Novel Polyesteramide-Based Diblock Copolymers: Synthesis by Ring-Opening Copolymerization and Characterization

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

Block copolymers based on a polyesteramide sequence and a polyether block were synthesized in bulk at 250 °C by ring-opening copolymerization (ROP) of ε-caprolactone (CLo) and ε-caprolactam (CLa) as initiated by Jeffamine® M1000, i.e., ω-NH_2 copoly[(ethylene oxide)-*co*-(propylene oxide)] copolymer [P(EO-*co*-PO)-NH_2]. For an initial molar ratio of $[CLa]_0/[CLo]_0 = 1$, the copolymerization allowed for the formation of a diblock copolymer with a statistical polyesteramide sequence, as evidenced by ^{13}C NMR. Investigation of the ROP mechanism highlighted that CLo was first polymerized, leading to the formation of a diblock copolymer P(EO-*co*-PO)-*b*-PCLo-OH, followed by CLa hydrolysis to aminocaproic acid that inserted into the ester bonds of PCLo via aminolysis and subsequent condensation reactions. The outcome is the selective formation of P(EO-*co*-PO)-*b*-P(CLa-*co*-CLo)-OH diblock copolymers where the composition and length of the polyesteramide sequence can be fine-tuned by the $[CLa]_0/[CLo]_0$ and $([CLa]_0 + [CLo]_0)/[P(EO\text{-}co\text{-}PO)\text{-}NH_2]_0$ initial molar ratios.

Introduction

A large proportion of plastic waste arises from materials used in packaging, especially household bags, agricultural films, or food containers. Taking into account environmental pollution concerns, designing polymers degrading in a controlled manner currently enjoys much attention. Accordingly, investigations on polymeric materials biodegrading in a specific environment have grown intensively.[1,2]

Aliphatic polyesters represent an interesting family of such biodegradable polymers and currently find a quite large range of applications in biomedical, agricultural, and packaging domains.[3] By contrast, aliphatic polyamides do not biodegrade in natural environment at an acceptable rate, this being the case for crystalline poly(ε-caprolactam) (PCLa), i.e., Nylon-6, the most industrially produced and commercially available polyamide.[4] The introduction of aliphatic ester units along the polymeric backbone has been reported as an interesting approach to increase the biodegradation ability of polyamide-based materials. Thus, aliphatic polyesteramides provide access to a new type of biodegradable polymers characterized by substantially higher mechanical and thermal properties with respect to aliphatic polyesters.[5–8] On one hand, polyesteramides tend to strengthen the materials thanks to the polarity of amide groups and their ability to strong hydrogen bonding.

G. Deshayes, C. Delcourt, P. Degée, P. Dubois
Center of Innovation and Research in Materials and Polymers (CIRMAP), Laboratory of Polymeric and Composite Materials, University of Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium
E-mail: gaelle.deshayes@chemistry.gatech.edu; philippe.dubois@umh.ac.be
I. Verbruggen, R. Willem
High Resolution NMR Centre (HNMR), Department of Materials and Chemistry (MACH), Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels, Belgium
L. Trouillet-Fonti, F. Touraud, E. Fleury, M. Destarac
Rhodia Recherche et Technologies, 85 Avenue des Frères Perret, F-69192 Saint Fons, France

Macromol. Chem. Phys. **2009**, *210*, 1033–1043

DOI: 10.1002/macp.200900065

On the other hand, the presence of hydrolytically cleavable ester links in the main chain has proven to reduce the extent of crystallinity of the resulting polyesteramides and to make them biodegradable. In addition to their slow biodegradation kinetics in a composting environment (standard EN13432), another disadvantage of aliphatic polyamides is their much higher propensity to be hygroscopic than their respective aliphatic polyesters. The ability to imprison water is an important drawback because the absorbed water acts as a plasticizer, reducing significantly the glass transition temperature.[9] The covalent inclusion of ester units within the polyamide chain thus represents a good alternative to address this issue.

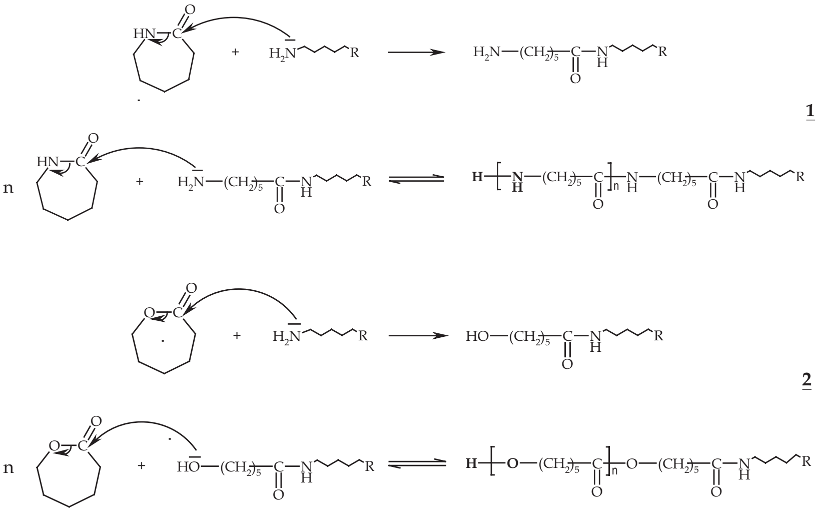
Various synthetic routes to biodegradable polyesteramides have been investigated so far either by polycondensation, by ring-opening polymerization (ROP) or by ester–amide exchange reactions between preformed polyester and polyamide chains.[10–12] Interestingly, polyesteramides based on poly(ε-caprolactone) (PCLo) and PCLa have demonstrated their inherent ability to be readily tuned up from a thermoplast to a rubber, depending on the relative content of lactone units present in the initial reaction medium and on the co-monomer distribution in the polymer chain.[5,6,13]

The present paper reports on the synthesis and characterization of block-copolymers based on a model polyether covalently bound to a polyesteramide sequence, the latter being obtained by ring-opening copolymerization of CLa and CLo according to an efficient hydrolytic reaction mechanism.[14] As previously reported, performing the H_3PO_2-catalyzed hydrolytic polymerization of CLa in bulk at 250 °C in the presence of ω-hydroxylated poly(ethylene oxide) (PEO-OH) resulted in a very low rate of CLa ROP. Such a slow polymerization kinetics proved to be the consequence of non-quantitative and very slow initiation from hydroxyl functions. By contrast, when the ROP of CLa was performed in the presence of a carboxylic ester, e.g., PEO$-$O$-$C(O)$-C_5H_{11}$, a significant activation of the hydrolytic polymerization of CLa by the ester was highlighted, giving rise to PEO-*b*-PCLa diblock copolymers isolated with very high yields.[14] In a similar way, another approach consisted first in initiating the polymerization of CLo from PEO-OH at 250 °C with H_3PO_2 as a catalyst, generating in situ a P(EO-*b*-CLo)-OH diblock copolymer and adding and polymerizing subsequently CLa at the same temperature. As a result, a novel polyesteramide-based block copolymer, i.e., (PEO-*b*-P[CLa-*co*-CLo]-OH), composed of a polyether block covalently linked to a polyesteramide sequence, was obtained. Interestingly, the CLa and CLo units were random distributed along the backbone of the polyesteramide, as evidenced by ^{13}C NMR.

With the purpose of widening the properties of these new hydrolytic "lactam insertion-type" materials and preserving their high reactivity, their reaction mechanism has been studied using Jeffamine M1000 or P(EO-*co*-PO)-NH_2, an ω-aminated polyether as a macroinitiator. By contrast to the previously investigated PEO-OH macroinitiator, this ω-aminated polyether is able to initiate the ROP of both CLo and CLa. Under these conditions, the co-monomer distribution in the polyesteramide sequence and the resulting material properties, can be tuned at will by varying the initial composition of the reaction medium ($[CLa]_0/[CLo]_0$), and also by varying the order of CLa/CLo co-monomer introduction into the reaction medium.

