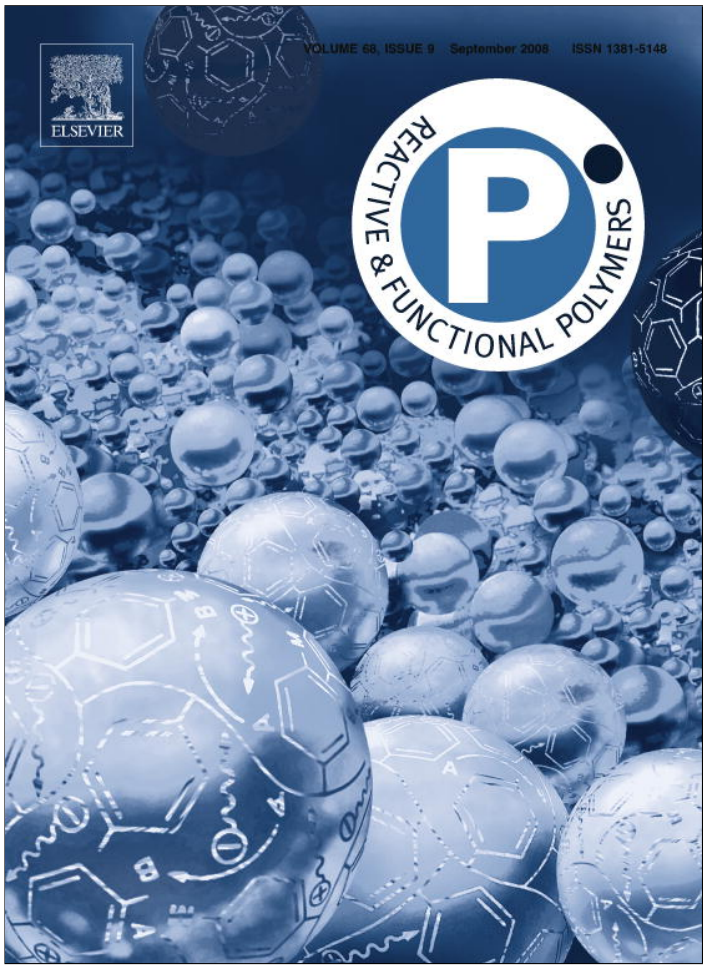

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# Activation of the hydrolytic polymerization of ε-caprolactam by ester functions: Straightforward route to aliphatic polyesteramides

Gaëlle Deshayes [a,*], Cécile Delcourt [a], Ingrid Verbruggen [b], Lise Trouillet-Fonti [c], Franck Touraud [c], Etienne Fleury [c], Philippe Degée [a], Mathias Destarac [c], Rudolph Willem [b], Philippe Dubois [a]

[a] Laboratory of Polymeric and Composite Materials (LPCM), Université de Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium
[b] High Resolution NMR Centre (HNMR), Department of Materials and Chemistry (MACH), Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels, Belgium
[c] Rhodia Recherche et Technologies, 85 rue des Fréres Perret, 69192 Saint Fons, France

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ABSTRACT

The hydrolytic polymerization of ε-caprolactam (CLa) was carried out in bulk (in absence of solvent) at 250 °C in the presence of carboxylic esters and aqueous $H_3PO_2$. It turned out that by conducting the ring-opening polymerization (ROP) of CLa in the presence of PEO–C(O)–O–$C_5H_{11}$, a selected model ester (PEO = poly(ethylene oxide)), a remarkable activating effect of the ester function on the hydrolytic polymerization of the lactam was observed yielding PEO–*b*–PCLa diblock copolymers. The comparison of the CLa monomer conversions obtained with or without the model ester activated by $H_3PO_2$, as determined by $^1$H NMR spectroscopy, has enabled to propose a multi-step mechanism in which three major reactions occurred: (i) ester and lactam hydrolysis, (ii) aminolysis of the carboxylic ester by the resulting primary amine of the hydrolyzed/opened lactam ring and (iii) condensation reactions between carboxylic acids and both amine/hydroxyl functions. The overall result of this multi-step mechanism can be assimilated as an "insertion" of the opened lactam into the ester function. By conducting the hydrolytic polymerization of CLa in the presence of an aliphatic polyester chain, such as poly(ε-caprolactone) (PCLo), polyesteramides were recovered with high yields and random distributions of the CLa and CLo repetitive units as determined by $^{13}$C NMR.



## 1. Introduction

Poly(ε-caprolactam) (PCLa, polyamide 6) is the most produced and commercially available polyamide. It is industrially synthesized by hydrolytic polymerization of ε-caprolactam (CLa). Numerous mechanistic studies on this ring-opening polymerization (ROP) have been performed and reported in [1,2]. The mechanism of the hydrolytic polymerization of CLa is summarized in Scheme 1. During the polymerization, three main equilibrium reactions occur: (i) ring-opening of CLa ($C_1$) in α-amino-ω-carboxylic acid ($P_1$), (ii) condensation of α-amino-ω-carboxylic acid oligomers ($P_n$, $P_m$), and (iii) ring-opening polymerization of CLa ($C_1$). In addition to these reactions and since the cyclic dimer ($C_2$) represents the major derivative within the cyclic byproducts [3,4], two additional equilibrium reactions have to be considered as well: (iv) ring-opening of $C_2$ in aminocaproylcaproic acid ($P_2$) and (v) ring-opening polymerization of $C_2$.

The ring-opening polymerization of lactams, instead of being initiated by water, can also be initiated by an amine or a carboxylic acid function. These functions are sufficiently active to initiate aminolytic (Scheme 2) and acidolytic (Scheme 3) polymerization of lactams, respectively.

In general, aliphatic polyamides, and especially polyamide 6, are semi-crystalline thermoplastics known for their relative fragility under mechanical stress at low temperature [5]. Aliphatic polyamides are characterized by high melting temperatures ($T_m$), as high as 220 °C in case of

* Corresponding author. Tel.: +32 404 822 8436.
*E-mail address:* gaelle.deshayes@chemistry.gatech.edu (G. Deshayes).

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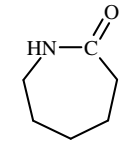
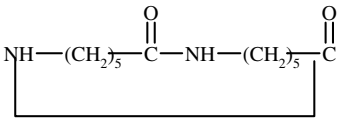
| | *Reaction* | *Equation* | *Other* |
|---|---|---|---|
| 1 | Ring-opening of CLa | $C_1 + H_2O \underset{k'_1 = k_1/K_1}{\overset{k_1}{\rightleftharpoons}} P_1$ | - |
| 2 | Condensation | $P_n + P_m \underset{k'_2 = k_2/K_2}{\overset{k_2}{\rightleftharpoons}} P_{n+m} + H_2O$ | n, m = 1,2,3… |
| 3 | Ring-opening polymerization | $P_n + C_1 \underset{k'_3 = k_3/K_3}{\overset{k_3}{\rightleftharpoons}} P_{n+1}$ | n = 1,2,… |
| 4 | Ring-opening of the cyclic dimer | $C_2 + H_2O \underset{k'_4 = k_4/K_4}{\overset{k_4}{\rightleftharpoons}} P_2$ | - |
| 5 | Ring-opening polymerization of the cyclic dimer | $P_n + C_2 \underset{k'_5 = k_5/K_5}{\overset{k_5}{\rightleftharpoons}} P_{n+2}$ | n = 1,2,… |

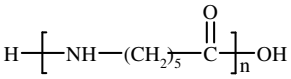
with:



$C_1$ = ε-caprolactam

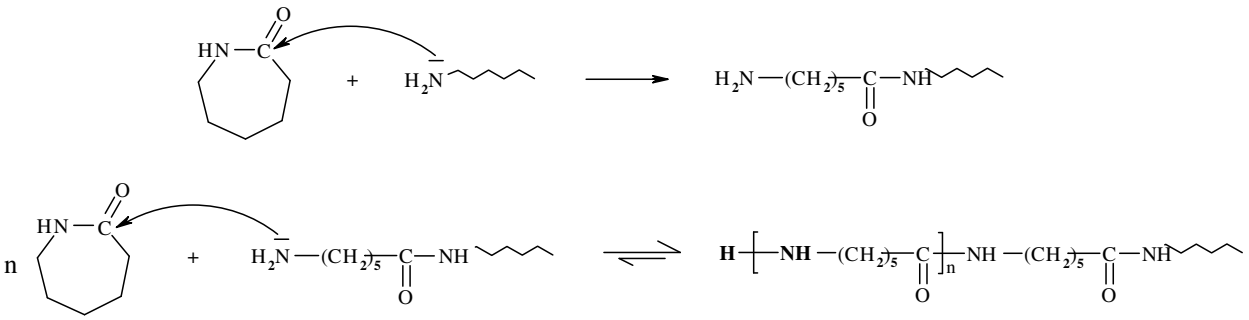


$C_2$ = cyclic dimer



$P_n$ = Polyamide 6

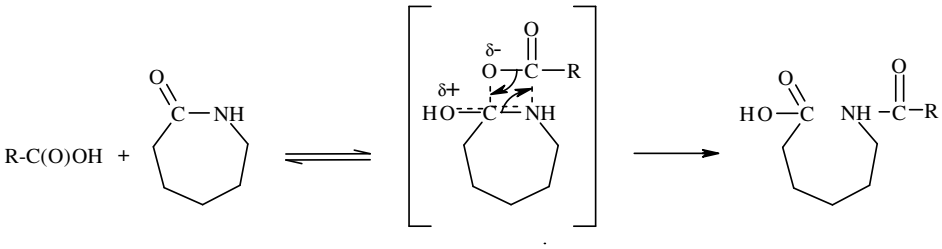
**Scheme 1.** Basic equations of the hydrolytic polymerization of ε-caprolactam ($C_1$).



**Scheme 2.** Aminolytic polymerization of CLa.

polyamide 6. In addition, one of the common properties of aliphatic polyamides is their high hygroscopicity. The absorbed water usually leads to undesirable modifications of the polyamide properties, for instance, decrease of the glass transition temperature ($T_g$) and of yield stress [6–8]. Furthermore, polyamides are not considered as biodegradable according to the European standard EN 13432 [9,10].

