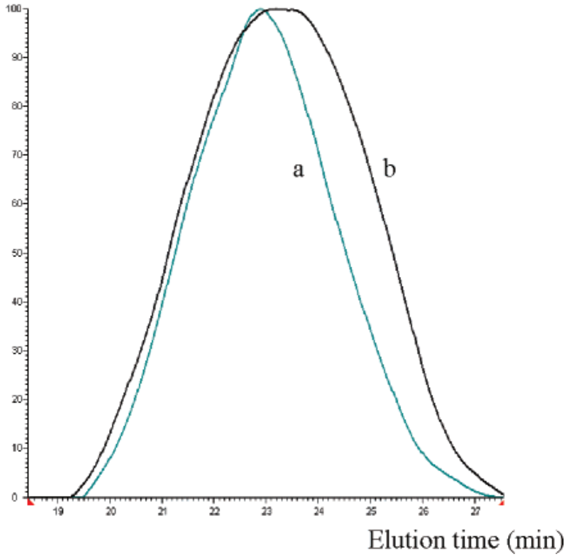


Figure 6. SEC traces for the tadpole-shaped copolyester before (a) and after (b) grafting of PEO by "click" cycloaddition.

The SEC trace (Figure 6) for the PEO-grafted copolymer **5** shows a slight increase in the polydispersity from 1.40 for the precursor **4** to 1.60, in line with previously reported data.[36] Nevertheless, the chromatogram remained symmetrical. An apparent shift of the chromatogram toward higher elution times

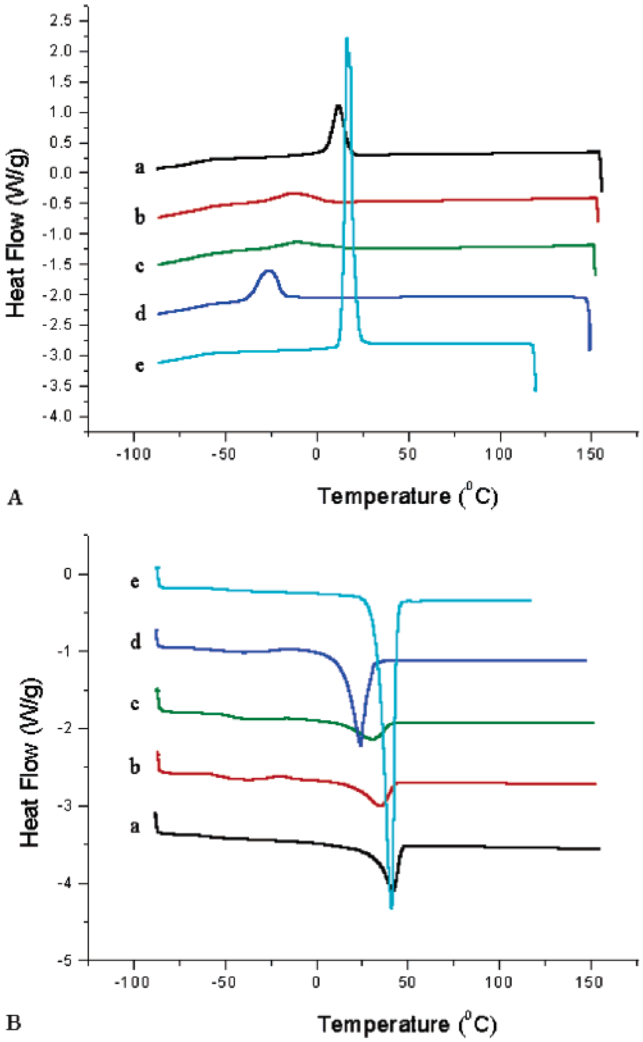


Figure 7. DSC traces during the cooling (A) and the second heating (B) runs for (a) macrocyclic PCL, (b) tadpole-shaped copolyester **3**, (c) azide-substitued copolyester **4**, (d) PEO-grafted copolymer **5**, and (e) linear homo-PEO.

was unexpectedly (and repeatedly) observed, which strongly suggests a highly compact conformation for the PEO-grafted copolymer **5** of a very complex architecture. This surprising observation calls for further investigation.

Thermal Properties. The thermal behavior of cyclic PCL, α-chloro-functionalized tadpole-shaped copolyester **3**, α-azide-substituted derivative **4**, PEO-grafted copolymer **5**, and homo-PEO (reference) was characterized by differential scanning calorimetry (DSC) (Figure 7). The (co)polymers were first heated to 150 °C and then cooled down to −90 °C at a rate of 10 °C/min. The DSC traces during cooling are shown in Figure 7(A). A crystallization peak was observed at 12.0 °C for the macrocyclic PCL **2** after hydrolysis of the tin dialkoxide, in contrast to a faint peak at a lower temperature (−12 °C) for the tadpole-shaped copolyesters with two amorphous tails, poly(αClϵCl-*co*-ϵCL) and poly(αN_3ϵCl-*co*-ϵCL), respectively. The crystallization enthalpy (ΔH_c) decreased by at least a factor of 2 upon the grafting of two tails onto the macrocyclic PCL (Table 2). The same observation was reported in the case of grafting of two semicrystalline poly(L-lactide) arms.[34] As a rule, the two tails of the tadpole-shaped PCL have a depressive effect on the crystallization of PCL, whatever they are amorphous or not. Crystallization of the PEO grafts of the PEO-grafted tadpole-shaped copolymer was observed although at a much lower temperature and to a lesser extent than homo PEO.