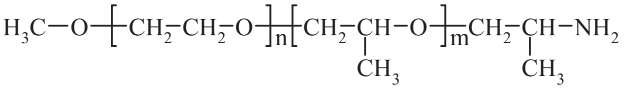
Results and Discussion

With respect to previously reported data exploring hydroxyl-terminated polyethers as macroinitiators in ROP of CLa/CLo,[14] the use of α-amino polyethers strongly modifies the ROP mechanism of both cyclic monomers. Indeed, lactams are known to readily polymerize through an aminolytic mechanism when initiated by primary amine functions, yielding high molecular weight polyamides.[15] Actually, the amine function of the macroinitiator promotes the ring-opening of the lactam by a nucleophilic attack onto the carbonyl carbon atom, followed by the amide cleavage and concomitant formation of an amide bond between the macroinitiator residue and the monomeric unit, and a new amine function capable to propagate the polymerization reaction (**Scheme 1.1**). As far as the polymerization of CLo is concerned, the amine function initiates the ROP of the lactone generating again an amide bond at one extremity of the growing polyester chain and an hydroxyl function at



Scheme 1. Aminolytic polymerization of CLa (1) and CLo (2).

DOI: 10.1002/macp.200900065



$$H_3C-O-\left[CH_2-CH_2-O\right]_n\left[CH_2-\underset{CH_3}{CH}-O\right]_m CH_2-\underset{CH_3}{CH}-NH_2$$

Scheme 2. P(EO-*co*-PO)-NH_2 Jeffamine (M).

Table 1. Molecular characteristics of P(EO-*co*-PO)-NH_2 Jeffamine M1000.

Jeffamine	$\overline{Mn}_{RMN}$[a)]	$\overline{Mn}_{titr}$[b)]	PO/EO[a)]
	$g \cdot mol^{-1}$	$g \cdot mol^{-1}$	
M1000	1 400	1 200	1/16

[a)] As determined by proton NMR; [b)] As determined by titration of the amine functions by an aqueous solution of oxalic acid.

the other one, which propagates the polymerization reaction (**Scheme 1.2**).[15] It is worth reminding that a hydroxyl function cannot initiate the ROP of CLa under most of the investigated polymerization conditions (see ref. [15] and papers cited herein).

Table 2. Monomer conversion and degree of polymerization of polyamides as obtained by aminolytic polymerization of CLa initiated by Jeffamine M1000 ($[CLa]_o/[P(EO\text{-}co\text{-}PO)\text{-}NH_2]_o = 5$) at 250 °C in the presence of 0.25 mol-% of H_3PO_2 (50 wt.-% in water) for different polymerization times.

Entry	Time	$Conv_{CLa}$[a)]	$\overline{DP}_{exp}$[a)]
	h	%	
1	1	29	2
2	3	53	3
3	5	65	3
4	7	68	3
5	9	69	3.5

[a)] As determined by ^1H NMR: $Conv_{CLa} = I_{PA2}/(I_{CLA2} + I_{PA2}) \times 100$, $\overline{DP}_{exp} = I_{PA2}/I_{AA3}$ (see Figure 1).

Investigation of CLa Polymerization as Initiated by P(EO-*co*-PO)-NH_2

In a first set of experiments, the aminolytic polymerization of CLa has been carried out in sealed glass ampoules, in bulk at 250 °C and in the presence of P(EO-*co*-PO)-NH_2, i.e., Jeffamine M1000. The *M* symbol stands for *M*onoamine and the number "1000" refers to the approximate molecular mass of the macroinitiator. The chemical structure and the molecular characteristics of Jeffamine M1000 are presented in Scheme 2 and Table 1.

Table 2 reports the monomer conversion and the degree of polymerization of polyamide samples as recorded for different polymerization times using H_3PO_2 (0.25 mol-% relative to the amide functions) as a catalyst. For this set of experiments, the $[CLa]_0/[P(EO\text{-}co\text{-}PO)\text{-}NH_2]_0$ initial molar ratio was kept as low as 5, in order to make NMR characterization easier, at least for the end-group identification. Monomer conversion was determined from the relative intensity of the ^1H NMR resonance from the methylene protons in α-position of the PCLa carbonyl (PA2) at 2.3 ppm and of the CLa cyclic monomer (CLA2) at 2.45 ppm. Conversion increases steadily with the polymerization time, at least up to 5 h (entry 3, Table 2). It turns out that all polyamide segments were end-functionalized by an amine function detected at 2.85 ppm ($-CH_2-NH_2$; AA3). Indeed no trace of carboxylic acid end-groups could be detected at 2.1 ppm ($-CH_2-COOH$) in the ^1H NMR spectra[14] (Figure 1).

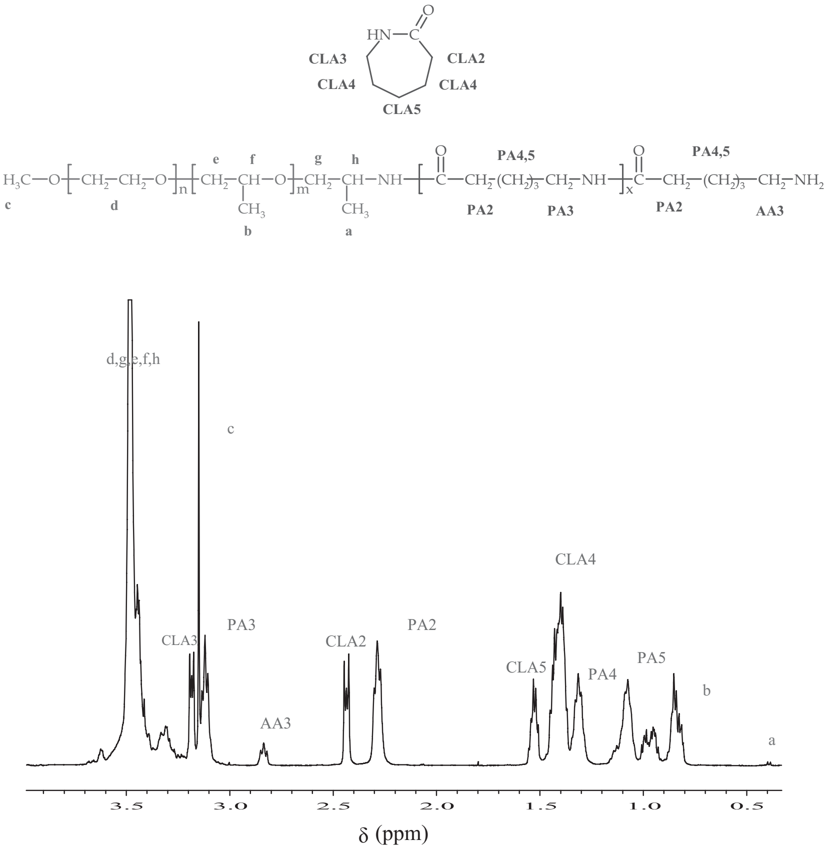


Figure 1. ^1H NMR spectrum of crude polyamide as obtained by aminolytic polymerization of CLa initiated by Jeffamine M1000 in the presence of 0.25 mol-% of H_3PO_2 at 250 °C for 7 h (entry 4, Table 2, solvent: TFA-*d*; 500.13 MHz).

Accordingly, the experimental degree of polymerization ($\overline{DP}_{\mathrm{exp}}$) could be determined and proved to be in a good agreement with the expected values assuming an aminolytic polymerization mechanism.