The introduction of ester units in the polyamide sequences, leading to the formation of aliphatic polyesteramides, can represent an efficient alternative to overcome these drawbacks. Indeed, aliphatic polyesteramides pave the way to a new type of biodegradable polymers, characterized by good thermal and mechanical properties [11–14]. By the polar nature of the amide groups and their



**Scheme 3.** Acidolytic polymerization of CLa.

capacity to form hydrogen bonds, amide units can reinforce the materials they are a part of. The ester links, on the other hand, sensitive to hydrolytic conditions, can induce the biodegradability of the copolymer [15].

Polyesteramides based on poly(ε-caprolactam) (PCLa) and poly(ε-caprolactone) (PCLo) have been widely studied, their properties varying from semi-crystalline thermoplastic to elastomeric, depending on the amount of ester units present in the copolymer and on the comonomer distribution along the macromolecular chain [12,13,16].

Biodegradable polyesteramides have been synthesized through either polycondensation, ring-opening polymerization, especially anionic polymerization, or ester-amide exchange reactions as conducted within direct melt blending of polyamide and polyester [17–19]. The major drawbacks of these methods lie in the intervention of numerous side reactions and so, in the lack of control of the polyesteramide chain structure.

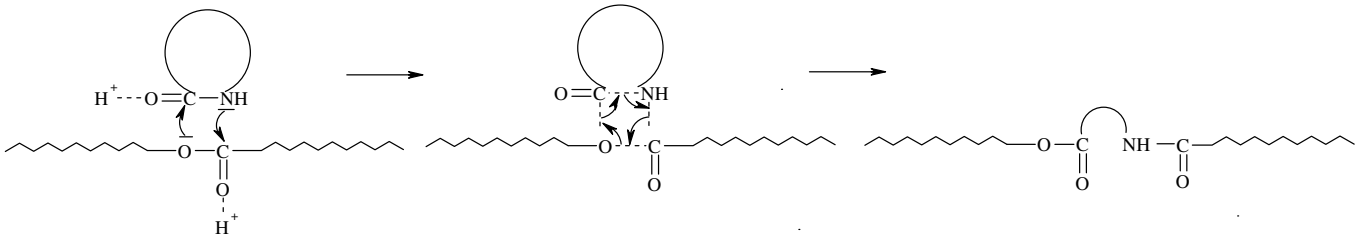
It has been recently observed that the hydrolytic polymerization of CLa conducted in the presence of aliphatic ester functions allows producing statistical polyesteramide chains [20,21]. Actually, the process takes place as if CLa polymerizes by an "insertion" mechanism of the lactam units into the carboxylic ester links (Scheme 4). In the present work, a mechanistic study of the polymerization of CLa in the presence of ester functions (activated by $H_3PO_2$) is carried out in order to get a better insight into this assumed "insertion" mechanism. Indeed, this novel type of copolymerization appears to be of particular interest because it should pave the way to new macromolecular architectures based on polyesteramide sequences.

## 2. Results and discussion

The influence of a monoester, with a long alkyl chain, on the hydrolytic polymerization of CLa was first investigated at 250 °C. This non-volatile ester, hereafter called model ester, was synthesized by a condensation reaction between ω-hydroxylated poly(ethylene oxide) (PEO–OH) and hexanoyl chloride in THF at 50 °C in the presence of triethylamine (PEO–O–C(O)–$C_5H_{11}$). The monohydroxylated poly(ethylene oxide) (PEO–OH) was chosen as a model based on criteria such as its low melting temperature ($T_m$ = 35 °C), its solubility in common organic solvents, but also because the proton and carbon atoms of this polyether display chemical shifts in NMR spectra in other value ranges than PCLa.

In a first set of experiments, the ring–opening polymerization (ROP) of ε-caprolactam (CLa) was carried out in sealed glass reactors, in bulk (i.e. in absence of solvent) at 250 °C in the presence of the model ester, PEO–O–C(O)–$C_5H_{11}$, and $H_3PO_2$ (0.25 mol% relative to the amide functions). Indeed, $H_3PO_2$ is largely industrially used for catalyzing the synthesis of polyamides via hydrolytic polymerization. The weight ratio of CLa/PEO–O–C(O)–$C_5H_{11}$ was fixed to the unity, which means a $[CLa]_0/[ester]_0$ molar ratio of 16. Table 1 reports the monomer conversion and the degree of polymerization of polyamides as recorded for different polymerization times (Table 1). For the sake of comparison, the hydrolytic polymerization of CLa was also performed in the presence of PEO–OH, i.e. without any ester functions in the reaction medium, under the same conditions (weight ratio CLa/ PEO–OH = 1, Table 1). Actually, the polymerization of CLa in the presence of PEO–OH was attempted in order to demonstrate that the hydroxyl functions of the PEO–OH are not sufficiently active to initiate the ROP of CLa. Indeed for promoting the ROP of lactams, it is known that hydroxyl functions require first their functionalization in *N*-acyllactam. Under such conditions, an anionic ring-opening polymerization mechanism initiated from the ω-*N*-acyllactam PEO chains does take place, leading to the formation of PEO-*b*-PCLa diblock copolymers [22–24].

In both cases, the $^1H$ NMR spectra show an increase of CLa monomer conversion with the polymerization time. When the ROP is conducted in the presence of PEO–OH



**Scheme 4.** Polymerization of CLa in the presence of carboxylic ester link (activated by $H_3PO_2$) via a hypothetical "insertion" mechanism.

**Table 1**
Monomer conversion ($Conv_{CLa}$) and degree of polymerization ($DP_{exp}$) of polyamides as obtained by hydrolytic polymerization of CLa at 250 °C in presence of 0.25 mol% of $H_3PO_2$ (50 wt% in water) and PEO–OH (CLa/PEO–OH = 1/1 w/w) or the model ester ($[CLa]_0/[PEO–O–C(O)–C_5H_{11}]_0 = 16$)

| Entry | Starting material | Time (h) | $Conv_{CLa}$[a] (%) | $DP_{exp}$[b] |
|---|---|---|---|---|
| 1 | PEO–OH | 7 | 14 | 2 |
| 2 | | 24 | 22 | 3 |
| 3 | | 48 | 20 | 3 |
| 4 | | 7 | 17 | 3 |
| 5 | PEO–O–C(O)–$C_5H_{11}$ | 24 | 35 | 5,5 |
| 6 | | 48 | 62 | 9 |

[a] As determined by proton NMR spectroscopy : conv = $I_{PA2}/(I_{CLa2} + I_{PA2}) \times 100$.
[b] $DP_{exp}$ determined by proton NMR spectroscopy based on the methylene ether protons of the polyether at 3.5 ppm: $DP_{exp} = [(160H/I_{3.5}) * I_{PA2}]/2$.

(Table 1, entries 1–3), the presence of signals assignable to –$CH_2$–COOH or –$CH_2$–COOR (AA2, PO5: 2.1 ppm) and –$CH_2$–$NH_2$ (AA3 : 2.85 ppm) protons is consistent with the formation of PCLa oligomers by condensation of α-amino-ω-carboxylic acid, and also consistent with the formation of PEO–O–C(O)–PCLa–$NH_2$ copolymers. These copolymers result from the condensation reaction between the PEO–OH hydroxyl end group and a carboxylic acid function issued from previously hydrolyzed CLa units (Scheme 5).

Interestingly, at identical polymerization time, a significant increase in the monomer conversion is observed when performing the ROP of CLa in the presence of the model ester (Table 1, entries 4–6), which suggests that the ester functions display an activating effect on the hydrolytic polymerization of CLa (Fig. 1).

The presence of the signal at 4.2 ppm, corresponding to α–OH methylene protons (–C*H*$_2$–OH, PO3), shows that some of the ester links were cleaved, leading to the formation of PEO–OH and hexanoic acid. However by comparing, on one hand, the relative intensities of $I_{PO4}$ and $I_{PO3}$ protons at 4.0 ppm and 4.2 ppm ($\Sigma = 5.25$ corresponding to 2H), and on the other hand, $I_{PO5}$ and $I_{AA2}$ protons ($\Sigma = 4.63$ corresponding to 2H), it comes out that part of the formed hexanoic acid is consumed, more likely via amide function formation as sketched for instance in Scheme 6.

In order to shed some light on the polymerization mechanism, the crude products have been subjected to Soxhlet extractions in THF. Table 2 summarizes the molecular characteristics of both filtrates and insoluble fractions as identified by $^1$H NMR in TFA-*d*.

After 7 h of hydrolytic polymerization in the presence of the model ester, the $^1$H NMR spectrum of the filtrate proved very similar to the crude product spectrum, except that the polyamide chains are characterized by a lower average DP ($DP_{exp} \sim 1$). Concerning the fraction remaining insoluble after the Soxhlet extraction in THF, it is characterized by the absence of –C*H*$_2$–OH proton at 4.2 ppm (PO3), i.e. absence of PEO–OH (Fig. 2). $^1$H NMR also shows –C*H*$_2$–$NH_2$ protons at 2.85 ppm (AA3) and –C*H*$_2$–COOH protons at 2.1 ppm (AA2). Comparing the relative intensities of the methylene ester protons (PO4) at 4 ppm ($I = 1.55$ corresponding to 2H) and of α-carbonyl ester and carboxylic acid methylene protons (PO5, AA2) at 2.1 ppm ($I = 3.78$ corresponding to 2H), evidences the presence of carboxylic acid end groups.

The following section presents separately findings on all reactions that could participate in the overall hydrolytic mechanism of CLa, as carried out in the presence of the carboxylic ester, the main objective aiming at understanding the activating effect displayed by this reactive ester function.