Table 2. Physical Properties of 2 (Macrocyclic PCL), 3 (Tadpole-Shaped Copolyester), 4 (Azide-Substituted Copolyester), and 5 (PEO-Grafted Copolymer) (See Scheme 1) and Homo-PEO

samples	T_g[a] [°C]	T_m[a] [°C]	ΔH_m[b] [J/g]	T_c[a] [°C]	ΔH_c[b] [J/g]
2	−57.0	42.0	34.5	12.0	36.5
3	−54.5	35.5	27.0	−12.0	16.5
4	−50.5	31.5	21.0	−11.0	12.0
5		24.5	53.5	−27.5	30.5
homo-PEO		41.5	165.5	16.5	157.5

[a] T_g and T_m were measured during the second heating run at 10 °C/min. T_c was measured during the cooling run after the first heating. [b] ΔH_m (ΔH_c) is the melting (crystallization) enthalpy measured under the same conditions as T_m (T_c).

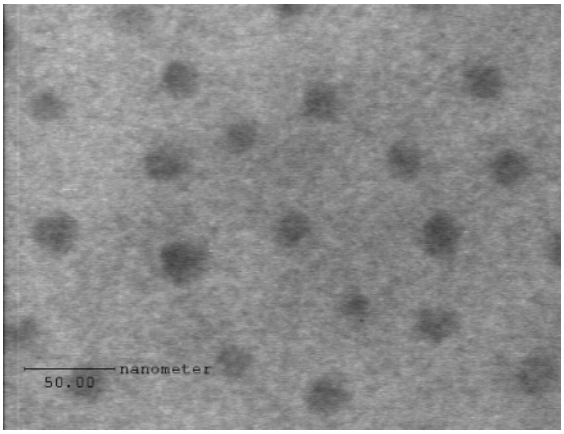


Figure 8. Micelles of PEO-grafted copolymer **5** observed by TEM.

All the samples were then heated from −90 °C at 10 °C/min, and the DSC traces are shown in Figure 7B. A melting endotherm was noted for the cyclic PCL at 42 °C with a melting enthalpy of 34.5 J/g. Once again, the negative impact of the tails was reported to an extent that depends on the substituents, thus chlorides vs azides. The melting temperature of PCL was indeed decreased by 6.5 °C in the case of α-chlorides and by 10.5 °C for the α-azide pendent groups. In parallel to T_m, the melting enthalpy for PCL was also decreased by 7.5 J/g for the α-chloride substituted copolyester and by 10.5 J/g for the α-azide version (Table 2). When PEO is part of the copolymer, only this constitutive component crystallizes, although with restrictions imposed by the complex architecture, as testified by a substantial decrease in T_m and ΔH_m compared to linear PEO (Table 2).

Additional although qualitative evidence for the successful grafting of PEO onto the tadpole-shaped PCL may be found in the micellization in water as result of the amphiphilicity and self-assembly of the copolymer. Spherical micelles were indeed observed by TEM (Figure 8), that are supposed to consist of a hydrophobic polyester core surrounded by a hydrophilic corona of PEO.

Conclusions

This work aimed at reporting for the very first time the synthesis of a tadpole-shaped copolyester with a high molecular weight cyclic head (M_n = 24 500) and two functionalized grafted tails. First, a cyclic tin(IV) dialkoxide initiated the ring-opening polymerization of ϵCL followed by a few units of αAϵCL, with formation of a large size living macrocycle. After the intramolecular photo-cross-linking of the pendent acrylic unsaturations, the copolymerization of ϵCL and αClϵCL was resumed, so yielding a tadpole-shaped copolyester with two activated chloride containing tails. The chloride groups were then converted into azides, that were added with alkyne end-capped PEO by a copper mediated "click" reaction. This new amphiphilic copolymer forms micelles in water, as testified by transmission electron microscopy (TEM). A detailed study of the impact of this quite unusual architecture on the macroscopic properties and self-assembly in solution and in bulk, will be reported in the near future, in comparison with acyclic counterparts. The "click" chemistry used for the grafting of the tails of the tadpole-shaped PCL is very tolerant to many functional groups and no cumbersome protection/deprotection reaction is required. This work paves thus the way to the synthesis of a variety of novel tadpole-shaped copolyesters and still more complex although well-defined architectures.

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