Investigation of CLo Polymerization as Initiated by P(EO-*co*-PO)-NH_2

The polymerization of CLo was performed in the presence of Jeffamine M1000 and 0.25 mol-% of H_3PO_2 in bulk at 250 °C for 7 h. Again, an initial molar ratio $[\mathrm{CLo}]_0/[\mathrm{P(EO\text{-}}co\mathrm{\text{-}PO)\text{-}NH_2}]_0$ of 5 was used (Table 3). For comparison, the results of the CLa polymerization obtained under identical conditions are also presented.

Table 3. Monomer conversion and degree of polymerization for the polyester and polyamide blocks as obtained by aminolytic polymerization of CLo and CLa, respectively, as initiated by Jeffamine M1000 ($[\mathrm{monomer}]_0/[\mathrm{P(EO\text{-}}co\mathrm{\text{-}PO)\text{-}NH_2}]_0 = 5$) at 250 °C in the presence of 0.25 mol-% of H_3PO_2 (50 wt.-% in water) for 7 h.

Entry	Monomer	Conv %	$\overline{DP}_{\mathrm{exp}}$
1	CLo	$>99^{a)}$	$5^{c)}$
2	CLa	$68^{b)}$	$3^{d)}$

a) As determined by ^{1}H NMR: no residual signals for CLo;
b) As determined by ^{1}H NMR: $\mathrm{Conv}_{\mathrm{CLa}} = I_{\mathrm{PA2}}/(I_{\mathrm{CLA2}} + I_{\mathrm{PA2}}) \times 100$; c) $\overline{DP}_{\mathrm{exp}}$ as determined by ^{1}H NMR: $\overline{DP}_{\mathrm{exp}}\mathrm{CLo} = I_{\mathrm{PE3}}/I_{\mathrm{PE4}}$ (see Figure 2); d) $\overline{DP}_{\mathrm{exp}}$ as determined by ^{1}H NMR: $\overline{DP}_{\mathrm{exp}}\mathrm{CLa} = I_{\mathrm{PA2}}/I_{\mathrm{AA3}}$ (see Figure 1).

CLo conversion was determined by ^{1}H NMR directly on the crude product. The absence of characteristic signals from the residual monomer shows that a quantitative CLo conversion was obtained (Figure 2). It turns out that the aminolytic polymerization of CLo is much faster than CLa polymerization performed under identical experimental conditions. Furthermore, ^{1}H NMR analysis of the crude product indicates the formation of P(EO-*co*-PO)-*b*-PCLo block copolymer end-capped by a hydroxyl function, as evidenced by the sole presence of a characteristic terminal $-CH_2-OH$ (PE4) signal at 4.05 ppm. Interestingly, the presence of the characteristic $-CH_2-C(O)-NH-$ proton signal at 2.30 ppm (PA2) is consistent with the expected formation of the amide bond between the polyether macroinitiator and the polyester segment, the ratio of

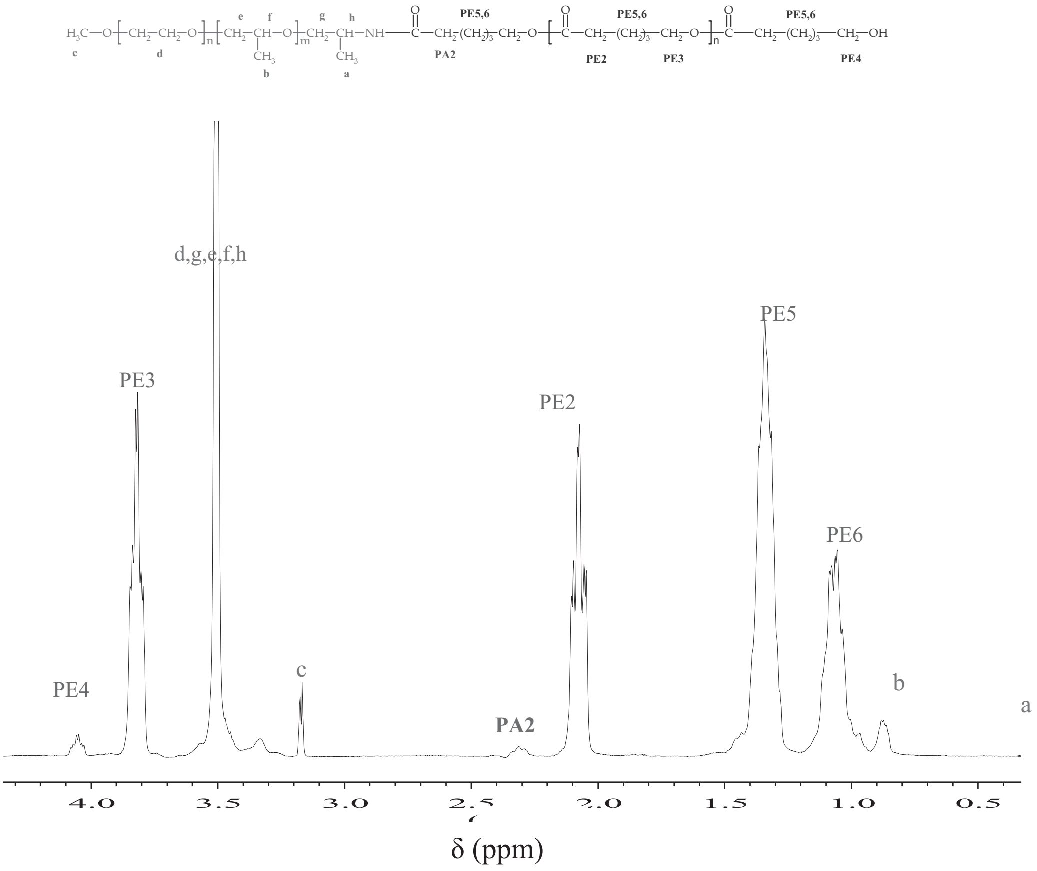


Figure 2. ^{1}H NMR spectrum of a crude polyester as obtained by aminolytic polymerization of CLo initiated by Jeffamine M1000 in the presence of 0.25 mol-% of H_3PO_2 at 250 °C for 7 h (entry 1, Table 3, solvent: TFA-*d*; 500.13 MHz).

DOI: 10.1002/macp.200900065

the relative intensity of the PA2 and PE4 proton signals being equal to unity (I_{PA2}/I_{PE4}). The amine function of the polyester block thus acts as the initiator for the ROP of the CLo through an aminolytic mechanism. Therefore, the experimental degree of polymerization ($\overline{DP}_{exp}$), as determined from the relative intensities of the resonances of the $-CH_2-O-C(O)-$ protons of the polyester chain (PE3: 3.8 ppm) and the $-CH_2-OH$ protons (PE4: 4.05 ppm), is equal to 5, in perfect agreement with the expected DP based on the initial monomer-to-amine molar ratio.

Copolymerization of CLa and CLo Initiated by P(EO-*co*-PO)-NH_2

Similarly to the aforementioned syntheses of the diblock copolymer, ''simultaneous'' copolymerization of CLa and CLo was also carried out in bulk at 250 °C. In this specific copolymerization reaction, various types of catalysts have been investigated: previously studied H_3PO_2 (50% in water), *p*-toluenesulfonic acid (PTSA), tin(II) octanoate [$Sn(Oct)_2$], di-*n*-butyltin(IV) dilaurate (Bu_2SnLaurate), and antimony(III) oxide (Sb_2O_3). These experiments were performed in the presence of Jeffamine M1000 for a polymerization time of 7 h, in the presence of 0.25 mol-% of the selected catalyst. The initial molar ratios used were fixed at $[CLa]_0/[CLo]_0 = 1$ and $[CLa + CLo]_0/[P(EO\text{-}co\text{-}PO)\text{-}NH_2]_0 = 10$ (Table 4). Again, in this first set of experiments, the initial co-monomer-to-macroinitiator molar ratio was kept low in order to identify the end-group by NMR.