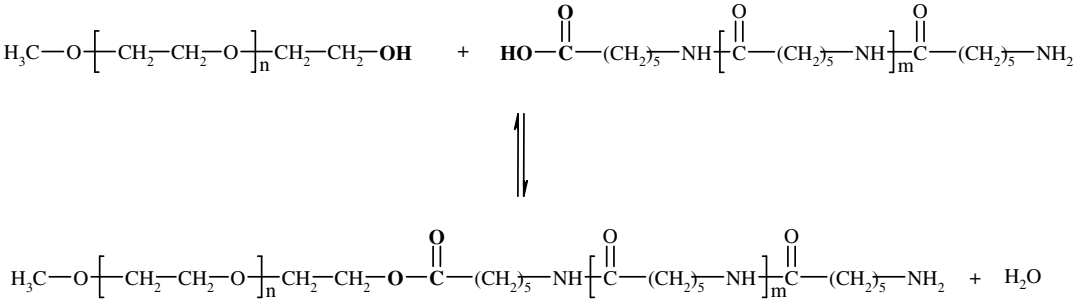
## 3. Mechanistic study

For this purpose, the polymerization medium is simply composed of PEO–O–C(O)–$C_5H_{11}$, actually a model ester based on monomethyl ether poly(ethylene glycol), CLa, $H_3PO_2$ and water. Clearly, the model ester is not a potential initiator of the CLa ROP because its two end groups are known to be inactive in ring-opening of a lactam. However, the catalyst used being $H_3PO_2$ in aqueous solution, water is inevitably introduced in the medium. In addition to its ability to initiate the ROP of CLa, this water can readily hydrolyze the ester link of PEO–O–C(O)–$C_5H_{11}$ at high temperature (250 °C). This hydrolysis should lead to the formation of PEO–OH and hexanoic acid (pathway 1).

### 3.1. Pathway 1: ester link hydrolysis

Water present in the catalyst solution can cleave the ester link of PEO–O–C(O)–$C_5H_{11}$ and involve the formation of PEO–OH and HO–C(O)–$C_5H_{11}$ (Scheme 7), this reaction being reversible.

The generated carboxylic acid can initiate the acidolytic polymerization of CLa or react with α-amino-ω-carboxylic



**Scheme 5.** Condensation of the hydroxyl group of PEO–OH and a carboxylic acid function – formation of a carboxylic ester bridge.

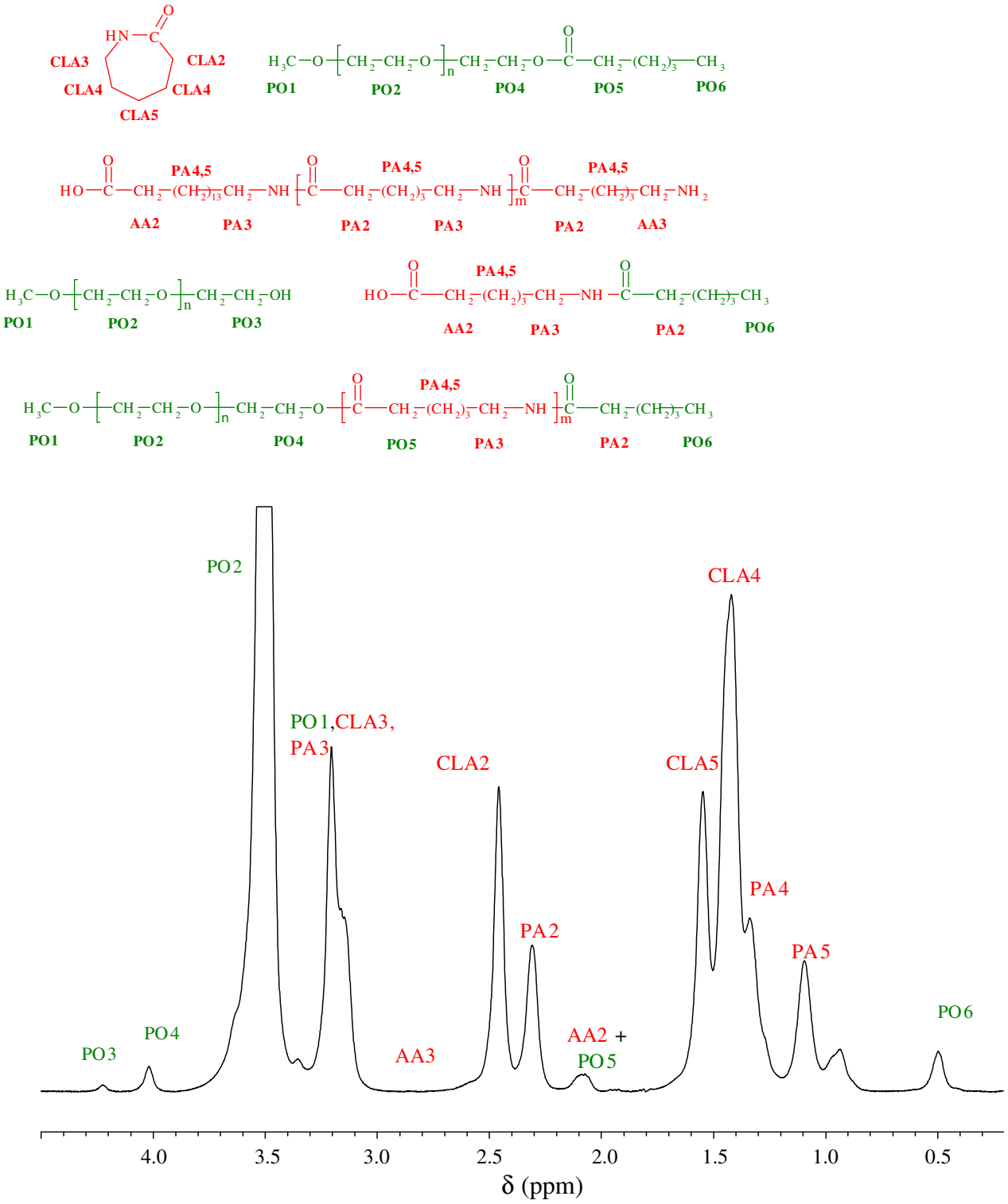
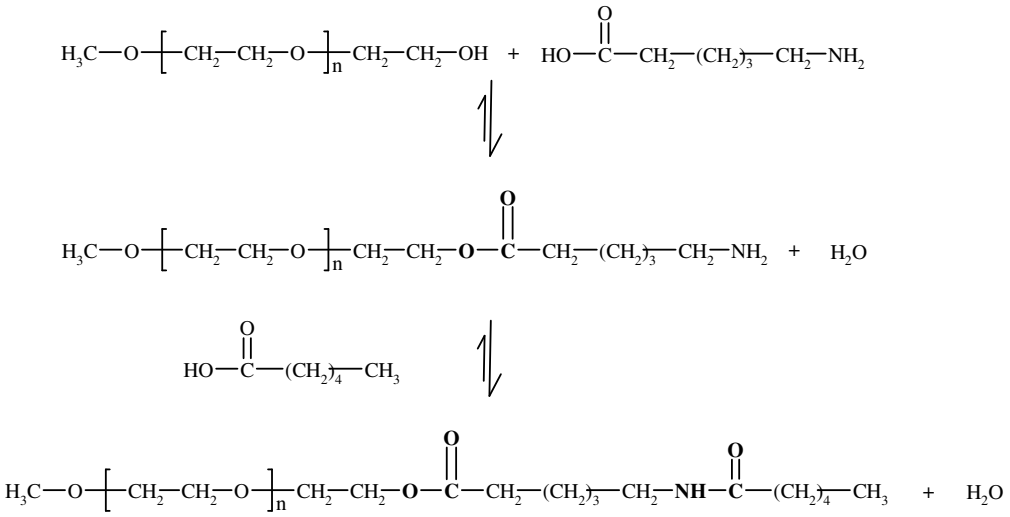



**Fig. 1.** $^1$H NMR spectrum of a crude polyamide sample as obtained by hydrolytic polymerization of CLa in the presence of PEO–O–C(O)–$C_5H_{11}$ and 0.25 mol% of $H_3PO_2$ at 250 °C for 24 h (Table 1, entry 5, solvent: TFA-*d*; 500.13 MHz).

acid units by condensation, generating a carboxylic acid initiator. In order to determine which of these reactions is predominant (acidolytic polymerization or condensation), the ring-opening polymerization of CLa has been carried out for different polymerization times in the presence of the model ester ($[CLa]_0/[ester]_0 = 16$) and an equimolar amount of stearic acid ($[Stear]_0 = [ester]_0$) (Table 3).

The $^1$H NMR spectrum of the crude PCLa sample obtained after 7 h (Table 3, entry 1) is characterized by the absence of –$CH_2$–OH protons at 4.2 ppm (PO3) corresponding to PEO–OH (Fig. 3). This observation can be explained by the condensation of the stearic acid with the PEO–OH, for example, yielding back an ester link at the end of the PEO chains. Contrary to the polymerization carried out



**Scheme 6.** Condensation reactions between PEO–OH and aminocaproic acid and the amine end function with hexanoic acid yielding an amide bond.

**Table 2**
Molecular characteristics of filtrates and insoluble fractions resulting from Soxhlet extraction in THF carried out of 1 g of the crude products as obtained by hydrolytic polymerization of CLa in the presence of PEO–O–C(O)–$C_5H_{11}$ and $H_3PO_2$ at 250 °C

| Entry | Time (h) | Filtrate weight fraction (%)[a] | Filtrate composition (molar%)[b] | | Solid weight fraction (%)[a] | Solid composition (molar%)[b] | |
|---|---|---|---|---|---|---|---|
| | | | PEO | Amide | | PEO | Amide |
| 1 | 7 | 68 | 48 | 52 | 24 | 46 | 54 |
| 2 | 24 | 57 | 57 | 43 | 36 | 39 | 61 |
| 3 | 48 | 49 | 64 | 36 | 48 | 36 | 64 |

[a] As determined by gravimetry after drying under vacuum at 40 °C.
[b] As determined by proton NMR spectroscopy in TFA-*d*: amide molar fraction = $(I_{PA2}/2)/[I_{PA2}/2) + (I_{PO2}/4)]$ and PEO molar fraction = $(I_{PO2}/4)/[I_{PA2}/2) + (I_{PO2}/4)]$.

without the addition of stearic acid, the relative intensities of the methylene ester protons (PO5 and PO4), methylene acid protons (AA2) and methyl protons (Stear 1 and PO6) remains in the same relative ratio as prior to the polymerization (I (Stear + PO6)/I (PO5 + AA2)/I (PO4) = 6H/4H/2H). The carboxylic acid function of stearic acid can react either with the hydroxyl extremity of PEO leading to the formation of an ester link (Scheme 8-1) or with the amine function of α-amino-ω-carboxylic acid units (Scheme 8-2).