Whatever the catalyst investigated, NMR spectra of the crude reaction products evidenced the formation of P(EO-*co*-PO)-*b*-P[CLa-*co*-CLo] block copolymers end-capped by a hydroxyl function. As shown by the representative ^{1}H NMR spectrum in Figure 3, the $-CH_2-OH$ (PE4) end-group resonance at 4.05 ppm could be detected, the $-CH_2-NH_2/-CH-(CH_3)-NH_2$ protons, initially displayed from the polyether macroinitiator, being not observed anymore. Moreover, the ratio between the relative intensity ratio of the $-CH_2-C(O)-O-$ (PE2) signal at 2.1 ppm and the $-CH_2-O-C(O)-$ (PE3) one at 3.8 ppm is equal to unity.

Table 4. Monomer conversion and degree of polymerization in copolymerization of CLa and CLo as initiated by Jeffamine M1000 ($[CLa]/[CLo]_o = 1$, $[Cla + CLo]_o/[P(EO\text{-}co\text{-}PO)\text{-}NH_2]_o = 10$) at 250 °C for 7 h in the presence of 0.25 mol-% of the selected catalyst.

Entry	Catalyst	Conv$^{a)}$		$\overline{DP}_{exp}$ $^{a)}$	
		%		%	
		CLa	CLo	CLa	CLo
1	H_3PO_2	55	>99	3	4.5
2	$Sn(Oct)_2$	30	>99	2.1	4.3
3	*n*-$Bu_2SnLaurate_2$	41	>99	2.4	4.5
4	Sb_2O_3	32	>99	2.1	4.5

$^{a)}$As determined by ^{1}H NMR: $Conv_{CLa} = I_{PA2}/(I_{CLA2} + I_{PA2}) \times 100$, $Conv_{CLo}$ quantitative, $\overline{DP}_{exp}$ determined based on $I_{3.5}$: $\overline{DP}_{CLa} = [(90H/I_{3.5})^* I_{PA2}]/2$, $\overline{DP}_{CLo} = [(90H/I_{3.5})^* I_{PE3}]/2$ (see Figure 3).

In agreement with NMR analyses previously discussed in homopolymerizations of CLa and CLo as initiated by P(EO-*co*-PO)-NH_2, CLo conversion appeared quantitative after 7 h at 250 °C, while CLa conversion is again lower as determined from the relative intensities of the $-CH_2-C(O)-NH-$ resonance (PA2) at 2.3 ppm and the residual CLa cyclic monomer resonance (CLA2), at 2.45 ppm. Among the catalysts investigated, H_3PO_2 in aqueous solution proved the most effective promoter with a CLa conversion of 55% after 7 h at 250 °C.

All these observations thus highlight that CLo is preferably polymerized by an aminolytic mechanism. The resulting PCLo hydroxyl end group being not sufficiently active to initiate ROP of CLa (vide supra), the lactam monomer is more likely to polymerize and, accordingly, to be inserted into the polyester block via the ''hydrolysis/condensation'' mechanism reported very recently.[14] Based on such a mechanism, the slower rate of CLa conversion recorded in the CLo/CLa copolymerization reaction with respect to CLa homopolymerization ($Conv_{CLa} = 65\%$ after 7 h), as initiated by P(EO-*co*-PO)-NH_2, can be accounted for. Importantly, the involvement of transamidation and/or transesterification reactions cannot be excluded, especially when organometallic [*n*-$Bu_2Sn(Laurate)_2$, $Sn(Oct)_2$, and Sb_2O_3] catalysts[16–19] are used. Accordingly, it has been chosen to focus only on H_3PO_2 in the next set of experiments. It is also worth mentioning that all copolymers obtained appeared insoluble in common solvents like THF, thus preventing their characterization by gel permeation chromatography (GPC).

In order to determine the distribution of CLa and CLo co-monomer units along the polyesteramide sequence, the diblock copolymers were further characterized by ^{13}C NMR spectroscopy, which demonstrated many times its effectiveness in the determination of the copolymer chain microstructure and the average length of a block incorporating the same repetitive unit.[20–23] In the case of the polyesteramide based on CLa and CLo units, the carbon atom of the methylene group in α position to the amide and ester functions, i.e., $-CH_2-C(O)-NH-$ and $-CH_2-C(O)-O-$, respectively, is monitored in terms of ^{13}C dyads (AA, AB, BA, and BB where A and B represent the two co-monomer units), meaning that the ^{13}C chemical shift is mainly determined by whether the adjacent repetitive unit originates from a CLo unit (AA and AB dyads) or a CLa one (BB and BA dyads; Figure 4), the small chemical shift difference within 1 ppm for each group of the

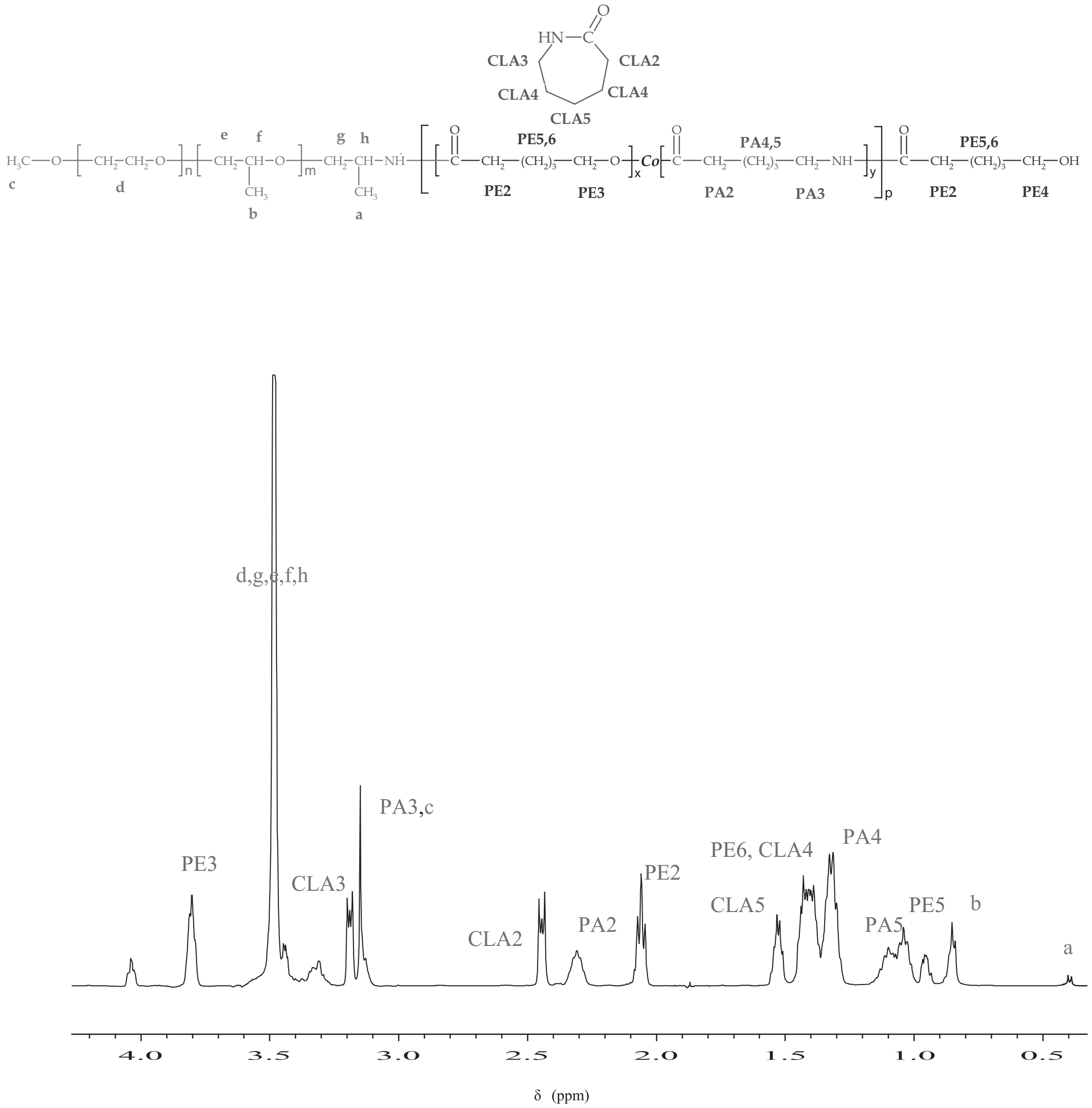


Figure 3. ^{1}H NMR spectrum of the crude product obtained by copolymerization at 250 °C for 7 h of CLa and CLo, initiated by Jeffamine M1000 in the presence of 0.25 mol-% of H_3PO_2 (entry 1, Table 4, solvent: TFA-*d*; 500.13 MHz).