When compared to the experiments carried out without stearic acid, the rate of polymerization slightly increases (Table 3). However, the activating effect of the ester function on the hydrolytic polymerization of Cla remains predominant in comparison with the benefit that the stearic acid could bring by initiating the acidolytic polymerization of CLa.

### 3.2. Pathway 2: ester link aminolysis

The ester link can also cleaved by aminolysis. The amine function of α-amino-ω-carboxylic acid units can react with the ester link of PEO–O–C(O)–$C_5H_{11}$ and generate PEO–OH and hexanoylamidocaproic acid (pathway 2). By condensation, these compounds can form an ester link (Scheme 9).

In order to account for the presence of the small amount of amine functions in the insoluble fractions recovered after Soxhlet extraction in THF (Fig. 2), one can further assume a condensation reaction between α-amino-ω-carboxylic acid units and the resulting ω-OH PEO chains generated by aminolysis. For assessing the intervention of such aminolysis reactions, the hydrolytic polymerization of CLa has been carried out in the presence of the model ester and an equimolar amount of hexadecylamine ($[R{-}NH_2]_0 = [ester]_0 = 1$) in the presence of 0.25 mol% $H_3PO_2$ (Table 4).

α-Amine methylene protons (AA3: 2.85 ppm) are present on the $^1$H NMR spectrum (Fig. 4). However, the relative intensity of these signals, when compared to the methyl group of the alkyl end groups (Hex1), does not fit the 2/3 ratio as expected if all the polymer chains were end-capped by a hexadecyl group at one end, and an amine at the other extremity. Moreover, the ratio of the $I_{AA3}/I_{Hex1}$ relative intensities decreases with polymerization time. It appears that the amine functions are consumed during the hydrolytic polymerization, likely by aminolysis of the ester link (Scheme 9).

The $^1$H NMR spectrum also shows the presence of –$CH_2$–OH protons (PO3 : 4.2 ppm). These end groups are the result of the ester link cleavage in PEO–O–C(O)–$C_5H_{11}$, the relative intensity of the PO3 signal increasing with polymerization time. As the ratio of the relative intensities $I_{PO4}/I_{PO3}$ also increases with time, it seems that the rate of the aminolysis reaction is relatively slow with regards to the rate of the aforementioned ester link hydroly-

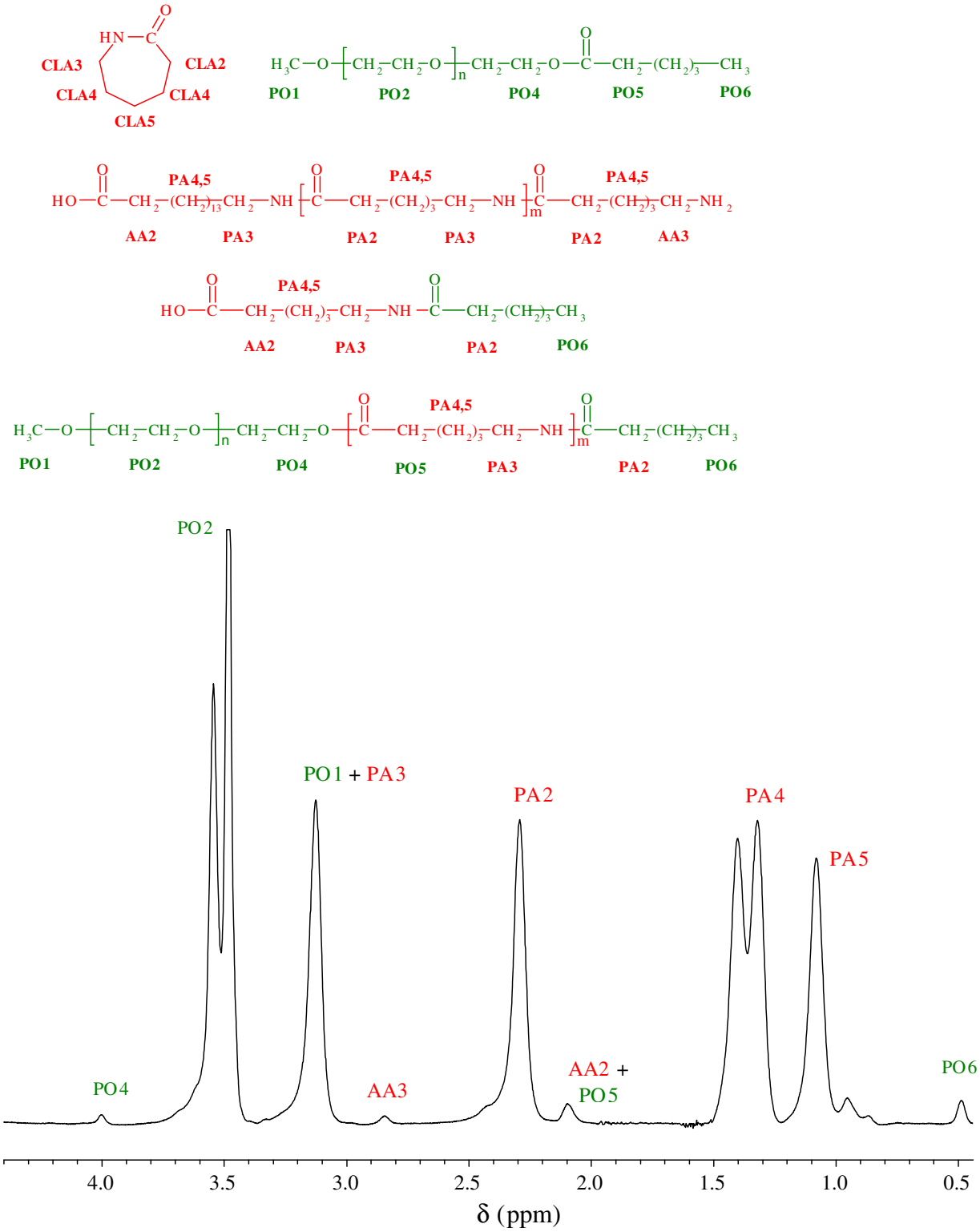
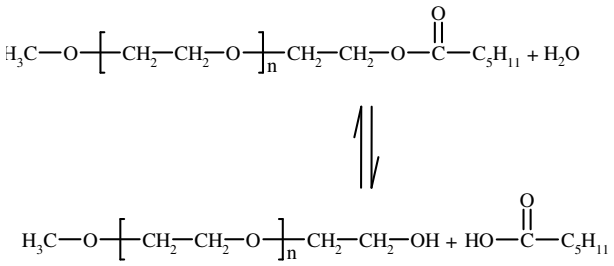



**Fig. 2.** $^{1}$H NMR spectrum of the insoluble fraction as recovered by Soxhlet extraction in THF of the crude product resulting from a 7-h hydrolytic polymerization of CLa in the presence of PEO–O–C(O)–$C_5H_{11}$ and 0,25 mol% of $H_3PO_2$ (solvent: TFA-*d*, Table 2, entry 1).

sis. As shown in Table 4, the addition of hexadecylamine during the hydrolytic polymerization of CLa in the presence of the model ester increases the rate of polymerization, in perfect agreement with an aminolytic ring-opening polymerization mechanism of lactams. However, in this case, the activating effect of the ester functions on the ROP of CLa seems to be negligible. The hydrolytic polymerization of CLa becomes faster than the acidolytic polymerization but is still slower than the aminolytic polymerization. Thus the reactivity order of the CLa polymerization mechanisms could be expressed as: aminolytic >> hydrolytic > acidolytic.



**Scheme 7.** Pathway 1 – ester hydrolysis reaction of PEO–O–C(O)–$C_5H_{11}$.

**Table 3**
Monomer conversion ($Conv_{CLa}$) and degree of polymerization ($DP_{exp}$) of polyamides as obtained by hydrolytic polymerization of CLa at 250 °C in the presence of stearic acid, the model ester and 0.25 mol% of $H_3PO_2$ (50 wt% in water) for different polymerization times

| Entry | Time (h) | $Conv_{CLa}$[a] (%) | $DP_{exp}$[b] |
|---|---|---|---|
| 1 | 7 | 10 | 3 |
| 2 | 24 | 44 | 7 |
| 3 | 48 | 82 | 21 |

[a] As determined by proton NMR spectroscopy: conv = $I_{PA2}/(I_{CLa2} + I_{PA2}) \times 100$.

[b] $DP_{exp}$ determined by proton NMR spectroscopy based on the methylene oxide protons of the polyether at 3.5 ppm: $DP_{exp} = [(160H/I_{3.5}) * I_{PA2}]/2$.

All these observations have highlighted an activating effect of the model ester, PEO–O–C(O)–$C_5H_{11}$, on the hydrolytic polymerization of CLa in presence of $H_3PO_2$, in contrast with more conventional aminolytic and acidolytic polymerizations. This can be explained by the involvement of two major reactions: (i) the lactam hydrolysis and (ii) concomitant aminolysis of the carboxylic ester function by the resulting primary amine. These two reactions occur in addition to the hydrolysis of the ester functions and the typical reactions known to take place in hydrolytic polymerization of CLa. On the basis of $^1$H NMR spectra recorded directly on crude reaction products but also on the soluble and insoluble fractions from Soxhlet extractions in THF, the ester hydrolysis has been evidenced by the presence (even if limited) of ω-hydroxylated poly(ethylene oxide). Interestingly, the major part of the polyamide chains proved to be linked to the polyether chains as a result of a condensation reaction. Even though some carboxylic acid end functions can be observed assuming the intervention of acidolytic polymerization, no trace of amine functions could be detected.

The addition of an equimolar quantity of stearic acid with regards to the ester functions is responsible for the complete disappearance of the PEO–OH in favor of the formation of PEO–O–C(O)–R. In comparison to the polymerization carried out in the presence of the model ester, the stearic acid does not increase the rate of the ring-opening polymerization.

The addition of hexadecylamine, in equimolar quantity with respect to the ester functions, initiates the aminolytic polymerization of CLa as evidenced by the higher rate of polymerization. However, a part of the amine function is involved in the ester aminolysis of PEO–O–C(O)–$C_5H_{11}$ leading to the formation of PEO–OH. This reaction appears however slower than the ester hydrolysis, as observed during the hydrolytic polymerization of CLa in the presence of PEO–O–C(O)–$C_5H_{11}$.