dyad resonance pairs being determined by whether the co-monomer raises from CLo (A) or CLa (B).[24] The ^{13}C NMR data of the isolated polyesteramide-based block copolymer were acquired from mixed $CDCl_3/(CF_3CO)_2O/CF_3COOD$ (70:17:13 v/v/v) solutions. Full relaxation conditions for ^{13}C signal quantification were determined by recording the ^{13}C NMR spectrum of a representative copolymer sample at different, increasing relaxation delays between two consecutive scans, until the differences in relative integrated areas of the ^{13}C resonances of interest to be quantified did not vary anymore within experimental error.

In this way, deconvolution of ^{13}C NMR resonances enables one to determine molar compositions in a similar way as obtained above from ^{1}H NMR spectra.

Based on the relative integrated areas of the ^{13}C resonances from the carbon atoms in α position of amide and ester functions, the average length of PCLo ($\bar{L}_{\text{PCLo}}$) and PCLa ($\bar{L}_{\text{PCLa}}$) blocks were determined using Equations (1) and (2).[23]

$$\bar{L}_{\text{PCLo}} = \frac{I_{\text{AA}}}{I_{\text{AB}}} + 1 \tag{1}$$

$$\bar{L}_{\text{PCLa}} = \frac{I_{\text{BB}}}{I_{\text{BA}}} + 1 \tag{2}$$

Interestingly, the ^{13}C NMR spectrum of the copolymer obtained after 7 h at 250 °C by copolymerization of CLa and

DOI: 10.1002/macp.200900065

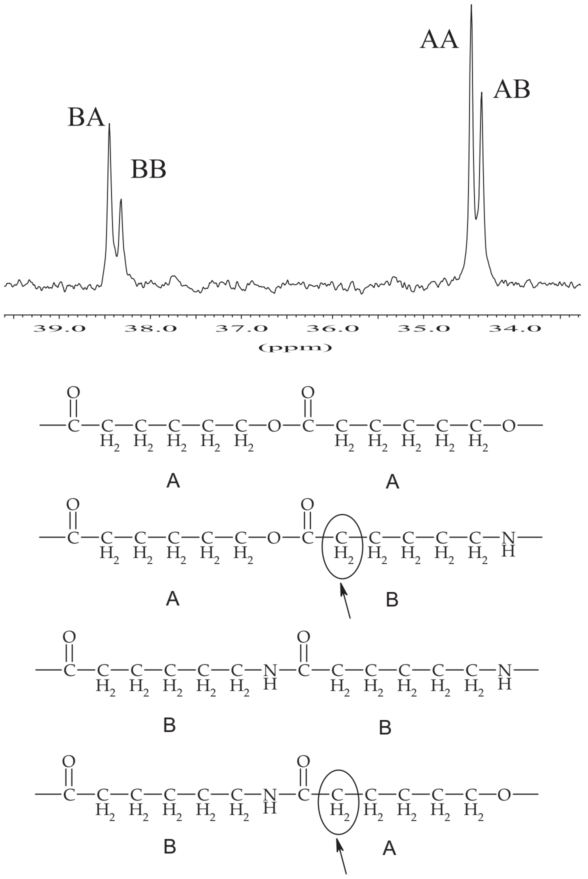


Figure 4. Expansion of the 30–40 ppm chemical shift range of a representative ^{13}C NMR spectrum displaying the ^{13}C resonances of the CH$_2$ groups in α-position to the carbonyl groups of the copolymer (in a 70:17:13 $CDCl_3/(CF_3CO)_2O/CF_3COOD$ mixture) obtained by copolymerization of CLa and CLo initiated by Jeffamine M1000.

CLo initiated by Jeffamine M1000 (entry 1, Table 4) confirms the random incorporation of CLa units into the polyesteramide sequence with PCLa and PCLo average lengths of 2.1 and 1.8, respectively. Interestingly, after deconvolution of the signals, a relative co-monomer composition identical to the one obtained by proton NMR is obtained, i.e., 63% CLo and 37% CLa units.

Synthesis of Higher Molecular Polyether/ Polyesteramide Block Copolymers

This part of the research aimed at focusing on the larger scale synthesis (in a 250 mL glass reactor) of block copolymers based on polyesteramide sequences. It is known that aliphatic polyesters like PCLo are characterized by rather weak thermo-mechanical performances in comparison with their polyamide analogs.[25,26] For instance, Table 5 (entries 1 and 2) confirms the sharp difference in thermal and mechanical properties of representative samples of industrially available PCLa and PCLo where T_g is the glass transition temperature and T_m, the melting temperature as determined by differential scanning calorimetry (DSC) while the elastic modulus (E') was recorded at 25 °C by dynamic mechanical analysis (DMA).

Depending not only on the type and quantity of ester and amide units but also on the co-monomer distribution along the chain, the polyesteramides are likely to present intermediate thermal and mechanical properties with respect to the corresponding homopolymers.[26]

First, the aminolytic homopolymerizations of CLa and CLo in the presence of H_3PO_2 and Jeffamine M1000 were performed in glass reactors equipped with a condenser, a three-way stopcock and a rubber septum in order to work under inert atmosphere. A heating mantle in connection with a temperature regulator and an anchor-like mechan-

Table 5. Thermal and mechanical properties of representative commercial PCLa and PCLo as well as high molecular weight P(EO-*co*-PO)-*b*-P(CLa-*co*-CLo)-OH diblock copolymers. Effect of the relative composition and the mean degrees of polymerization in CLa and CLo.

Entry	**(Co)polymer**[a)]	$\overline{DP}_{CLa}$	$\overline{DP}_{CLo}$	T_g[b)] °C	T_m[c)] °C	E'[b)] MPa
1	PCLa	165	–	70	225	1 900
2	PCLo	–	440	−40	60	360
3	P(EO-*co*-PO)-*b*-P(CLa-*co*-CLo)-OH	150	10	59	213	1 600
4	P(EO-*co*-PO)-*b*-P(CLa-*co*-CLo)-OH	170	50	9	183	770
5	P(EO-*co*-PO)-*b*-P(CLa-*co*-CLo)-OH	180	100	−6	152	400

[a)] PCLa: commercial polyamide (Rhodia France, $\overline{M}_n = 18\,500$ g · mol^{-1}); PCLo: commercial poly(ε-caprolactone) (CAPA 6500, Solvay Interox, UK, $\overline{M}_n = 50\,000$ g · mol^{-1}); [b)] As determined by DMA (dual cantilever mode, 2 °C · min^{-1}, 1 Hz, 20 μm, from −100 to 150 °C); value measured at 25 °C; [c)] As determined by DSC (10 °C · min^{-1}, from −120 to 280 °C, first scan).