In summary, the activating effect of the ester function on the kinetics of the hydrolytic polymerization of CLa can be assigned to the following polymerization mechanism scheme (Scheme 10-1 and 2). On one hand, the ester hydrolysis leads to the formation of alcohol and carboxylic acid functions, which can further condense and/or promote the acidolytic polymerization of CLa, the latter being slow (Scheme 10-1). On the other hand, the ester aminolysis is promoted by the amine function of the α-amino-ω-carboxylic acid present, leading to the formation of an amide bond and a hydroxyl function also followed by condensation reactions (Scheme 10-2). As a further confirmation, this mechanism has been interestingly extrapolated to the hydrolytic polymerization of CLa conducted in the presence of a polyester sequence. As a result, aliphatic polyesteramides are synthesized in a very practical way as reported in the following section.

## 4. Synthesis of a polyesteramide sequence

The hydrolytic polymerization of CLa has been carried out in sealed glass reactors, in bulk at 250 °C, in the presence of a poly(ethylene oxide)-*b*-poly(ε-caprolactone) diblock copolymer (PEO–*b*–PCLo–OH) and $H_3PO_2$ (0.25 mol% relative to the amide functions).

The PEO–*b*–PCLo–OH diblock copolymer has been first synthesized by ring-opening polymerization of ε-caprolactone (CLo) in dichloromethane at room temperature. The poly(ethylene oxide) was used as initiator, its hydroxyl function being preliminarily activated by the addition of triethylaluminum ($AlEt_3$) (see experimental section). The copolymer composition was $M_{nPEO}$block = 1800 g/mol and $M_{nPCLo}$block = 1300 g/mol with a polydispersity index equal to 1.3.

The ring-opening polymerization of CLa has thus been carried out in the presence of this PEO–*b*–PCLo–OH diblock copolymer. The weight ratio of CLa/PEO–*b*–PCLo–OH was fixed to unity, which means a $[CLa]_0/[CLo]_0$ molar ratio of 2.4. After a polymerization time of 7 h, a monomer conversion as high as 80% was determined by $^1$H NMR spectroscopy. As previously observed in the presence of the model ester ($[CLa]_0/[ester]_0 = 16$), the polyester block acts as an activator of the hydrolytic polymerization of CLa. Actually, the activation is more pronounced since the relative amount of ester units in the reaction medium is higher ($[CLa]_0/[ester\ link]_0 = 2.4$).

In agreement with aforementioned $^1$H NMR data, α-amine methylene protons (–$CH_2$–$NH_2$ AA3: 2.85 ppm) are again observable in the $^1$H NMR spectrum (Fig. 5), even though the relative intensity of this signal being low. Based on the relative intensities of the protons –$CH_2$–O–C(O)– (PE3) at 3.8 ppm and –$CH_2$–C(O)–O– (PE2, AA2) at 2.1 ppm, a significant amount of –$CH_2$–COOH (AA2) chain extremities is formed. It is likely that, besides the multistep polymerization mechanism of CLa, the hydrolysis of CLa is also always involved, followed by its polycondensation in α-carboxylic acid, ω-amine PCLa.

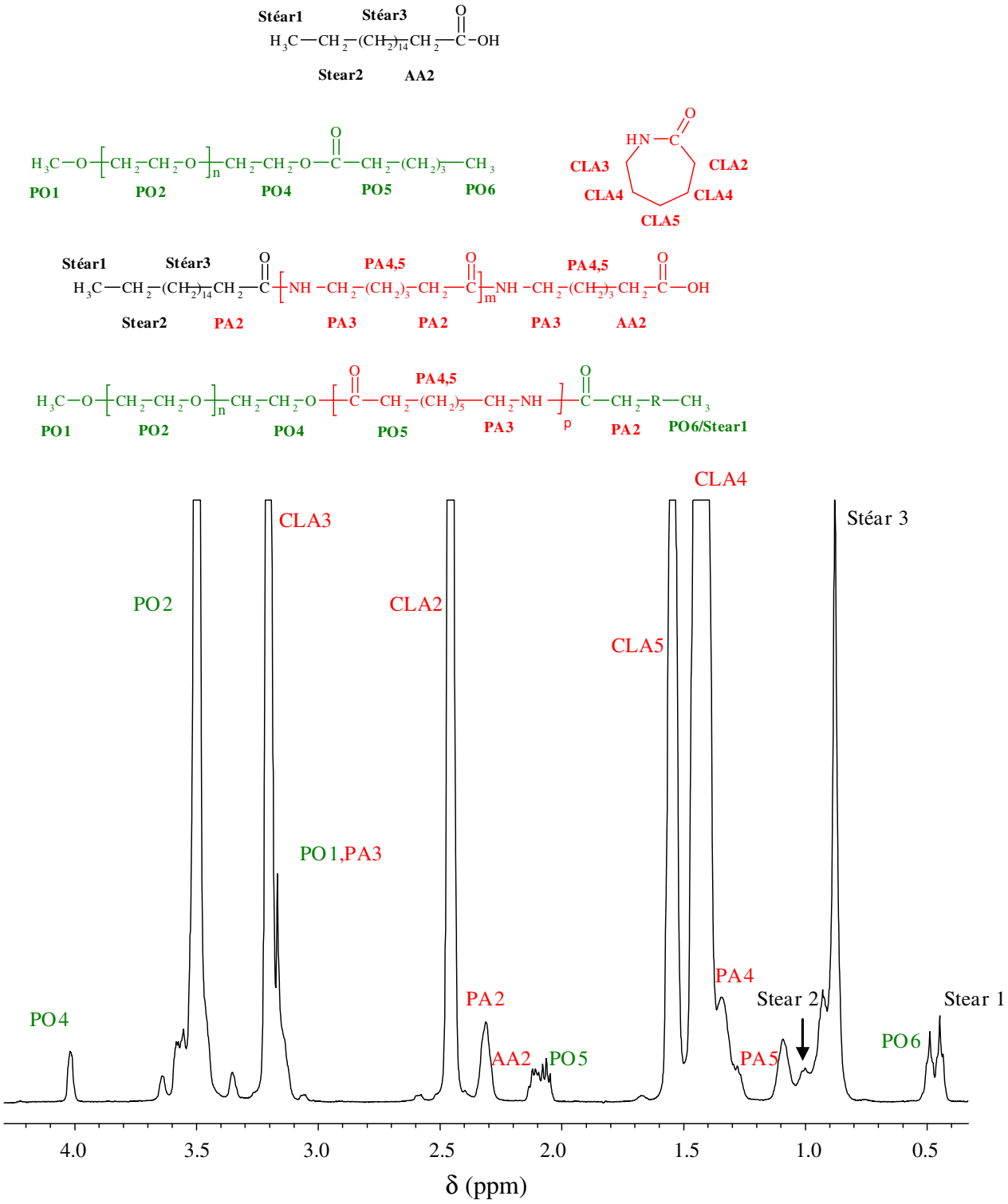
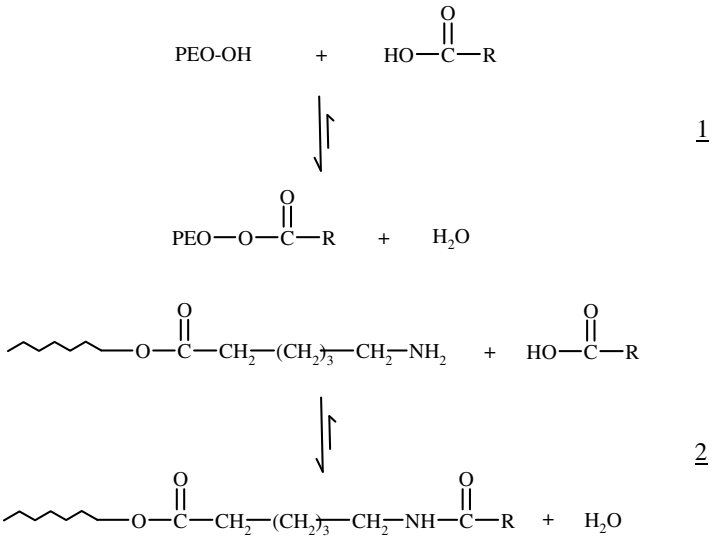
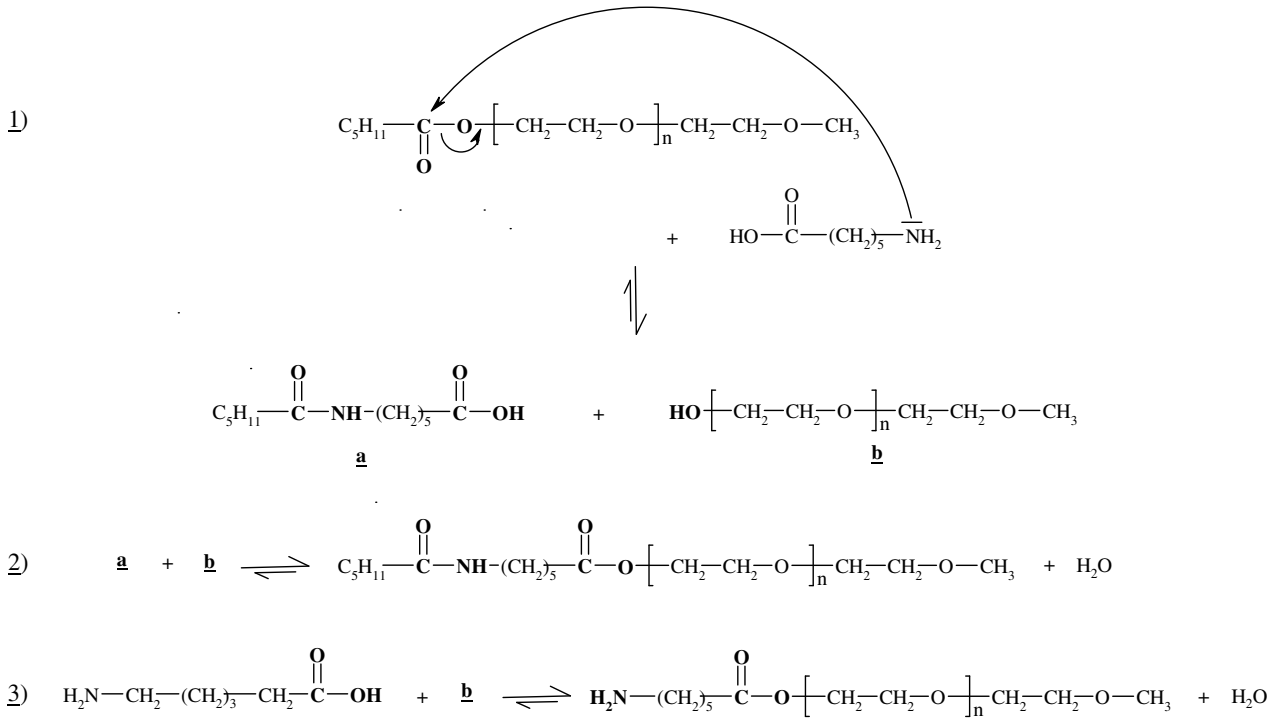



**Fig. 3.** $^1$H NMR spectrum of a crude polyamide sample as obtained by hydrolytic polymerization of CLa in the presence of the model ester (PEO–O–C(O)–$C_5H_{11}$), stearic acid, 0.25 mol% of $H_3PO_2$ and water at 250 °C for 7 h (solvent: TFA-*d*, Table 3, entry 1).

Furthermore, after the CLa polymerization, one can notice a significant increase of the relative intensity of the –C$H_2$–OH (PE4) at 4.05 ppm. Accordingly, by comparing the relative intensities of the PCLo ester methylene protons (–C$H_2$–O–C(O)–, PE3) at 3.8 ppm, and the α-hydroxyl methylene protons (PE4) at 4.05 ppm, the average molecular mass of the polyester sequence decreases from 1300 to 300 g/mol ($M_{n\mathrm{PCLo}} = I_{\mathrm{PE3}}/I_{\mathrm{PE4}} \times \mathrm{MW}_{\mathrm{CLo}}$, with $\mathrm{MW}_{\mathrm{CLo}}$ = 114.14 g/mol). This observation can be explained by the hydrolysis and the aminolysis of the ester links along the polyester sequence. It is worth noting that, comparatively to the hydrolytic polymerization of CLa performed in the presence of the model ester ($[\mathrm{CLa}]_0/[\text{ester link}]_0 = 16$), no polyether end chains –C$H_2$–OH $^1$H



**Scheme 8.** Condensation reaction between carboxylic acid functions and PEO–OH – formation of an ester bond ester (**1**), and/or condensation reaction between carboxylic acid functions and amine functions – formation of an amide bond (**2**).



**Scheme 9.** Pathway 2 - PEO–O–C(O)–$C_5H_{11}$ ester link aminolysis (1) and consecutive condensation reactions (**2** and **3**).

resonance is observed at 4.2 ppm. This observation confirms that increasing the amount of ester functions in the reaction medium has an activating effect on the ROP of CLa and allows the formation of a copolymer composed of a polyether block covalently linked to a polyesteramide sequence.

In order to determine the distribution of the CLa and CLo units in the polyesteramide sequence, the copolymer was characterized by $^{13}C$ NMR spectroscopy, which demonstrated many times its effectiveness in characterizing the copolymer chain microstructure and the average length of a block incorporating the same repetitive unit [25–28]. In the case of polyesteramide based on CLa and CLo units, the methylene carbon atoms in α position of amide and ester functions (–*C*$H_2$–C(O)–NH– (A) and –*C*$H_2$–C(O)–O– (B)) shows up as dyads (AA, AB, BA and BB) in the $^{13}C$ NMR spectrum (Fig. 6) [29]. This spectrum has been recorded by dissolving the polyesteramide $CDCl_3$/$(CF_3CO)_2O$/$CF_3COOD$: (70/17/13 v/v/v). Full relaxation conditions for $^{13}C$ signal quantification were confirmed by recording a copolymer sample at different, increasing relaxation delays between two consecutive scans, which resulted in differences in the relative integrated areas of the $^{13}C$ resonances within experimental error.

**Table 4**
Monomer conversion ($Conv_{CLa}$) and degree of polymerization ($DP_{exp}$) of polyamides as obtained by hydrolytic polymerization of CLa at 250 °C in presence of hexadecylamine, the model ester and 0.25 mol% of $H_3PO_2$ (50 wt% in water) for different polymerization times

| Entry | Time (h) | $Conv_{CLa}$ [a](%) | $DP_{exp}$ [b] |
|---|---|---|---|
| 1 | 7 | 75 | 13 |
| 2 | 24 | 78 | 16 |
| 3 | 48 | 81 | 21 |

[a] As determined by proton NMR spectroscopy: conv = $I_{PA2}/(I_{CLa2} + I_{PA2}) \times 100$.
[b] $DP_{exp}$ determined by proton NMR spectroscopy based on the methylene oxide protons of the polyether at 3.5 ppm: $DP_{exp} = [(160H/I_{3.5}) * I_{PA2}]/2$.

First of all, it is worth noting that deconvolution of the $^{13}C$ NMR spectrum allows determining a molar composition similar to the value obtained by $^1H$ NMR.

Based on the relative intensities of the carbon atoms in α position of amide and ester signals, the average length of PCLo ($\bar{L}_{PCLo}$) and PCLa ($\bar{L}_{PCLa}$) blocks could be determined by Eqs. (1) and (2) [28]:

$$\bar{L}_{PCLo} = \frac{I_{AA}}{I_{AB}} + 1 \quad (1)$$

$$\bar{L}_{PCLa} = \frac{I_{BB}}{I_{BA}} + 1 \quad (2)$$

Eqs. (1) and (2): determination of the average length of PCLo and PCLa sequences as determined by $^{13}C$ NMR.

The $^{13}C$ NMR spectrum of the copolymer obtained by hydrolytic polymerization of CLa in the presence of PEO–*b*–PCLo–OH shows that the incorporation of the CLa units into the polyesteramide sequence is random with PCLa and PCLo average lengths of 2.6 and 1.2, respectively, for an initial molar ratio of $[CLa]_0/[CLo]_0 = 2.4$.

## 5. Experimental

### 5.1. Synthesis of PEO–C(O)–O–$C_5H_{11}$

#### 5.1.1. Materials

Poly(ethylene glycol) ω-hydroxylated (PEO–OH, Fluka), hexanoyl chloride (99+%, Aldrich) and heptane (99+%, Labscan) were used as received. Triethylamine ($NEt_3$, 99%, Acros) was dried over barium oxide at room temperature during 72 h, distilled under reduced pressure and stored under $N_2$. Tetrahydrofuran (THF, 99+%, Labscan) was dried on 4 Å molecular sieves during 72 h at room temperature.

#### 5.1.2. Synthesis

In a preliminarily flamed and nitrogen purged round-bottom flask equipped with a three-way stopcock and a rubber septum, PEO–OH (15 g, 8.3 mmol) and dry toluene (15 mL) were added. After three successive azeotropic distillations of toluene, dry THF (150 mL), 5 equivalents of hexanoyl chloride (5.9 mL, 0.042 mol) and 5 equivalents of triethylamine (5.9 mL, 0.042 mol) were added. The reaction medium was heated up to 50 °C. After 48 h reaction time, the insoluble ammonium salts were filtered off and the filtrate was washed on carbon black. The PEO–C(O)–O–$C_5H_{11}$ was recovered by precipitation into heptane, filtered off and dried until constant weight (yield = 80%, $M_n$ NMR = 1900 g/mol).

### 5.2. Polymerization of CLa in the presence of PEO–C(O)–O–$C_5H_{11}$

#### 5.2.1. Materials

ε-Caprolactam (CLa, 99%, Acros) was dried under reduced pressure at 60 °C overnight Three successive azeotropic distillations of toluene were performed and CLa was stored under $N_2$. PEO–O–C(O)–$C_5H_{11}$ was dried by three successive azeotropic distillations of toluene. Hypophosphorous acid ($H_3PO_2$, 50 wt% in water, Aldrich) was used as received.

#### 5.2.2. Synthesis

In a glass tube equipped with a three-way stopcock and a rubber septum, CLa (2 g, 17.67 mmol), PEO–O–C(O)–$C_5H_{11}$ (2 g, 1 mmol, $[CLa]_0/[ester]_0 = 16$) and $H_3PO_2$ (0.25 mol% with regards to the amine functions) were added. After three vacuum-$N_2$ cycles, the tube was sealed and placed in a ventilated oven for a predetermined time at 250 °C. Then, the tube was cooled down to room temperature and broken. The reaction product was recovered and analyzed by $^1H$ NMR in deuterated trifluoroacetic acid (TFA-*d*). Soxhlet extractions on 1 g of the product were carried out in THF at reflux overnight. Filtrates and solids were dried until constant weight and analyzed by $^1H$ NMR.

### 5.3. Polymerization of CLa in the presence of PEO–C(O)–O–$C_5H_{11}$ and addition of hexadecylamine or stearic acid

#### 5.3.1. Materials

Hexadecylamine (R–$NH_2$, 90%, Sigma–Aldrich) and stearic acid (R–COOH, 97%, Acros) were dried by three successive azeotropic distillations of toluene and stored under $N_2$.

#### 5.3.2. Synthesis

In a glass tube equipped with a three-way stopcock and a rubber septum, CLa (2 g, 17.67 mmol), PEO–O–C(O)–$C_5H_{11}$ (2 g, 1 mmol, $[CLa]_0/[ester]_0 = 16$), hexadecylamine (0.25 g, 1 mmol, $[ester]_0/[R–NH_2]_0 = 1$) or stearic acid (0.3 g, 1 mmol, $[ester]_0/[R–COOH]_0 = 1$) and $H_3PO_2$ (0, 25 molar% compared to the amide functions) were added. After three vacuum-$N_2$ cycles, the tube was sealed and placed in a ventilated oven for 7 h at 250 °C. subsequently, the tube was cooled down to room temperature and opened. The reaction product was analyzed by $^1H$ NMR in deuterated trifluoroacetic acid (TFA-*d*). Soxhlet extractions on 1 g of the product were carried out in THF at reflux overnight. Filtrates and solids were dried until constant weight and analyzed by $^1H$ NMR.