Table 6. Expected degree of polymerization, monomer conversion, and average length of PCLo ($\bar{L}_{PCLo}$) and PCLa ($\bar{L}_{PCLa}$) blocks as obtained in homopolymerizations of CLo and CLa for 7 h ([monomer]$_o$/[P(EO-*co*-PO)-NH$_2$]$_o$ = 25), simultaneous copolymerization for 24 h of CLa and CLo initiated by Jeffamine M1000 for different [CLa]$_o$/[CLo]$_o$ and [CLa + CLo]$_o$/[P(EO-*co*-PO)-NH$_2$]$_o$ molar ratios at 250 °C (0.50 mol-% H_3PO_2).

Entry	$\overline{DP}_{\text{CLa theor}}$	$\overline{DP}_{\text{CLo theor}}$	Conv$^{a)}$ %		$L_{PCLa}$$^{b)}$	$L_{PCLo}$$^{b)}$
			CLa	CLo		
1	–	25	–	99	–	
2	25	–	30	–	–	–
3	25	25	79	>99	1.8	1.9
4	50	25	80	>99	3.4	1.6
5	200	10	75	>99	–$^{c)}$	–$^{c)}$
6		50	86	>99	3.3	1.2
7		100	90	>99	2.6	1.6
8		150	88	>99	2.2	2.0

[a)] As determined by ^{1}H NMR: $\text{Conv}_{CLa} = I_{PA2}/(I_{CLA2} + I_{PA2}) \times 100$; Conv_{CLo}: quantitative; [b)] As determined by ^{13}C NMR via Equations 1 and 2; [c)] Limited resolution of ^{13}C NMR spectra preventing resonance deconvolution.

ical stirrer were used. The homopolymerizations were carried out at 250 °C for 7 h starting with an initial molar ratio [monomer]$_0$/[P(EO-*co*-PO)-NH$_2$]$_0$ of 25. In a second step, the simultaneous copolymerization of CLa and CLo initiated by Jeffamine M1000 was performed for 24 h in the 250 mL glass reactor at different [CLa]$_0$/[CLo]$_0$ and [CLa + CLo]$_0$/[P(EO-*co*-PO)-NH$_2$]$_0$ molar ratios, at 250 °C, in the presence of 0.50 mol-% H_3PO_2 (Table 6).

As expected, the ^{1}H NMR spectrum of the crude product obtained after the polymerization of CLo initiated by Jeffamine M1000 in the reactor shows the formation of a diblock copolymer P(EO-*co*-PO)-*b*-PCLo-OH (entry 1, Table 6). The ^{1}H NMR spectrum not only displays the signals characteristic for $-CH_2-C(O)-O-$ (PE2: 2.1 ppm) and $-CH_2-O-C(O)-$ (PE3: 3.8 ppm) ester unit protons but also the signal characteristic from the $-CH_2-NH-C(O)-$ (PA2: 2.30 ppm) protons. The presence of the latter is the result of the formation of an amide bond between the initiator and the polyester block. Moreover, the $-CH_2-OH$ resonance (PE4: 4.1 ppm) of the end-group, resulting from the aminolytic polymerization of the CLo initiated by the Jeffamine M1000, is also observed. Similarly, the ^{1}H NMR spectrum of the crude product obtained after the CLa polymerization under identical conditions shows the formation of P(EO-*co*-PO)-*b*-PCLa-NH$_2$ (entry 2, Table 6). The presence of the amine end-group resonance at 2.85 ppm (AA3) in the ^{1}H NMR spectrum evidences the aminolytic polymerization of CLa initiated by Jeffamine M1000. The CLa conversion, calculated from the ratio of the signal amplitude from the α-carbonyl amide methylene protons of the polymer at 2.3 ppm (PA2) to that from the monomer at 2.45 ppm (CLA2) remains low, even after 7 h. Accordingly, a two-fold increase in the quantity of catalyst, while keeping all other conditions unchanged, resulted in a CLa conversion as high as 80% after 7 h.

In a second step (entries 3–8, Table 6), the simultaneous copolymerization of CLa and CLo initiated by Jeffamine M1000 was performed for 24 h in the 250 mL glass reactor for different [CLa]$_0$/[CLo]$_0$ and [CLa + CLo]$_0$/[P(EO-*co*-PO)-NH$_2$]$_0$ molar ratios. The ^{1}H NMR spectrum reveals high conversions in both co-monomers after reaction completion under these conditions (Figure 5). Signal from $-CH_2-OH$ (PE4: 4.05 ppm) end-groups are readily observed but signal from $-CH_2-NH_2$ (AA3: 2.85 ppm) amine end-groups are not. Again, in perfect agreement with the ''lactam insertion-type'' reaction mechanism activated in the presence of ester functions,[14] the distribution of the co-monomers in the polyesteramide sequence appears to be random, as revealed by ^{13}C NMR of copolymers isolated after extraction of residual CLa under reduced pressure (Table 6). Furthermore, the length of the polyamide and polyester ''blocks'' in the polyesteramide sequence depends on the co-monomer composition in the feed.

Preliminary thermal and mechanical characterizations have been performed on some representative high molecular weight polyesteramide-based block copolymers. Both DSC and DMA were used for the determination of the T_g, T_m, and E' values, respectively (see Table 5, entries 3–5). Interestingly, the investigated copolymers display intermediate thermal transitions with respect to the corresponding PCLa and PCLo homopolymers. Both T_g and T_m of the polyesteramide blocks proved to decrease upon increasing the relative content in ester units. Furthermore, the same trend is observed when comparing the elastic modulus recorded at 25 °C by DMA in dual cantilever mode. Clearly, this first set of thermal and mechanical characterizations offers prospects to fine-tune the thermo-mechanical properties of the P(EO-*co*-PO)-*b*-P(CLa-*co*-CLo)-OH copolymers by controlling their composition and block length.

Experimental Part

Materials

ε-Caprolactam (CLa, 99%, Acros) was dried overnight under reduced pressure at 60 °C. Three successive azeotropic distillations of toluene were performed and CLa was stored under N_2. CLo (99%, Acros) was dried over calcium hydride at room temperature for 48 h and distilled under reduced pressure and stored under N_2. Jeffamine M1000 (Jeff-NH$_2$, $Mn_{titr} = 1\,200$ g · mol^{-1} from Hunst-