### 5.4. Synthesis of PEO–b–PCLo–OH diblock copolymer

#### 5.4.1. Materials

ε-Caprolactone (CLo, 99%, Acros) was dried over calcium hydride at room temperature during 48 h and distilled

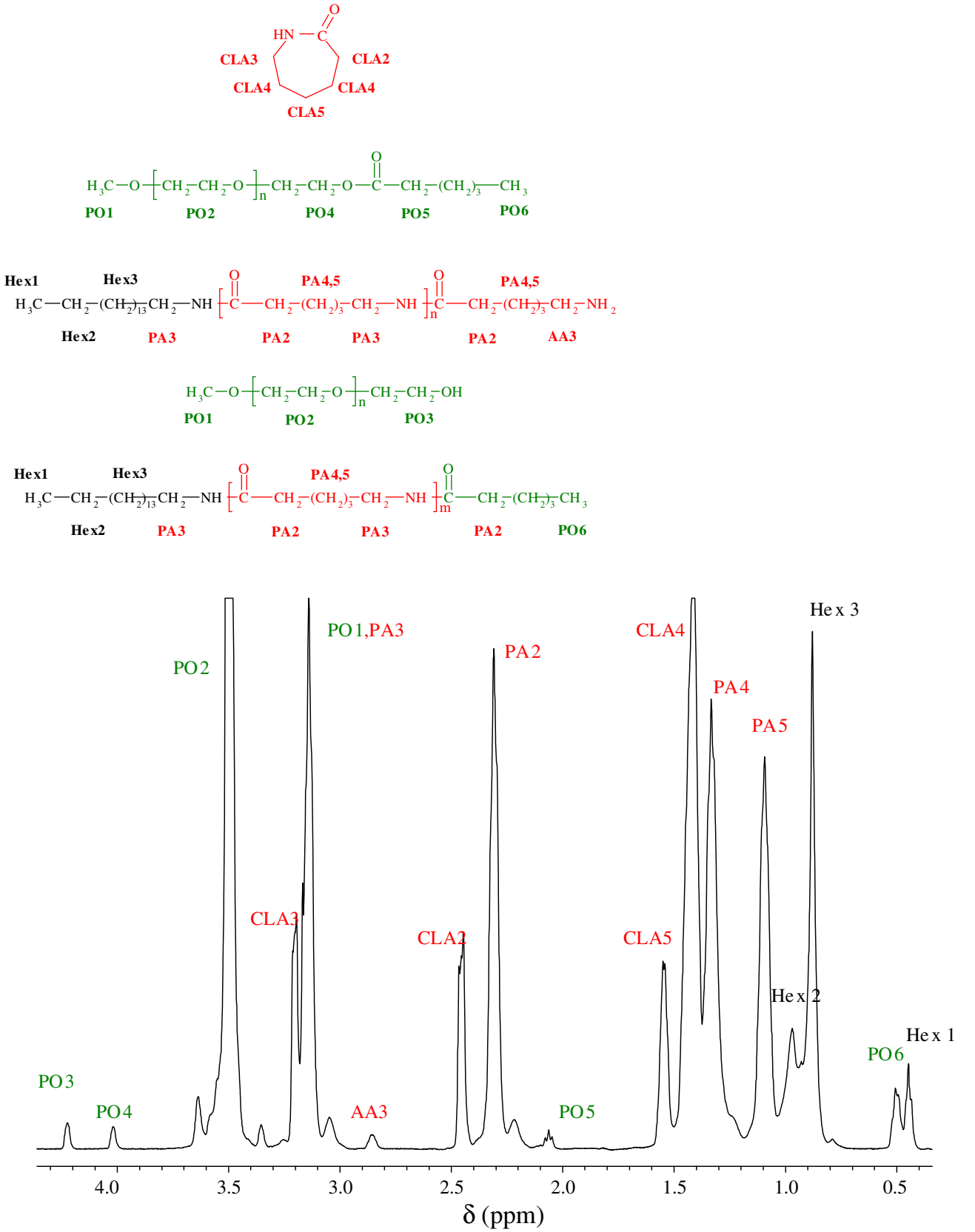
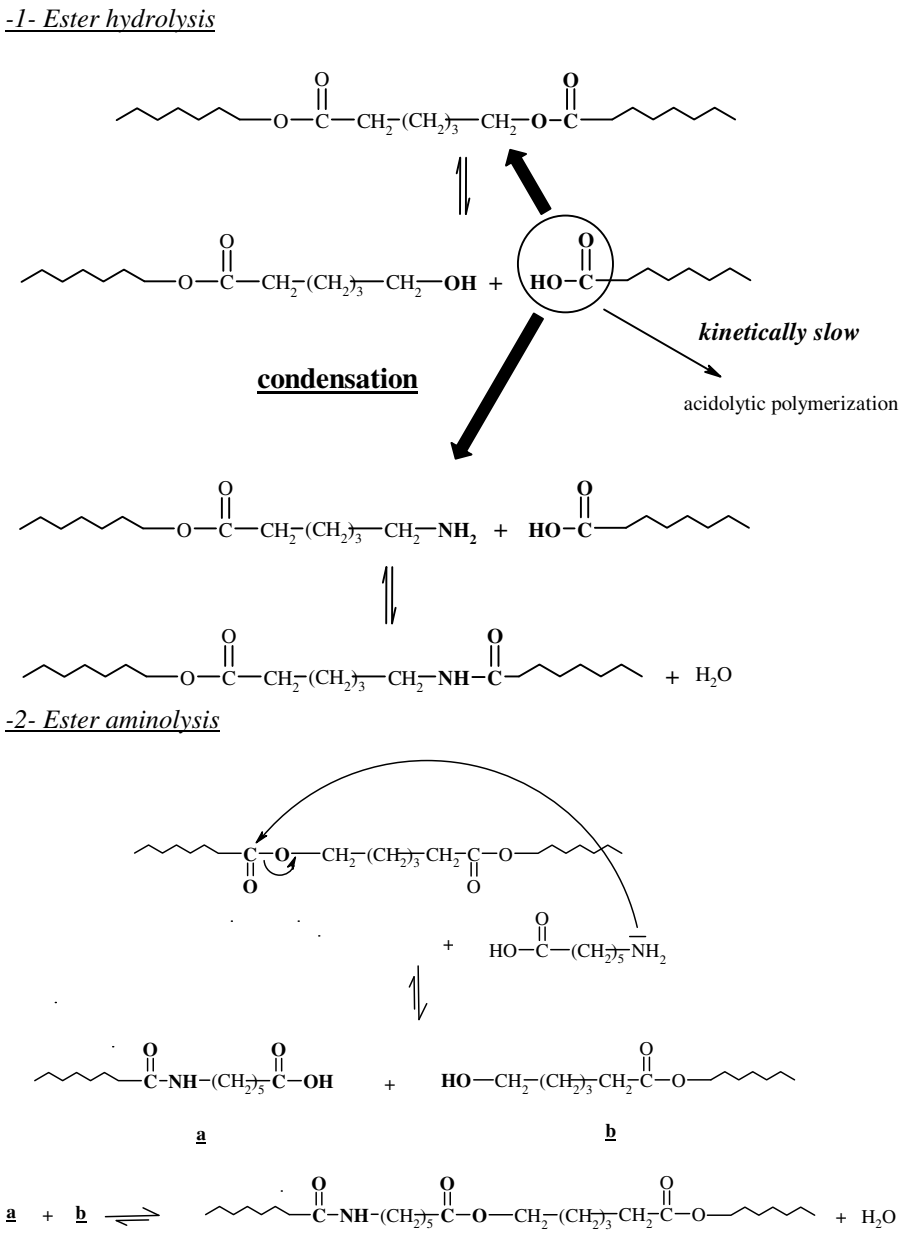



**Fig. 4.** 1H NMR spectrum of crude PCLa sample as obtained by ring-opening polymerization of CLa in the presence of PEO–O–C(O)–C5H11, hexadecylamine, 0.25 mol % of $H_3PO_2$ and water at 250 °C for 7 h (solvent: TFA-*d*, Table 4, entry 1).

under reduced pressure and stored under $N_2$. Poly(ethylene glycol) ω-hydroxylated (PEO–OH, Fluka), was recrystallized two times from ethyl acetate (10% w/v solution) and dried by three successive azeotropic distillations of toluene




**Scheme 10.** Ester hydrolysis (**1**) and aminolysis (**2**).

($M_n$ = 1800 g/mol, $M_w/M_n$ = 1.08). Dichloromethane ($CH_2Cl_2$, 99.6%, Aldrich) was dried over calcium hydride during 48 h and distilled under reduced pressure and stored under $N_2$. Triethylaluminum ($AlEt_3$, 20wt% in toluene, Aldrich) was diluted in toluene (99+%, Labscan), preliminarily dried over calcium hydride and distilled. The concentration of the $AlEt_3$ solution was determined by a complexometric back titration of $Al^{3+}$ using an aqueous solution of ethylenediaminetetraacetic acid disodic salt ($Na_2EDTA$, 0,15 M, 99+%, Acros) and $ZnSO_4$ (0,25 M, 99+%, Acros). The pH was kept at 4.8 by addition of sodium acetate during the titration. The solution of $AlEt_3$ was stored under $N_2$. Heptane (99+%, Labscan) was used as received.

*5.4.2. Synthesis*

In a preliminarily flamed and nitrogen purged round-bottom flask equipped with a three-way stopcock and a rubber septum, PEO–OH (10 g, 5.5 mmol) was dissolved in 200 mL of $CH_2Cl_2$ (5% w/v solution). The temperature was reduced to −78 °C (acetone, liquid nitrogen bath) and 5.5 mL of $AlEt_3$ solution (1.1 M, 6.05 mmol) were added. The mixture was then brought to room temperature and 7.3 mL of CLo (0.07 mol, $[CLo]_0/[R–OH]_0$ = 13) were added. The polymerization was carried out at room temperature. After 72 h, the polymerization was quenched by the addition of a few drops of an aqueous solution of HCl (1 M). The solution was concentrated and the polymer chains were dissolved in toluene at 40 °C. The PEO–*b*–PCLo–OH diblock copolymer was recovered by precipitation into heptane, filtered off and dried until constant weight. The insoluble aluminum salts were filtered off and the copolymer was recovered by precipitation in heptanes (yield = 80%). The copolymer was characterized by $^1H$ NMR spectroscopy

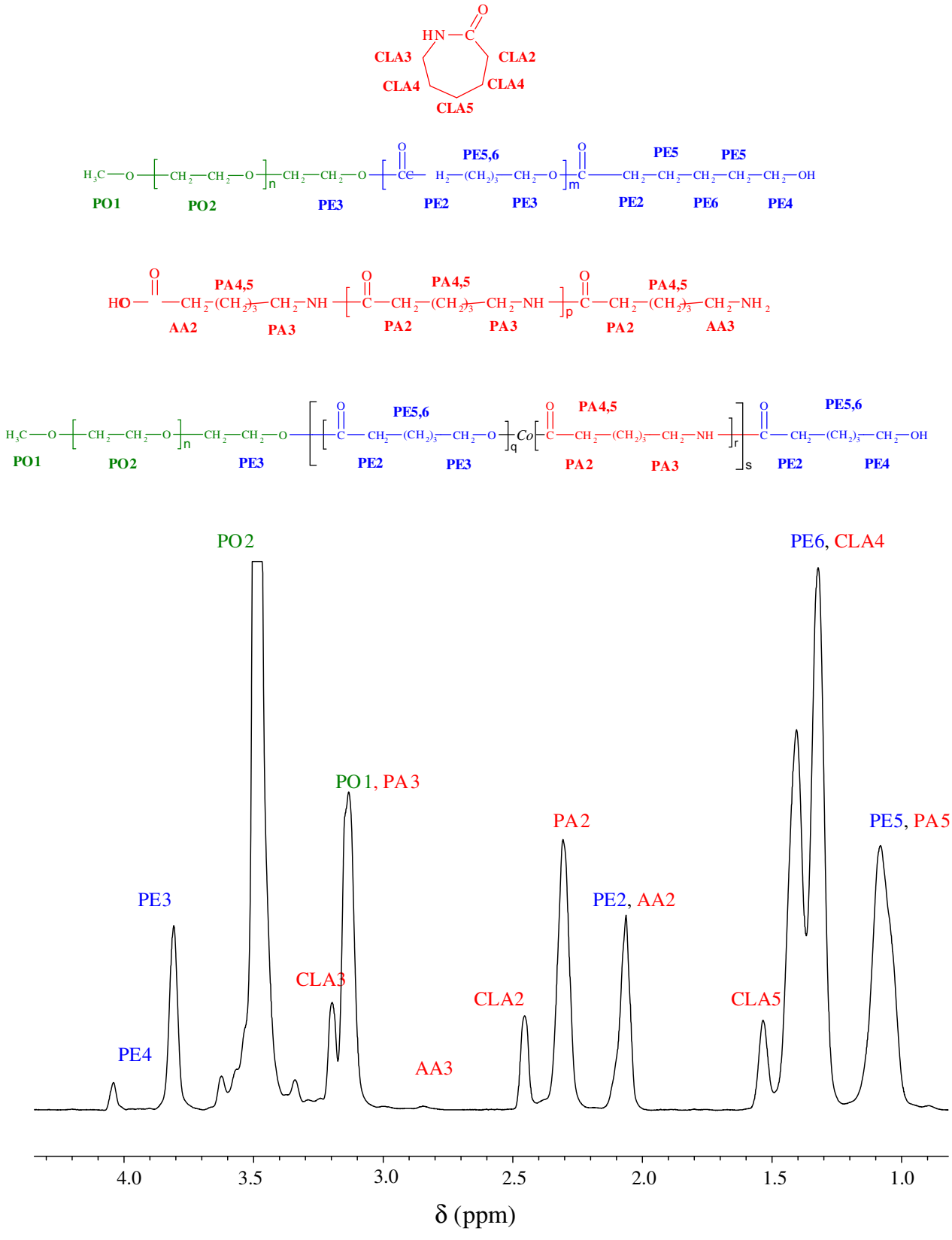



**Fig. 5.** $^1$H NMR spectrum of a crude polyamide sample as obtained by hydrolytic polymerization of CLa in the presence of P(EO–*b*–CLo)–OH and 0.25 mol% of $H_3PO_2$ at 250 °C for 7 h (solvent: TFA-*d*).

in $CDCl_3$ and by size exclusion chromatography (SEC) in tetrahydrofuran (polystyrene standards, $M_{napp}$ = 5200 g/mol, $M_w/M_n$ = 1,31, $M_{nPEO}$ = 1800 g/mol et $M_{nPCLo}$ = 1300 g/mol).

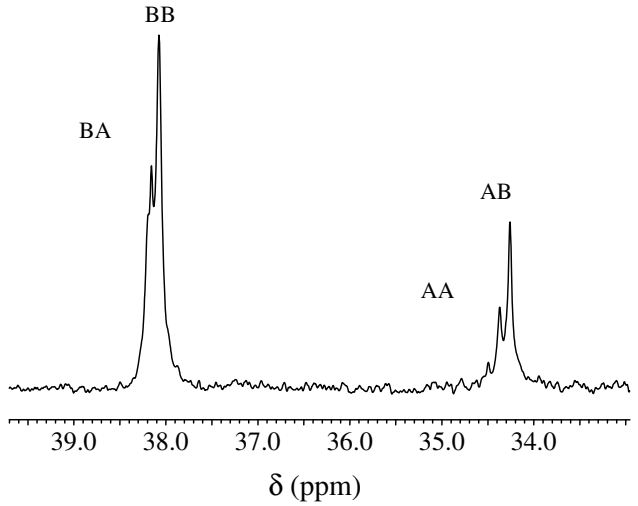



**Fig. 6.** Expansion of the 30–40 ppm range of the $^{13}C$ NMR spectrum of the copolymer obtained by hydrolytic polymerization of CLa in the presence of PEO–*b*–PCLo–OH during 7 h at 250 °C – carbon signals of the methylene in α position of amide and ester carbonyls.

### 5.5. Polymerization of CLa in the presence of PEO–b–PCLo–OH

#### 5.5.1. Materials

ε-Caprolactam (CLa, 99%, Acros) was dried under reduced pressure at 60 °C overnight Three successive azeotropic distillations of toluene were carried out and CLa was stored under $N_2$. PEO–*b*–PCLo–OH was dried by three successive azeotropic distillations of toluene. Hypophosphorous acid ($H_3PO_2$, 50 wt% in water, Aldrich) was used as received.

#### 5.5.2. Synthesis

In a glass tube equipped with a three-way stopcock and a rubber septum, CLa (2 g, 17.67 mmol), PEO–*b*–PCLo–OH (2 g, 7.3 mmol of CLo, $[CLa]_0/[ester]_0 = 2.4$) and $H_3PO_2$ (0.25 molar% compared to the amide functions were added). After three vacuum-$N_2$ cycles, the tube was sealed and placed in a ventilated oven for a predetermined time at 250 °C. Then, the tube was cooled down to room temperature and broken. The reaction product was recovered and analyzed by $^1H$ NMR in TFA-*d*.

*NMR spectroscopy*: The $^1H$ and $^{13}C$ NMR spectra were recorded on AMX500 or Avance2 Bruker instrument operating respectively at 500.13 and 125.66 MHz for $^1H$ and $^{13}C$ nuclei, using hexamethyldisiloxane as an internal reference. For $^1H$ NMR analysis, samples were prepared by dissolving about 10 mg of the product in deuterated trifluoroacetic acid (0.5 mL) and for $^{13}C$ NMR, the samples were prepared by dissolving 50–100mg of the product in 0.6 mL of deuterated chloroform/ trifluoroacetic anhydride/deuterated trifluoroacetic acid (70/17/13 v/v/v). The PERCH deconvolution software was used for $^{13}C$ resonance deconvolution in order to determine the composition in CLo and/or CLa diads.

*Size exclusion chromatography* (SEC) was performed in THF at 35°C by using a polymer laboratories liquid chromatograph equipped with a PL-DG802 degasser, an isocratic HPLC pump LC 1120 (flow rate = 1 mL $min^{-1}$), a Marathon autosampler (loop volume = 200 μL, solution concentration = 1 mg $mL^{-1}$), a PL-DRI refractive index detector and three columns: a PL gel 10 um guard column and two PL gel Mixed-B 10 μm columns (linear columns for separation of PS molecular weight ranging from 500 to $10^6$ Da). Poly(styrene) standards were used for calibration.

## 6. Conclusions

The addition of carboxylic ester functions, as a model ester (PEO–O–C(O)–$C_5H_{11}$) or as a preliminarily synthesized diblock copolymer based on poly(ethylene oxide)-*b*-(poly ε-caprolactone) (PEO–*b*–PCLo–OH), has highlighted an activating effect on the hydrolytic polymerization of CLa as catalyzed by aqueous solution of $H_3PO_2$.

The polymerization of CLa in the presence of ester functions actually follows a hydrolytic mechanism, with the major involvement of hydrolysis of the ester/lactam ring with further condensation reaction between the resulting amine and the carboxylic acid functions.

On one hand, the ester hydrolysis leads to the formation of alcohol and carboxylic acid functions, amenable to polycondensation, the carboxylic acid functions being also able to initiate the acidolytic polymerization of CLa. On the other hand, the ester aminolysis promoted by the α-amino-ω-carboxylic acid leads to the formation of an amide link and a hydroxyl function. In addition to both reactions, all typical reactions occurring during the hydrolytic polymerization of CLa are involved, the ester hydrolysis appearing faster than the ester aminolysis.

Increasing the $[ester\ link]_0/[CLa]_0$ molar ratio starting from PEO–*b*–PCLo–OH, as an example, allowed synthesizing a diblock copolymer composed of a polyether block and a polyesteramide sequence characterized by a random distribution of the repetitive CLa and CLo comonomer units. The thermal and mechanical properties of the resulting block copolymers, i.e. PEO–*b*–P(CLa–*co*–CLo) diblock copolymers but also P(CLa–*co*–CLo)–*b*–PEO–*b*–P(CLa–*co*–CLo) symmetrical triblock copolymers, have been characterized and will be reported in a forthcoming paper.

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