DOI: 10.1002/macp.200900065

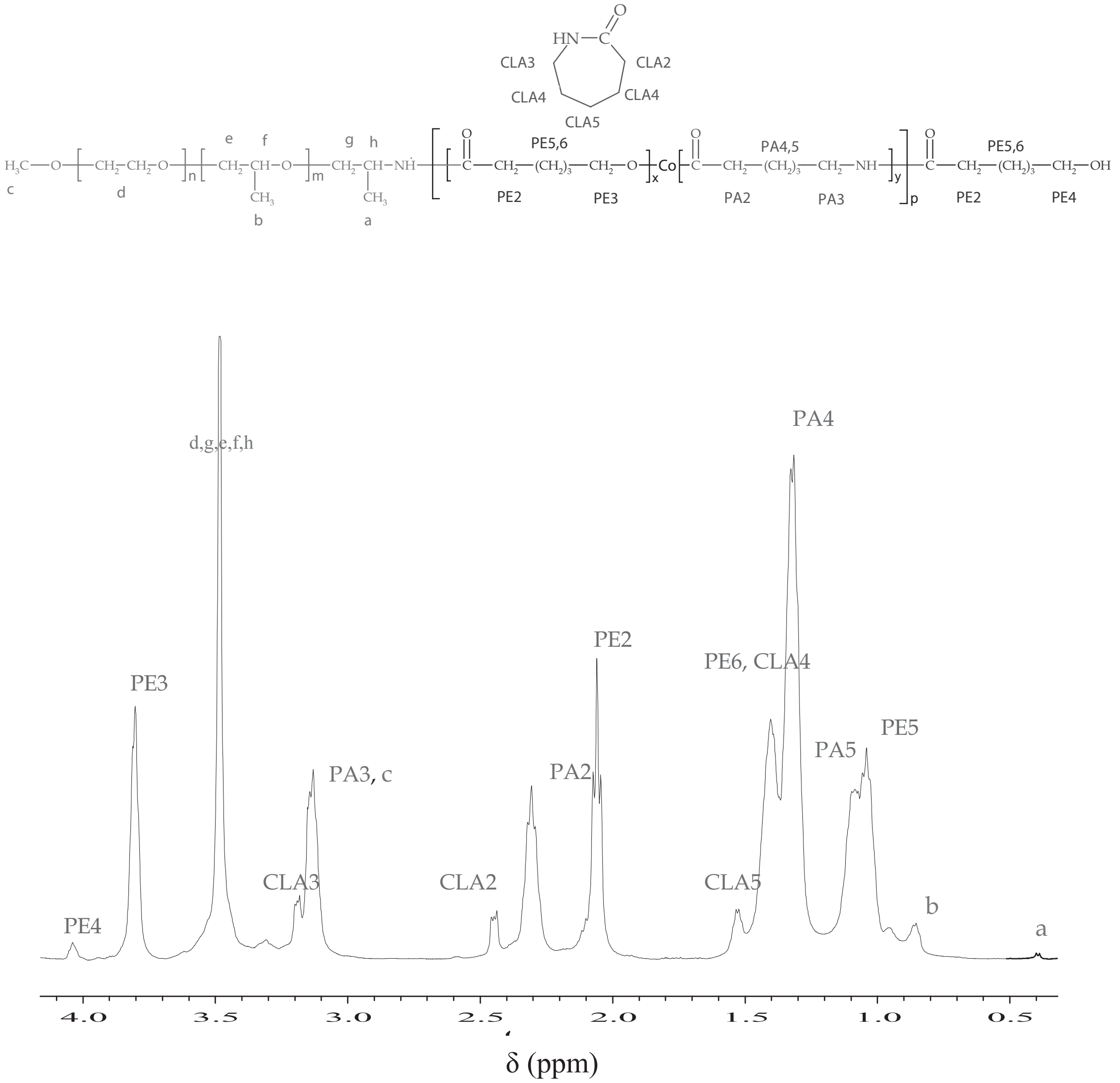


Figure 5. ^{1}H NMR spectrum of crude product as obtained by simultaneous copolymerization for 24 h of CLa and CLo initiated by Jeffamine M1000 in the presence of 0.50 mol-% of H_3PO_2 at 250 °C (entry 2, Table 7, solvent: TFA-*d*; 500.13 MHz).

man) was likewise dried by three successive azeotropic distillations of toluene. *p*-Toluene sulfonic acid (APTS, 99+%, Acros) was dried for 4 h under reduced pressure at 100 °C, and then by three successive azeotropic distillations of toluene. Hypophosphorous acid (H_3PO_2, 50 wt.-% in water, Aldrich), tin octanoate [Sn(Oct)$_2$, 95%, Sigma–Aldrich], di-*n*-butyl dilaurate tin (*n*-Bu$_2$SnLaurate$_2$, Aldrich), and antimony (III) oxide (Sb_2O_3, 99+%, Acros) were used as received. For larger scale syntheses of polyesteramides, monomers, initiators, and catalyst were used as received.

Syntheses

Polymerization of CLa Initiated by Jeffamine M1000

CLa (2 g, 17.67 mmol), Jeffamine M1000 (4.2 g, 3.5 mmol, $[CLa]_0/[Jeff\text{-}NH_2]_0 = 5$) and H_3PO_2 (0.25 mol-% with respect to the amide functions) were added to a glass tube equipped with a three-way stopcock and a rubber septum. After three vacuum–N_2 cycles, the tube was sealed and placed in a ventilated oven for a predetermined time at 250 °C. Subsequently, the tube was cooled down to room temperature and opened. The reaction product obtained was analyzed by ^{1}H NMR using deuterated trifluoroacetic acid (TFA-*d*) as a solvent.

Polymerization of CLo Initiated by Jeffamine M1000

In a glass tube equipped with a three-way stopcock and a rubber septum, CLo (1.9 mL, 17.14 mmol), Jeffamine M1000 (4.2 g, 3.5 mmol, $[CLo]_0/[P(EO\text{-}co\text{-}PO)\text{-}NH_2]_0 = 5$), and H_3PO_2 (0.25 mol-% with respect to the ester 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. Subsequently, the tube was cooled down to room temperature and opened. The reaction product obtained was analyzed by ^{1}H NMR using TFA-*d*.

Simultaneous Copolymerization of CLa and CLo Initiated by Jeffamine M1000

CLa (0.83 g, 17.14 mmol), CLo (0.8 mL, 7.4 mmol), Jeffamine M1000 (4.2 g, 3.5 mmol, $[CLa]_0/[CLo]_0 = 1$ and $[CLa + CLo]_0/[P(EO\text{-}co\text{-}PO)\text{-}NH_2]_0 = 10$), and catalyst (0.25 mol-% with respect to the amide functions) were added to a glass tube equipped with a three-way stopcock and a rubber septum. After three vacuum–N_2 cycles, the tube was sealed and placed in a ventilated oven for a predetermined time at 250 °C. Subsequently, the tube was cooled down to room temperature and de-sealed. The reaction product obtained was analyzed by ^{1}H NMR using TFA-*d*.

Synthesis of Polyesteramide-Based Copolymers in Reactor

For larger scale syntheses of polyesteramides, a 250-mL glass reactor was equipped with a condenser, a three-way stopcock and a rubber septum allowing to work under N_2 atmosphere. A heating mantle connected to a heating regulator and an anchor stirrer were used. A platinum probe coated with Teflon, connected to the temperature regulator was dipped into the reactor via a third inlet, the desired temperature being reached after 15 min. The stirring speed was fixed at 50 rpm. As CLa can sublimate at 60 °C, a rubber-skin balloon preliminarily filled with N_2 was placed at the extremity of the condenser instead of using a continuous N_2 flow.

Polymerization of CLa Initiated by Jeffamine M1000 in Reactor

CLa (100 g, 0.88 mol) and Jeffamine M1000 (42.4 g, 35 mmol) were successively poured into the reactor. The reactor was placed in a heating mantle preliminarily heated to 100 °C. 0.50% of H_3PO_2 (relative to the amide functions) was added and the reactor is kept under N_2 atmosphere with a balloon. The temperature was raised to 250 °C. After 7 h, the product was transferred into a rectangular aluminum mold. The crude product was analyzed by ^{1}H NMR using deuterated TFA-*d*.

Polymerization of CLo Initiated by Jeffamine M1000 in Reactor

CLo (98 mL, 0.88 mol) and Jeffamine M1000 (42.4 g, 35 mmol) were successively poured into the reactor. The reactor was placed in a heating mantle preliminarily heated to 100 °C. 0.50% of H_3PO_2 (relative to the ester functions) was added and the reactor was kept under N_2 with a balloon. The temperature was raised to 250 °C. After 7 h, the product was transferred into a rectangular aluminum mold. The crude product was analyzed by ^{1}H NMR using TFA-*d*.

Simultaneous Copolymerization of CLa and CLo Initiated by Jeffamine M1000 in Reactor for Different $[CLa + CLo]_0/[P(EO\text{-}co\text{-}PO)\text{-}NH_2]_0$ and $[CLa]_0/[CLo]_0$ molar Ratios

Described example for the simultaneous copolymerization of CLa and CLo initiated by Jeffamine M1000 in a reactor for $[CLa + CLo]_0/[P(EO\text{-}co\text{-}PO)\text{-}NH_2]_0 = 300$ and $[CLa]_0/[CLo]_0 = 2$ molar ratios.

CLa (116.2 g, 1 mol), CLo (58.6 g, 1 mol), and Jeffamine M1000 (5.2 g, 5 mmol) were introduced successively into the reactor. The reactor was placed in a heating mantle preliminarily heated to 100 °C. 0.50% of H_3PO_2 (relative to the amide functions) was added and the reactor is kept under N_2 in a balloon. The temperature was raised to 250 °C. After 24 h, the product was transferred into a rectangular aluminum mold. The crude product was analyzed by ^{1}H NMR using TFA-*d*.

NMR Spectroscopy

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX500 instrument operating, respectively, at 500.13 MHz using hexamethyldisiloxane as internal reference. For ^{1}H NMR analysis, the samples were prepared by dissolving about 10 mg of the product in deuterated trifluoroacetic acid (0.5 mL) while for ^{13}C NMR, the samples were prepared by dissolving 50–100 mg of the product in 0.6 mL of a mixture of three solvents, deuterated chloroform, trifluoroacetic anhydride, and deuterated trifluoroacetic acid (70:17:13 v/v/v).

Differential Scanning Calorimetry (DSC)

DSC measurements were performed on a TA Instrument Q100 apparatus under N_2 atmosphere at a heating rate of $10\ K \cdot min^{-1}$ from −120 to 280 °C. The first scan was recorded.

Dynamic Mechanical Analysis (DMA)

DMA was carried out with a TA Instrument 2980 apparatus operating in the dual cantilever mode. A frequency of 1 Hz, an amplitude of 20 μm and a heating rate of $2\ K \cdot min^{-1}$ from −100 to 150 °C were used. The elastic modulus values gathered in Table 5 were recorded at 25 °C.

Conclusion

The use of an ω-aminated macroinitiator, $P(EO\text{-}co\text{-}PO)\text{-}NH_2$ like Jeffamine M1000, in ROP of CLa or CLo as catalyzed by H_3PO_2 at 250 °C allows synthesizing original P(EO-*co*-PO)-*b*-PCLa and P(EO-*co*-PO)-*b*-PCLo diblock copolymers. The rate of CLo polymerization proved much higher, when compared to CLa ROP. When copolymerization of CLa and CLo is performed in the presence of $P(EO\text{-}co\text{-}PO)\text{-}NH_2$, a block copolymer P(EO-*co*-PO)-*b*-PCLo-OH is quickly formed in the first steps of the reaction and subsequently, the polymerization of CLa follows a hydrolytic reaction mechanism, with the major involvement of hydrolytic cleavage of the lactam ring with further condensation/amination reactions between the resulting amine and carboxylic acid ester functions. Interestingly, a block copolymer with a statistical polyesteramide sequence is obtained, as evidenced by ^{13}C NMR. This synthetic approach, promoted by a catalyst as simple as H_3PO_2 in aqueous solution, could be also performed in a higher capacity 250 mL glass reactor allowing not only to increase the amount of the isolated materials (ca. 150 g scale) but also to readily tune up the composition of the polyesteramide block by the CLa/CLo co-

DOI: 10.1002/macp.200900065

monomer composition in the feed. As far as the molecular weight of the polyesteramide blocks is concerned, it proved to be dependent on the initial co-monomer-to-amine molar ratio. Such a molecular parameter control proved to be a remarkable tool for tuning both the thermal and mechanical properties of the resulting polyesteramide-based materials. In conclusion, this contribution paves the way to a new family of biodegradable polyesteramide-based copolymers with remarkable thermo-mechanical and (bio)degradable properties, as will be reported in a forthcoming paper.

Acknowledgements: G. D. is much indebted to *Rhodia Recherche et Technologies, France*, for financial support of her PhD grant. The authors are very grateful for the financial support from "*Région Wallonne*" and *European Community* (FEDER, FSE) in the frame of "Pôle d'Excellence Materia Nova". LMPC thanks the *Belgian Federal Government Office of Science Policy* (STC-PAI 6/27). R. W. and I. V. are indebted to the Research Council of the *VUB* for financial support of the *High Resolution NMR Centre at the Vrije Universiteit Brussel* (GOA31).

Received: February 16, 2009; Revised: April 16, 2009; DOI: 10.1002/macp.200900065

Keywords: block copolymer; ε-caprolactam; ε-caprolactone; polyesteramide; ring-opening polymerization

[1] G. Scott, *Polym. Degrad. Stab.* **2000**, *68*, 1.
[2] L. A. Bosnea, I. Arvanitoyannis, A. Nakayama, *Curr. Trends Polym. Sci.* **1999**, *4*, 89.
[3] A.-C. Albertson, I. K. Varma, *Adv. Polym. Sci.* **2001**, *157*, 1.
[4] "Polymerization, Structure and Properties" in: *Lactam-based Polyamides*, B. Lanska, Ed., Vol. 1, CRC Press, Boca Raton 1991, p. 261.
[5] I. Arvanitoyannis, A. Nakayama, N. Kawasaki, N. Yamamoto, *Angew. Makromol. Chem.* **1994**, *222*, 111.
[6] I. Goodman, R. N. Vachon, *Eur. Polym. J.* **1994**, *20*, 529, 539, 549.
[7] J. Tuominen, J. V. Seppala, *Macromolecules* **2000**, *33*, 3530.
[8] Z. Y. Qian, S. Li, Y. He, C. Li, X. B. Liu, *Polym. Degrad. Stab.* **2003**, *81*, 279.
[9] J. Zimmerman, "*Encyclopedia of Polymer Science and Engineering*", Vol. II, H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, J. I. Kroschwitz, Eds., Wiley and Sons, New York 1988, p. 372.
[10] I. Arvanitoyannis, A. Nakayama, N. Kawasaki, N. Yamamoto, *Polymer* **1995**, *36*, 2947.
[11] K. E. Gonsalves, X. Chen, J. A. Cameron, *Macromolecules* **1992**, *25*, 3309.
[12] I. Goodman, M. T. Rodriguez, *Macromol. Chem. Phys.* **1996**, *197*, 881.
[13] X. Chen, K. E. Gonsalves, J. A. Cameron, *J. Appl. Polym. Sci.* **1993**, *50*, 1999.
[14] G. Deshayes, C. Delcourt, I. Verbruggen, L. Trouillet-Fonti, F. Touraud, E. Fleury, P. Degée, M. Destarac, R. Willem, P. Dubois, *React. Funct. Polym.* **2008**, *68*, 1392.
[15] S. W. Shalaby, H. K. Reimschussel, E. M. Pearce, *Polym. Eng. Sci.* **1973**, *13*, 88.
[16] H. R. Kricheldorf, M. Berl, N. Scharnagl, *Macromolecules* **1988**, *21*, 286.
[17] J. Baran, A. Duda, A. Kowalski, R. Szymanski, S. Penczek, *Macromol. Rapid Commun.* **1997**, *18*, 325.
[18] J. Baran, A. Duda, A. Kowalski, R. Szymanski, S. Penczek, *Macromol. Rapid Commun.* **1997**, *18*, 93.
[19] C. Wang, Y. Sun, *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1295.
[20] K. L. L. Eersels, A. M. Aerdts, G. Groeninckx, *Macromolecules* **1996**, *29*, 1046.
[21] H. R. Kricheldorf, T. Mang, J. M. Jonté, *Makromol. Chem.* **1985**, *186*, 955.
[22] A. Le Borgne, N. Spassky, C. L. Jun, A. Momtaz, *Makromol. Chem.* **1988**, *189*, 637.
[23] H. R. Kricheldorf, I. Kreiser, *Makromol. Chem.* **1987**, *188*, 1861.
[24] F. Samperi, C. Puglisi, R. Alicata, G. Montaudo, *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2778.
[25] S. Y. Lee, J. W. Park, Y. T. Yoo, S. S. Im, *Polym. Degrad. Stab.* **2000**, *78*, 63.
[26] A. Bernaskova, D. Chromcova, J. Brozek, J. Roda, *Polymer* **2004**, *45*, 2141.